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...

Degree and/or honorific distinctions ....

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

....	Signatures of three Members.

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

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

Chairman.

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

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

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

49.

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 1932

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EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

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36 VICTORIA STREET, LONDON, S.W.1
1932

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

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

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

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

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Walter Rosenhain, D.Sc., F.Inst.Met., F.R.S., 1928–1930.

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THE INSTITUTE OF METALS
1932-1933

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H. B. Weeks	London.

Secretary and Editor.

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

Assistant Secretary.

S. C. Guillan.

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

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

December, 1932.

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SECTION I.

MINUTES OF PROCEEDINGS.

ANNUAL AUTUMN MEETING.

THE TWENTY-FOURTH ANNUAL AUTUMN MEETING of the Institute of Metals was held, jointly with the Iron and Steel Institute, in London, from September 12 to 15, 1932.

Monday, September 12.

The meeting opened in the evening, in the Hall of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W.1, the President of the Institute of Metals, Sir Henry Fowler, K.B.E., LL.D., D.Sc., occupying the Chair, when Dr. H. J. GOUGH, M.B.E., delivered the Institute of Metals ELEVENTH AUTUMN LECTURE on " Corrosion-Fatigue of Metals," a full report of which is given on pp. 17–92.

On the motion of the PRESIDENT, seconded by Professor HENRY LOUIS, M.A., D.Sc., A.R.S.M., a hearty vote of thanks was accorded to Dr. H. J. GOUGH for his lecture.

Tuesday, September 13.

At the morning session held in the Hall of the Institution of Civil Engineers, Great George Street., S.W.1, members of the Iron and Steel Institute and the Institute of Metals met to discuss a programme of five papers, two of the Iron and Steel Institute and three of the Institute of Metals, that were considered to be of interest to the members of both Institutes.

In the afternoon the Iron and Steel Institute papers were presented and discussed, under the chairmanship of Colonel Sir CHARLES WRIGHT, Bart., K.B.E., C.B., in the Hall of the Institution of Civil Engineers, whilst the Institute of Metals papers were presented and discussed, under the chairmanship of Sir HENRY FOWLER, K.B.E., LL.D., D.Sc., in the Hall of the Institution of Mechanical Engineers.

Morning.

The CHAIRMAN (Colonel Sir Charles Wright, Bart., K.B.E., C.B., President of the Iron and Steel Institute): As you all know, by the very kind invitation of the American Iron and Steel Institute and the American Institute of Mining and Metallurgical Engineers, arrangements had been initiated for holding this year's autumn meetings of the Iron and Steel Institute and the Institute of Metals in America. Circumstances unfortunately prevented this and it was found necessary to abandon the plans already made. I am sure that the President of the Institute of Metals, Sir Henry Fowler, will wish to join with me in expressing our gratitude to our American friends for the very cordial gesture they made to us, and perhaps it may still be possible to witness the fulfilment of the original plan in the not very far distant future.

As an alternative, the Councils of our respective Institutes considered that the idea of a simultaneous meeting might still be maintained. It is a real pleasure to me in my year of Presidency to have this joint meeting, more especially as Sir Henry Fowler is a very old and great friend of mine, with whom I worked very closely in the many high positions he occupied during the Great War. There are many who are members of both Institutes, and I feel that there will be general agreement that the meeting together of the two bodies this year will be enjoyed and appreciated by us all.

Sir HENRY FOWLER, K.B.E., LL.D., D.Sc. (President of the Institute of Metals): We of the Institute of Metals appreciate the opportunity of holding this joint meeting with the Iron and Steel Institute. One feels that the establishment of personal contact between those of us interested in ferrous and non-ferrous metals cannot fail to be of benefit to us scientifically as well as socially.

The President of the Iron and Steel Institute occupied the chair during the presentation and discussion of the Institute of Metals papers, whilst the President of the Institute of Metals occupied the chair during the presentation and discussion of the Iron and Steel Institute papers.

COMMUNICATIONS.

The communications by the following authors were presented and discussed: J. R. Handforth; A. L. Norbury and E. Morgan (Iron and Steel Institute papers); W. R. Barclay, G. A. V. Russell, and H. Williamson; G. L. Bailey; and E. J. Daniels (Institute of Metals papers). In each case a hearty vote of thanks to the authors was proposed by the Chairman and carried with acclamation.

Afternoon.

At the resumed meeting at the Institution of Mechanical Engineers, Sir HENRY FOWLER, K.B.E., LL.D., D.Sc., President, in the Chair:

NOMINATIONS OF OFFICERS FOR 1933–34.

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 1933–34:

President.

Sir HENRY FOWLER, K.B.E., LL.D., D.Sc.

Vice-Presidents.

C. H. DESCH, D.Sc., Ph.D., F.R.S.
Professor R. S. HUTTON, D.Sc., M.A.

Members of Council.

Engineer Vice-Admiral Sir ROBERT DIXON, K.C.B., D.Eng.
WESLEY LAMBERT, C.B.E., A.K.C.
H. C. LANCASTER.
A. H. MUNDEY.
A. J. G. SMOUT.
F. TOMLINSON.

The PRESIDENT: The result of the ballot for the election will be announced at the Annual General Meeting to be held in London on March 8 and 9, 1933. I have to remind members that any ten members are entitled at this meeting to nominate a candidate other than one of those nominated by the Council, so long as this is done before the conclusion of our meeting here at midday on Wednesday, September 14.

Election of Members and Student Members.

The Secretary announced that the following members and student members had been elected on July 14 and August 25, 1932:

Members Elected on July 14, 1932.

Claussmann, Paul, Dr.-es-Sci	Paris, France.
Engel, Walter, Dr.-phil.	Copenhagen, Denmark.
Higgins, Harold	Leeds.
Hudson, Frank	Kilmarnock.
Hughes, David Wynne	Liverpool.
Nemilow, Wladimir A.	Leningrad, U.S.S.R.
Quinney, Harry, M.A.	Cambridge.
Sadler, Arthur Vernon	Leicester.

Student Members Elected on July 14, 1932.

Barham, Basil Stanley	London.
Cherry, Alexander William	Birmingham.

Members Elected on August 25, 1932.

Cuthbertson, Joseph William, M.Sc.	Manchester.
Edmunds, William Thomas, B.Sc.	Maesteg.
Greenwood, Harry Delbert, B.S.	Carteret, N.J., U.S.A.
Heaton, Ralph, B.Com.	Birmingham.
Howard, Captain Herbert Seymour (C.C.), U.S.N., M.S.	London.
Moore, Norman Clement	London.
Morgan, Frank Ewen	Khargpur, India.
Perry, Everett Robbins	Los Angeles, Cal., U.S.A.
Pisart, Fernand	Liége, Belgium.
Spurr, Edward	Coventry.
Thompson, Maurice Bernard, Ph.D., B.Sc., A.R.S.M.	Rotherham.

Student Members Elected on August 25, 1932.

Stevens, Harry, B.Sc.	Birmingham.
Temple, Samuel Geoffrey	Birmingham.

Communications.

The communications by the following authors were presented and discussed: N. P. Allen; J. D. Grogan and T. H. Schofield; H. A. Sloman; R. J. M. Payne and J. L. Haughton; D. Stockdale; M. Cook and H. J. Miller; and J. H. Watson. In each case a hearty vote of thanks to the authors was proposed by the President and carried with acclamation.

Evening.

In the evening the Presidents of the Iron and Steel Institute and the Institute of Metals received the members and their ladies at a Conversazione held at the Science Museum, South Kensington.

Wednesday, September 14.

The meeting was resumed in the morning under the chairmanship of the President.

COMMUNICATIONS.

The communications by the following authors were presented and discussed: C. E. Ransley and C. J. Smithells; H. J. Gough and D. G. Sopwith; Professor G. I. Taylor and H. Quinney; H. W. Brownsdon and L. C. Bannister; and W. H. J. Vernon. Papers by K. L. Meissner, and T. G. Bamford were presented, but not discussed. In each case a hearty vote of thanks to the authors was proposed by the President and carried with acclamation.

VOTES OF THANKS.

The PRESIDENT: I wish to move: "That the best thanks of the Members in General Meeting assembled be accorded to:—

(1) The Director (Sir Joseph E. Petavel, K.B.E., D.Sc., F.R.S.) of the National Physical Laboratory, for granting permission to members to visit the Laboratory;

(2) The Director (Sir Henry Lyons, D.Sc., F.R.S.) of the Science Museum, for granting permission for a Conversazione to be held at the Science Museum, and for many facilities;

(3) The Director (C. C. Paterson, Esq., O.B.E.) of the Research Laboratories of the General Electric Company, Ltd., Wembley, for granting permission for members to visit the Research Laboratories and the Lamp and Glass Works, and for his hospitality;

(4) The Mond Nickel Company, Ltd., for granting permission for members to visit their Acton Refinery, and for their hospitality;

(5) The Ford Motor Company (England), Ltd., for granting permission for members to visit their Dagenham Works;

(6) The President (Vice-Admiral Sir William Boyle, K.C.B.) of the Royal Naval College for granting permission for the ladies to visit Greenwich Hospital with its Painted Hall, Royal Naval Museum, and Chapel.

(7) The Council of the Institution of Civil Engineers, and the Council of the Institution of Mechanical Engineers, for so kindly permitting the use of their splendid halls and buildings and for many facilities."

Dr. H. MOORE, C.B.E., Vice-President, seconded the motion, which was put to the meeting and carried with acclamation.

The business meeting then terminated.

In the afternoon visits were paid, by kind permission, to the National Physical Laboratory, Teddington; the Research Laboratories and the Lamp and Glass Works of the General Electric Company, Ltd., Wembley, and the Acton Refinery of the Mond Nickel Company, Ltd.

Thursday, September 15.

Members of the Iron and Steel Institute and the Institute of Metals, and their ladies, took part in an all-day excursion on the River Thames to the works of the Ford Motor Company (England), Ltd., at Dagenham. Three steamers left Westminster carrying a party of over 400 members and their ladies. Luncheon was provided on board. The main party disembarked at Dagenham at 2 p.m., while the ladies visited Greenwich Hospital, all returning to Westminster at 7 p.m., when the meeting terminated.

AUTUMN LECTURE, 1932

CORROSION-FATIGUE OF METALS

ELEVENTH AUTUMN LECTURE TO THE INSTITUTE OF METALS, DELIVERED SEPTEMBER 12, 1932.

By H. J. GOUGH,* M.B.E., D.Sc., Ph.D., Member.

Synopsis.

Corrosion-fatigue of metals is defined as the behaviour of metals subjected to cyclical stresses while exposed to an environment of an oxidizing nature, and is discussed accordingly in the present lecture. Following a brief historical account, the nature of the general problem, the nomenclature employed, and the characteristics of laboratory tests are stated; representative failures in service are described. Consideration is then given to the general influences of chemical composition, heat-treatment, and cold-working on the resistance of metals to corrosion-fatigue, also of the effect of time, number of cycles, and corrosivity of environment as factors in the process. The available knowledge regarding the special case of corrosion-fatigue in steam is discussed, also the general characteristics of corrosion accelerators and inhibitors. It is shown that a recognition of the importance of oxygen as a factor in fatigue renders entirely reconcilable the results of many apparently unrelated observations which have been obtained in independent researches. Some fundamental facts regarding the nature of corrosion fatigue can be deduced from observations of the changes of microstructure occurring under these conditions. Primary importance is attached to the behaviour of protective films under the straining actions associated with cyclical stressing. Although a large field of research remains to be explored, yet, even at the present time, it is concluded that the mechanism of corrosion-fatigue can be reduced to an ordered sequence of chemical and physical events which are explicable in the light of existing knowledge relating to corrosion and fatigue phenomena.

Table of Contents.

Note.—The reference numbers in the text relate to the bibliography given at the end of the paper.

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* Superintendent, Engineering Department, National Physical Laboratory, Teddington.

1.—INTRODUCTORY.

CORROSION being essentially a process of oxidation, and fatigue a generic term employed to denote those phenomena exhibited by metals and other materials, when subjected to cyclical variations of stress, the subject of the present lecture may be properly and concisely defined as *the behaviour of metals subjected to cyclical stresses while exposed to an environment of an oxidizing nature.* Objections have been raised to the use of the term "corrosion-fatigue," on the grounds that undue restrictions are thereby placed on the range of the phenomena which fall within the meaning of the term, but these objections are fallacious, apparently being based on the assumption that fatigue occurs only when the applied conditions are such that complete *fracture* will ultimately result. This definition of fatigue is much too restrictive, for extensive researches have shown that, under certain conditions, metals can be exposed to an indefinitely great number of repetitions of a range of cyclic stress without producing fracture, although the physical properties of the metal may be greatly changed in the process; these changes are indications of fatigue. Corrosion-fatigue of metals will therefore be discussed according to the definition stated above.

The separate damages to metals caused by corrosion and by cyclic stresses have been the subject of much experimental study, yet the results offer little indication of the greatly accelerated damage which *may* result when these influences act simultaneously; it is important to realize that these separate effects are not merely additive, and to appreciate the reason. In the usual type of corrosion test, the specimen may be subjected to stress, but the conditions are essentially *static*; it is common experience to find that the presence of the resulting corrosion products tends to retard the attack or to cause it to cease completely. Directly cyclic stresses are superimposed, the induced cyclic *strains* tend to rupture, or render more permeable, the protective film, and to dislodge or remove the other products of corrosion; hence, the cyclic stresses may be said to accelerate corrosion in an indirect manner. Again, the pitting of the surface by corrosion gives rise to mechanical stress concentration effects, and corrosion may therefore be said to increase the effect of the applied stresses. Of these two accelerating factors, that of the cyclic strains on the corrosion products is usually much the more potent in the general case of corrosion-fatigue.

In many cases of corrosion-fatigue, the amount of metal combining to form corrosion-products is extremely small—to such an extent that certain fractured laboratory specimens retain undiminished their surface brightness, although their fatigue resistance has been considerably reduced. The serious damage sustained has been caused by the presence of sharp, deep pits or crevices, produced under the conjoint action. The mechanism of the production of these pits is the major problem of the subject. At first sight, therefore, corrosion-fatigue phenomena appear to differ essentially from those of static corrosion or of ordinary fatigue, but it is hoped to show that the same fundamental operative factors are involved.

Stressed parts subjected to marine conditions are liable to corrosion-fatigue, and the fitting of ship's tail shafts with brass liners has been common practice for many years. In naval practice, the shaft is usually totally enclosed, whilst two-part liners are common in the merchant service, although the continuous liner is now being more generally adopted. A reason for the use of these liners was the superior wearing quality of the brass, as compared with the steel shaft, in *lignum vitæ,* permitting wear without weakening of the shaft itself. The author has been unable, however, to find any reference to an early recognition, in marine engineering circles, of the conjoint action of corrosion and fatigue, and the long-established precautions taken to exclude sea-water appear to have been adopted with the object of restricting the mere wastage of dimensions resulting from ordinary corrosion.

Some early references occur in the literature to alleged failures of railway carriage axles due to corrosion-fatigue, and I have endeavoured to obtain particulars of these failures. Our president—Sir Henry Fowler—has kindly interested himself in this matter and has had a careful search made of the records, but without success; at the time of writing, it seems extremely doubtful whether any axle failures, due to this cause, actually occurred. I am informed * that the late Mr. H. R. Haigh, of Derby, held the definite opinion that fatigue of metals could be influenced and accelerated by chemical action; he frequently directed, in discussion, the attention of engineers to the importance of the conjoint action. At his suggestion, Dr., now Professor, B. P. Haigh made some laboratory tests and found that accelerated fatigue *did* occur in the presence of chemical reagents, also that the action was less marked in soft than in hard steels.

The experience thus gained by Dr. B. P. Haigh was destined to be of valuable service [5] when, in 1916, he was "lent"—by the Royal Naval College—to assist Lieutenant Burney, the designer of the paravane, in the various problems of the strengths of materials which arose in that connection. The paravane towing ropes and attachments, although subjected to only moderate nominal forces, were maintained in a state of violent vibration while exposed to the action

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* I am indebted to Professor Haigh for this interesting information.

of sea-water eddying round the rope, and the effective life of the ropes was disquietingly small. An abnormally small endurance was also exhibited if the submerged ropes came into contact with any part of the fittings of the paravane or of the forefoot of the vessel. It was also found that the use of steels produced by different processes, and of widely differing mechanical strengths, gave endurances which did not differ appreciably. The life of the ropes was finally increased very greatly by the use of galvanized wire: the protection afforded by the zinc coating enabled the superior fatigue resistance of high-tensile wire to be developed, thus producing greater flexibility and decreased towing resistance. This use of galvanizing is extremely interesting: the resistance to corrosion was thereby increased, although the normal fatigue resistance in air was undoubtedly decreased; * the total result being that superior resistance to corrosion-fatigue was obtained. A full description of this work has since been published by Haigh.[18]

The first published account of laboratory experiments on corrosion-fatigue was given by Haigh [17] in a paper published in 1917. The subject received no further research attention for some years, after which investigations were started quite independently, and almost contemporaneously, in England and America. The Aeronautical Research Committee of the Air Ministry has for many years supervised a number of researches, carried out at various laboratories, into many aspects of the problem of fatigue. In 1925, a research was commenced, on behalf of the Committee, by Lehmann—working in Professor J. F. Jenkin's laboratory at Oxford—into the fatigue strength of metals tested in the presence of hot aqueous solutions. The results of the research, published [23] in 1926, directed attention to the important part played by air in corrosion-fatigue phenomena: strongly corrosive liquids were found to exhibit surprisingly small effect on the fatigue resistance when they contained little dissolved air. The importance of oxygen was further demonstrated in work carried out by Binnie.[4] A comprehensive investigation into corrosion-fatigue, on behalf of the Aeronautical Research Committee of the Air Ministry, was commenced, as a joint research, at the National Physical Laboratory at Teddington and the Royal Aircraft Establishment at Farnborough. This programme includes the study of fundamental aspects by metallographic examinations and the use of single crystals, the effect of different environments and of protective coatings, in addition to the collection.

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* See very recent paper by W. H. Swanger and R. D. France on "Effect of Zinc Coatings on the Endurance Properties of Steel," *Amer. Soc. Test. Mat. Preprint*, 1932.

of data for use in the design of aircraft operating under marine conditions. Some results of this work have already been published.[13, 14, 15]

The origin of the American work is of great interest, as it was not planned initially as an investigation into corrosion-fatigue, but as an examination of the effects of temperature on the shape of the curve connecting range of stress and number of cycles to fracture of specimens fatigued in air. McAdam[27] investigated the effects of altering the temperature of the test-piece by various means, which included the use of various cyclic speeds, cooling the specimen by a water stream, and altering the thermal conductivity of the specimen by changes in its shape. When, however, the experiments on the water-cooled specimens were extended to include lower stress ranges and correspondingly greater endurances, McAdam encountered abnormal results, which indicated that a chemical as well as a thermal action of the water stream was involved, and that this chemical action had "unexpected influence on the fatigue-resisting properties." To this conjoint action McAdam applied the new term "corrosion-fatigue." McAdam's first report[27] was published in 1926; it was the first of a long series of papers[27–41] which described the most systematic and comprehensive investigation on corrosion-fatigue which has yet been published. McAdam's work has exerted a profound influence on other workers in this field. He has investigated the corrosion-fatigue properties of a comprehensive range of metals and alloys, and explored the general effects of composition, heat-treatment, and cold-working. Even more important is his general investigation of the inter-relationship of the factors, stress, time, and number of cycles on damage. It will be a matter of general regret if his recent transfer from the U.S. Naval Experiment Station to the Bureau of Standards involves the cessation of his invaluable researches into corrosion-fatigue phenomena.

The foregoing traces the early history of the subject and the two main investigations in England and America carried out in the laboratories of, or supervised by, State Departments. Corrosion-fatigue is, however, of such direct importance in industry that it is not surprising to find that other valuable investigations have been made in industrial research laboratories or on behalf of industry. In this connection passing reference may be made to the following: in England, the work of Haigh and Jones,[19] also of Beckinsale and Waterhouse,[2] in connection with the special problem of lead alloys for cable sheathing, carried out on behalf of the British Non-Ferrous Metals Research Association; of Inglis and Lake,[21] conducted in the laboratories of Messrs. Synthetic Ammonia and Nitrates, Ltd. The application of the subject to the special needs of turbine constructors has been studied in America by Fuller,[8, 9] of the Research Laboratories of the General Electric Company, and, in Switzerland, by Honegger, on behalf of Messrs. Brown, Boveri & Co. To the researches of Speller, McCorkle, and Mumma,[49, 50] carried out in the laboratories of the National Tube Company, we are indebted for considerable knowledge of the influence of corrosion accelerators and inhibitors, and the important reminder that extremely local conditions may produce effects far outweighing those due to the general environment. The resistance of structural steels to corrosion-fatigue has received attention, in Germany, by Schulz and Buchholtz,[47] working in the Research Institute of the Vereinigte Stahlwerke A.G. Researches are also in progress in various European and American Universities. The above brief references to research activities will explain why it is that, although the important investigations of corrosion-fatigue have all been made within a period covered by the past seven years, considerable knowledge of the subject is now available. Ample scope, however, remains for further investigation. Some suggestions for research have been stated;[12] these and many others await attention.

In preparing what is the first general survey of corrosion-fatigue phenomena, the author has discussed the subject under certain sections, and a word of explanation is due concerning what may be regarded as two omissions. First, no special reference has been made to the protection afforded by coatings. A little work has already been carried out on this aspect by Fuller, Inglis, Honegger, and McAdam; extensive investigations, however, are in progress at the Royal Aircraft Establishment, at the Bureau of Standards, in the Research Department of the National Tube Company, and, on behalf of the British Non-Ferrous Metals Research Association, in the Research Department, Woolwich, and some of the results obtained should soon be ready for publication. Any survey made at the present time would necessarily be incomplete and probably misleading, and, hence, none has been attempted. Secondly, much might have been written concerning the possible relation between boiler failures and corrosion-fatigue. The author has deliberately refrained from so doing, because of the essential differences which exist between actual boiler conditions and the conditions of corrosion-fatigue tests the data of which would form the only basis of comparison. Much more knowledge is required of the effect of temperature, of varying *general* concentrations of dissolved oxygen, of *local* concentrations of oxygen at seams and rivets, of turbulence, of the influence of corrosion products of the type formed under boiler conditions, of different types of water, and of extremely low cyclic frequencies; until more of this knowledge is available, considerable speculation would be involved in attempting to correlate failures under corrosion-fatigue and under boiler conditions.

2.—GENERAL CONSIDERATION OF THE PROBLEM, THE NOMENCLATURE EMPLOYED, AND THE CHARACTERISTICS OF ENDURANCE TESTS.

Much confusion has resulted from a tendency to consider " fatigue " and " corrosion-fatigue " as separate and distinct actions; a correct appreciation can be obtained only if the whole subject is treated, on a perfectly general basis, under one general title. It cannot be denied that the term " fatigue " is open to grave criticism, but it has acquired universal use. The fatigue properties of a metal are obtained from a series of groups of experiments; in the individual experiments of each group only one variable is explored. The essential variables then become: (1) the applied stress system; (2) the environment, or contact substance, of the specimen; (3) the test temperature, and (4) the frequency of the stress cycle. Other important variables relating to the specimen are its size, shape, and surface condition, but, to simplify the subject in the present treatment, these will be considered as constants. The applied stress system can consist primarily of direct, flexural, or torsional stresses, or a combination of these. With any one type of stress, this can be sub-divided essentially into stress cycles involving impact, or stress cycles varying between certain minimum and maximum values without shock. The latter is the general case (usually, under laboratory conditions, the stress–time function is represented by a sine curve) when the cycle is conveniently represented by $\left(M \pm \frac{R}{2}\right)$, where M is the mean or average stress, and R is the algebraic difference between the maximum and minimum stresses of the cycle. With regard to variable (2), it has been too lightly assumed that none but stress effects are in operation when the atmosphere constitutes the environment: very recent research [14] has shown that this is not the case, and that a perfect vacuum is probably the real standard of comparison. Probably the ideal environment would be one which is absolutely inert (chemically) to the specimen, and also ensures that the temperature of the specimen remains throughout at a pre-determined value. The effect, in ordinary fatigue, of the primary variables (1), (3), and (4) has long been recognized, and a vast number of researches have shown clearly that, even when air is the constant environment, it is impossible to express the fatigue resistance of a material as a single quantity. Still less simple, therefore, becomes the statement of the fatigue resistance when another important variable—environment—is introduced, and it is essential that this fact shall be realized at the outset. Whatever data are derived from a corrosion-fatigue test must be held to apply only to the precise conditions of test; the application of the experimental data to any other conditions or to design must be made with the very greatest care, and only after serious consideration has been given to any differences of conditions that may exist.

Holding air as a constant environment, considerable information exists regarding the effect of the other primary variables; this information is summarized elsewhere.[10, 11, 12] With other environments a large field for research exists, in spite of the exhaustive work already accomplished. For example, practically nothing is known of the effect of the mean stress of the cycle, M; most corrosion-fatigue tests have been made using cycles of reversed stress * ($M = 0$), and in most of these flexural stresses have been employed, although torsional stresses have received some attention (a report from the National Physical Laboratory on some tests employing reversed direct stresses will be published shortly). The effect of the frequency of the cycle is negligible, in fatigue tests conducted in air, and at atmospheric temperature, at cyclic frequencies up to about 3000 cycles per minute: at higher frequencies, Jenkin has shown that the fatigue resistance *increases* steadily up to very high frequencies (why this should be so is a fundamental problem of the subject, although the effect of speed on plastic deformation is most probably largely concerned). With environments of a corrosive nature, a marked speed effect in the opposite direction is observed; this would be expected, however, as penetration by corrosion is essentially a process involving time.

Bearing in mind the above broad general treatment, we can proceed to obtain some nomenclature for use in the present paper. A typical group of fatigue experiments will consist of tests on a number of specimens, the following factors being held constant in each test: the type of straining or stressing action (direct, flexural, torsional, &c.), the value of the mean stress M, the frequency of the stress cycle, and the nature and temperature of the environment. The stress range $\left(R \text{ or } \pm \frac{R}{2}\right)$ is calculated from the applied loading on the original area of the specimen and—in the case of flexural or torsional stresses—

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* If $M = O$, the stresses are referred to as "reversed" stresses; if $M < \frac{R}{2}$, a cycle of "alternating" stresses is obtained; if $M = \frac{R}{2}$, the stresses are said to be "repeated." If $M > \frac{R}{2}$, the stresses are said to be "pulsating" or "fluctuating." Reversed stresses are merely a special case of "alternating" stress, the correct definition for the latter being a cycle in which the maximum and minimum stresses are of opposite signs.

assuming that elastic conditions obtain in the specimen. After a certain number of stress cycles, N, the specimen fractures; N cycles is then termed the "endurance" of the specimen. Other specimens are then tested under other ranges of stress, some probably remaining unbroken. The results of the experiments are then plotted on a diagram of which the ordinates S usually refer to the values of $\frac{R}{2}$, values of N being plotted as abscissæ. Usually, the results fall fairly evenly on a locus known as an "S/N" curve. In the case of tests conducted in air, the form of the curve is generally such that its inclination to the N axis becomes less as the range of stress is decreased, and tends, at some stage, to become parallel * to the N axis and to remain parallel for greater values of N. The final asymptotic value of the curve, representing that value of S which will not produce fracture after an indefinitely great number of stress cycles, is denoted as the "fatigue limit" of the material under the test conditions. It is often convenient—especially in cases where the curve does not tend to an asymptote or where the experiments have not been carried on long enough to determine the asymptotic value—to express an ordinate value of the curve in terms of the value of S, which is just insufficient to produce fracture at a certain number of stress cycles. This value will be referred to as the "endurance limit (N)," where N is the quoted number of cycles. Now these two terms—"fatigue limit" and "endurance limit (N)"—are sufficiently precise to be used whatever the test environment may be. Unfortunately, another term, "corrosion-fatigue limit," was coined by McAdam, and is in general use. McAdam's earlier test data appeared to indicate that when the environment was a stream of fresh water, the corrosion-fatigue S/N curve also became definitely asymptotic, and he undoubtedly used the term originally as denoting a real fatigue limit. As his own work proceeded, and as the work of other investigators became available, it became increasingly doubtful whether the S/N curves obtained in corrosion-fatigue tests did in fact tend to an asymptote: in some cases [21] the S/N curve, plotted on a log–log scale, is a straight line. The term, however, is in such general use that the author, after registering protest, has decided to retain it in the present connection, but will use it always in the form "corrosion-fatigue limit (N)," thereby indicating that it is really exactly equivalent in meaning to the term "endurance limit (N)" by which it should be entirely supplanted: its present use must not be

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* There are certain exceptions to this behaviour: see tests by Johnson and Oberg [22] on some aluminium alloys where the S/N curves had not become horizontal even at 500 millions of stress cycles.

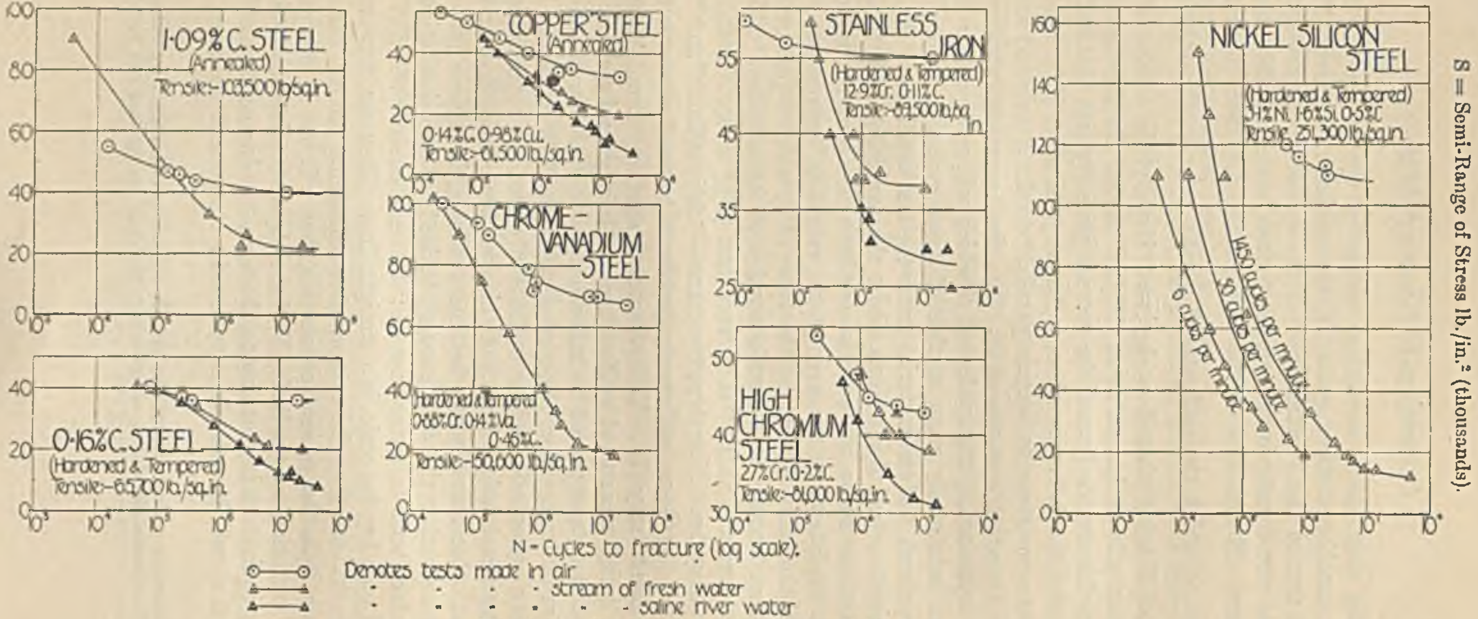

Fig. 1 (a).—Typical Stress–Endurance (S/N) Curves.

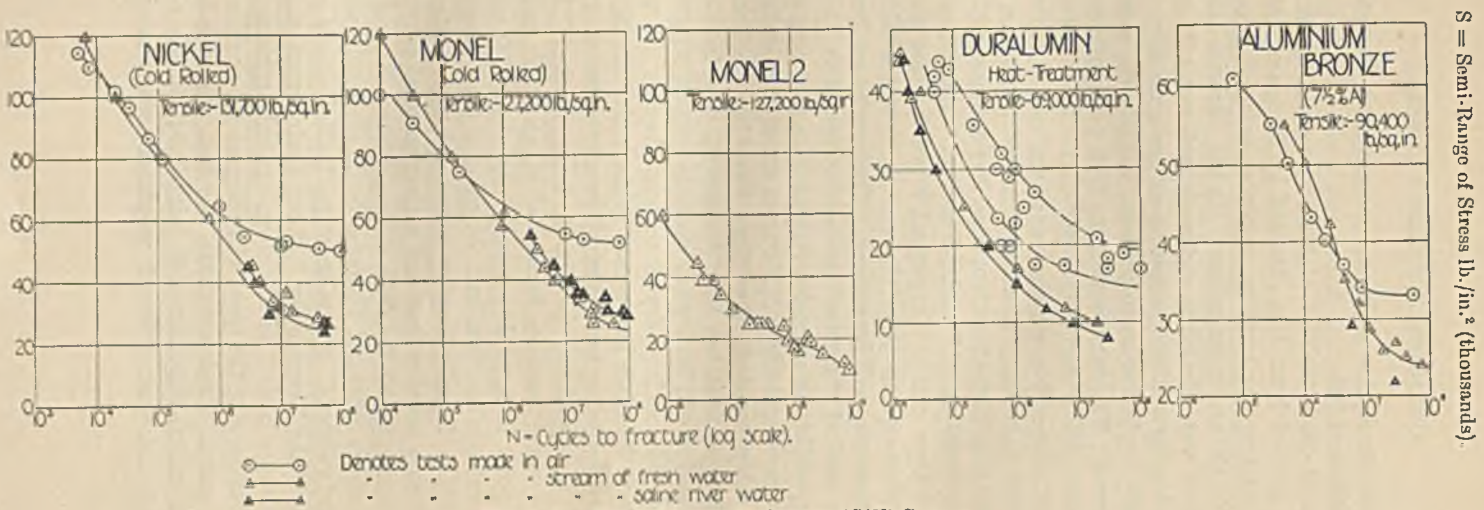

Fig. 1 (*b*).—Typical Stress–Endurance (S/N) Curves.

taken to indicate that a definite "fatigue limit" exists under the stated conditions of test.

The general characteristics of *S*/*N* curves will be seen in Figs. 1 (*a*) and (*b*), plotted from data obtained by McAdam. All tests were made in a rotating bar machine, applying reversed flexural stresses, at a speed of 1450 cycles per minute. In the corrosion-fatigue tests, a stream of fresh water (calcium carbonate well water [28]) or salt water (river water having a saline content about one-sixth that of sea water) was diagonally applied so as to surround entirely the stressed portion of the specimen. The curves relate to 0·16 per cent. carbon steel,[30] 1·09 per cent. carbon steel,[30] 0·14 per cent. carbon steel containing 0·98 per cent. copper,[30] a chrome–vanadium steel [30] (chromium 0·88, vanadium 0·14 per cent.), a stainless iron [30] (chromium 13, carbon 0·11 per cent.), a high-chromium steel [30] (chromium 27 per cent.), Duralumin,[29] Monel metal,[29] nickel,[29] and an "aluminium–bronze" [30] (aluminium 7·5 per cent.). In general, it will be seen that increased destructive effects result from the water of greater salinity: some exceptions, however, will be noticed. The results on Duralumin are interesting: marked "scatter" of results occurs in the tests conducted in air, whilst the corrosion-fatigue tests plot very consistently. Many of the corrosion-fatigue *S*/*N* curves are of such a shape that one might reasonably conclude that they have become horizontal and that a real fatigue limit has been developed. The fresh-water curve for Monel metal would be a good example: at 65,000,000 cycles an asymptotic curve could be drawn to pass through the points. Yet more recently [40] McAdam had reason to determine the *S*/*N* curve for the same alloy, including tests at much greater endurances: the curve he obtained is reproduced in Fig. 1, being marked "Monel (2)." Although the curve becomes horizontal at about 50 million cycles, beyond this point it turns downwards. At about 800 million cycles the ordinate value is less than half the value of the "corrosion-fatigue limit (5×10^7)." Equally lengthy corrosion-fatigue tests (not reproduced) made on a stainless iron and a stainless steel showed a similar reversal of curvature of the *S*/*N* curve between 10 and 50 million cycles. The above notes and diagrams should show with what extreme caution quoted values of "corrosion-fatigue limits" should be accepted; the influence of the "corrosivity" of the environment and the value of the "endurance basis" will be clear. It only remains to mention the marked influence of the speed of testing on the position and shape of the *S*/*N* curve. To demonstrate this fact, corrosion-fatigue *S*/*N* curves, for a nickel–silicon steel [30] (nickel 3·1, silicon 1·58, carbon 0·47 per cent.), at three different speeds of testing are included in

Fig. 1. These curves afford one reason why independent laboratories, employing similar machines but operated at different speeds, report differing values for similar materials.

3.—CORROSION-FATIGUE FAILURES IN SERVICE AND UNDER LABORATORY CONDITIONS.

Corrosion-fatigue is the direct cause of a large variety of failures in service, although until fairly recently the potency of the combined effects of corrosion and cyclic stress, also various characteristics of such failures, have been so little understood that their cause has often remained obscure and unappreciated. As would be expected, this type of failure is common under marine conditions, and precautions, such as the sheathing of propeller shafts with bronze liners and means of preventing sea-water from entering joints, were common practice long before the principles governing corrosion-fatigue were realized. In those earlier times, what was aimed at chiefly was undoubtedly the prevention of the *wastage* of metal and its resulting decrease of effective resistance by mere reduction of *dimensions*, and it must have been a complete mystery how total failure occurred with such a slight degree of apparent surface damage. The particularly destructive mechanism of corrosion-fatigue, by which very sharp, narrow fissures are formed, is now becoming more generally known, and the mystery no longer remains. Previous reference has been made to the aspect of the paravane problem which arose from corrosion-fatigue. The following are further examples of service failures which have been definitely and reliably traced to corrosion-fatigue action :—

Marine propeller shafts;
Ship's rudder main piece;
Steering arms and stub axles of motor vehicles;
Boiler and superheater tubes;
Turbine rotors, discs, and blading;
Tramway and locomotive springs;
Various kinds of piping conveying corrosive liquors;
Flying wires of aeroplanes;
Pump shafts, pump rods, and pump bodies exposed to water;
Water-cooled piston rods of Diesel engines;
Steel railway sleepers, &c., &c.

From careful examination of certain boiler explosions and similar failures, McAdam believes that these failures may be regarded as extreme cases of corrosion-fatigue, in which the cyclic stresses are of such extremely low frequency that the fatigue or final stage is practically absent. A great difference exists between boiler conditions and those of ordinary corrosion-fatigue, but McAdam concludes that laboratory tests made in *cold* water and at low cyclic frequencies give considerable support to his view. This aspect of our subject is too involved and insufficiently explored for brief discussion, and the reader is referred to the original publication.[38] It may be noted that tests * made at Illinois have shown, as would be expected, that boiler feed water, so treated as to prevent caustic embrittlement, causes corrosion-fatigue in laboratory specimens of boiler material. The possible connection between boiler failure and corrosion-fatigue is receiving some attention at the National Physical Laboratory at the present time.

Very few photographs of service failures have been published, although the characteristic features of the fractures are particularly instructive. The author has been extremely fortunate, however, in obtaining a representative collection from his valued correspondents, and some selected photographs may be reproduced and discussed with advantage.

Conditions which tend to promote failure by corrosion-fatigue are imposed on water-cooled piston-rods of internal combustion engines, and many failures have occurred in service. The alternating stresses are twofold, due to the piston and crankshaft loads and centrifugal force, also to the stresses caused by the cyclic changes in temperature. Fig. 2 (Plate I) shows a section of a failed rod: attention is directed to the pitting or roughening of the inner surface, and to the fine cracks which are visible having their origin at the bottom of such pits. Fig. 3 (Plate II) shows the appearance of the face of the fracture. In its *general* smooth appearance it is indistinguishable from an ordinary fatigue fracture; the serrated nature of the fracture is, however, characteristic of many corrosion-fatigue failures, showing that fracture has commenced at a *number* of cracks. Fig. 4 (Plate II), to which further reference is made later, is a composite photomicrograph of one of the small cracks seen in Fig. 2 (Plate I). Another interesting example of this type of failure is shown in Fig. 5 (Plate III). This refers to a gas-engine piston rod which failed after about 12 years' service. River water, used for cooling purposes, passed through the central hole and emerged at the smaller diametral holes, in which corrosion-fatigue failure has commenced. An extremely smooth fracture, indistinguishable, except at its origin, from an ordinary fatigue failure, has resulted.

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* Unpublished thesis by B. B. Betty, for which the author is indebted to Professor H. F. Moore.

Figs. 7 and 8 (Plate IV) show a fractured ship's tail shaft of 9 in. diameter. The bronze liners fitted to this shaft were not of the "continuous" type, but were divided into two parts. For lubrication purposes, a trickle of water flowed past the outer liner, and the shaft fractured, as shown, at the unprotected section situated between the liners. Fig. 7 shows the outer surface of the shaft, including the edge of the actual fracture: special attention is directed to the very sharp and deep X-shaped corrosion-fatigue fissures which are responsible for the fracture (the significance of these star-shaped notches is discussed later). An excellent idea of the "sharpness" of the fissures is obtained from Fig. 8, which shows the face of the fracture; "ripple" markings are visible, indicating that the final stage of the corrosion-fatigue process is progressive damage by means of a spreading crack or cracks, similar to that of ordinary fatigue. The initial stage is represented by the formation of the fissures under the combined effects of corrosion and stress.

Fig. 6 (Plate III) shows a 14-in. diameter propeller shaft which failed at the junction of the brass propeller hub and the brass liner: the liner is visible in the photograph. The hub projected over the liner by about 1·5 in., a red-lead packing being used to keep out the water. Water, however, had penetrated the packing and come into contact with the shaft, leading to corrosion-fatigue failure after 15 months' service. Fig. 6 is an excellent example of the serrated type of fracture which is so often observed in service failures. Fig. 9 (Plate V) shows a fractured propeller shaft of 16 in. diameter. In this case, the shaft had failed, between two sections of the brass protective sleeves, after 3¾ years' service: the serrated shape of the edge of the fracture is shown clearly in Fig. 10 (Plate V). Now, while there are special reasons why shafts fractured under combined corrosion and alternating torsional stresses show what may be termed "double helicoidal" fractures, yet this "zigzag" type of failure must not be regarded as characteristic of corrosion-fatigue in service; in some cases it is not exhibited. As an example, Fig. 11 (Plate VI) shows a marine shaft which failed in the tapered portion underneath the hub. In this case, water entered between the sleeve and hub and penetrated to that portion of the tapered shaft where the presence of the keyway set up stress concentrations. A fairly smooth-edged single helicoidal fracture has resulted; the appearance of the fracture indicates, unmistakably, that the cause is corrosion-fatigue and not ordinary fatigue.

Fig. 12 (Plate VII) is of special interest. It shows the failure of a tail shaft caused by water penetrating the rubber sealing ring and obtaining access to the neighbourhood of the keyway. Surface corrosion and several corrosion-fatigue cracks are clearly visible in the photograph. When the shaft was bent during examination, it was found that the whole of the semi-circular end of the keyway was severely cracked, as shown in Fig. 13 (Plate VII). This type of failure—by a large number of cracks—which is quite characteristic of corrosion-fatigue, is extremely rarely seen in failures due to ordinary fatigue.

Examples of service failures by corrosion-fatigue in railway engineering are shown in Figs. 14, 15, and 16 (Plate VIII). Fig. 14 shows corrosion-fatigue cracks in a steel railway sleeper: the failure has been considerably assisted by the cold-work involved in punching the holes. Figs. 15 and 16 show the complete failure, also cracks, in helical springs: these are further examples of the manner in which the paths of alternating torsional corrosion-fatigue cracks coincide with the planes of the principal stresses.

A very large number of pump rod failures is recorded by the Gulf Oil Corporation of America; Horst and Westcott[20] report that 10,000 rods fractured in the Texas and Louisiana Wells during 1930. They state that nearly all these rods are required to operate in the presence of well-water which is usually brine of high saline content and considerable corrosivity; the cause of a large proportion of the failures is attributed to corrosion-fatigue. Fig. 17 (Plate IX) is a photograph of three of these pump rods illustrating various stages in the development of failure by corrosion-fatigue. Fig. 18 (Plate IX) shows another example of service failure by corrosion-fatigue—namely, in superheater tubes. Reference will be made at a later stage to a tube made of 18 : 8 : 1 chromium–nickel–tungsten which failed while conveying a rapid stream of boiling ammonium sulphate liquor; the alternating stresses in operation were due to vibration of the tubes.

Fig. 19 (Plate X) shows a portion of a lead pipe which cracked in service, in an intercrystalline manner. The pipe carried 70 per cent. sulphuric acid at 140° C. and was laid in a trough. The alternating stress in this case was due to vibration caused by an adjacent motor; removing the cause of the vibration prevented further failures. Fig. 20 (Plate X) is of exceptional interest, as it shows a service failure which was reproduced exactly in the laboratory. It shows a mild steel pump shaft (8 in. diam.) which failed, on the River Tees, due to the river water leaking at a joint between the sleeve and the bronze pump impeller: the service stresses on the shaft were estimated not to exceed $\pm$ 2 tons/in.^{2} and the service life of the shaft—6 months—was equivalent to about 125,000,000 revolutions. Inglis and Lake[21] carried out laboratory corrosion-fatigue tests on a similar steel in which a drip of River Tees water was allowed to fall on to the test-specimens. The

PLATE I.

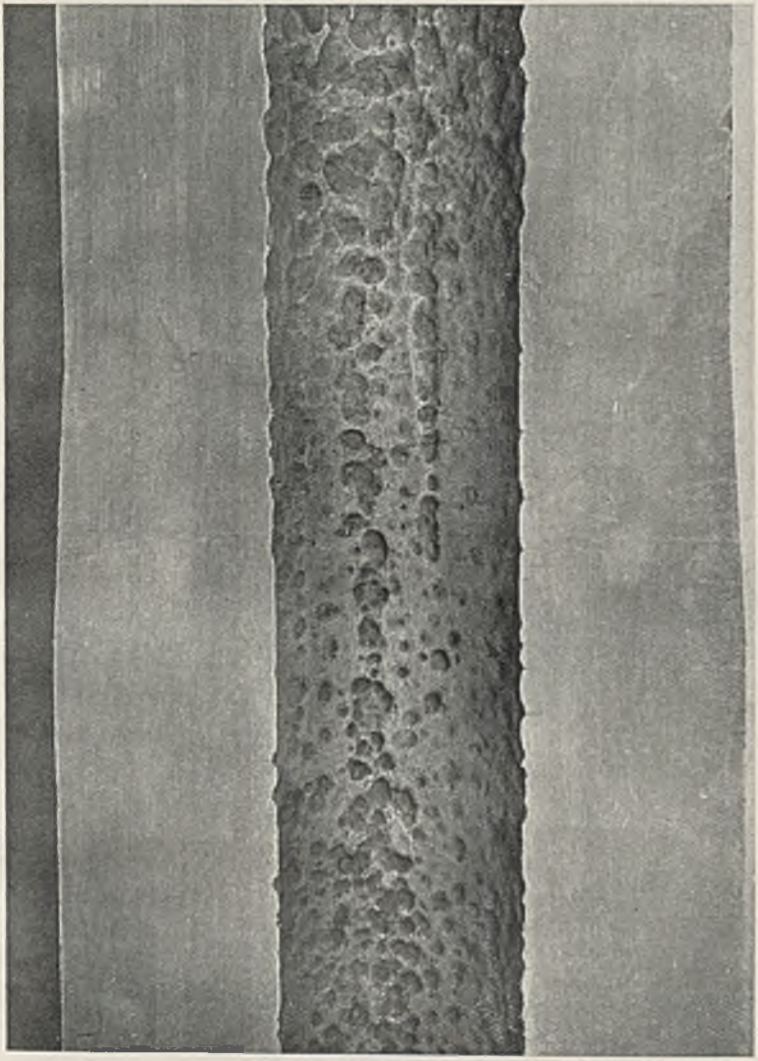


FIG. 2.—Water-Cooled Piston Rod of an Internal Combustion Engine. Failed in Service by Corrosion-Fatigue.

[To face p. 32.

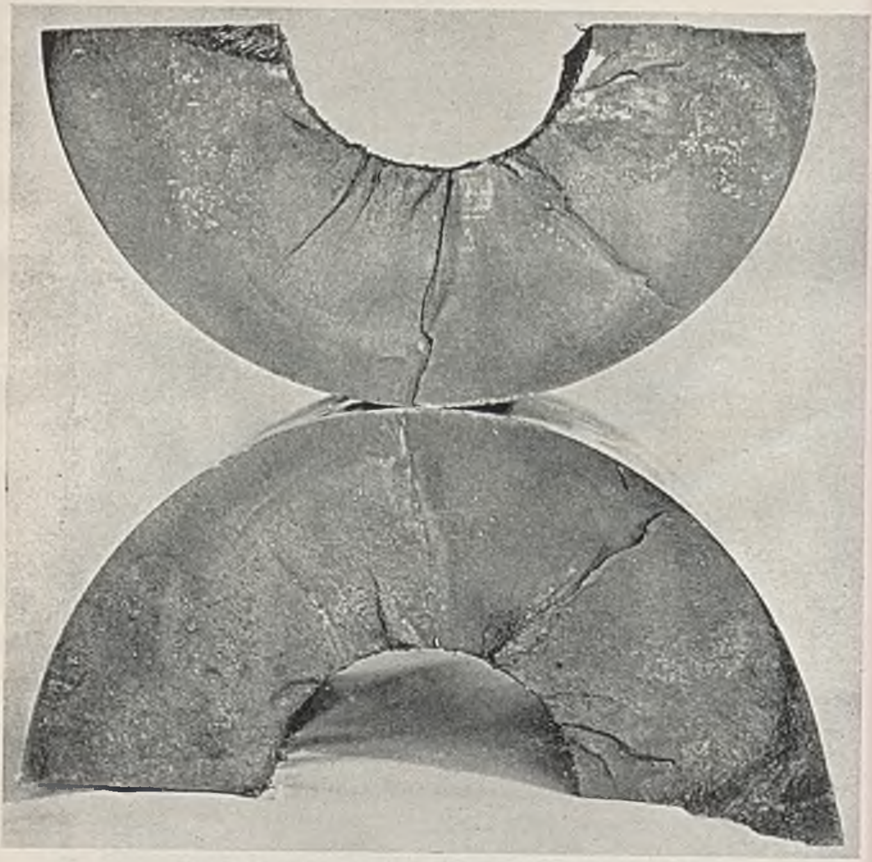


Fig. 3.—Fractured Surface of the Rod shown in Fig. 2.

Fig. 4.—Corrosion Pit and Fatigue Crack in Piston Rod (Water-Cooled).

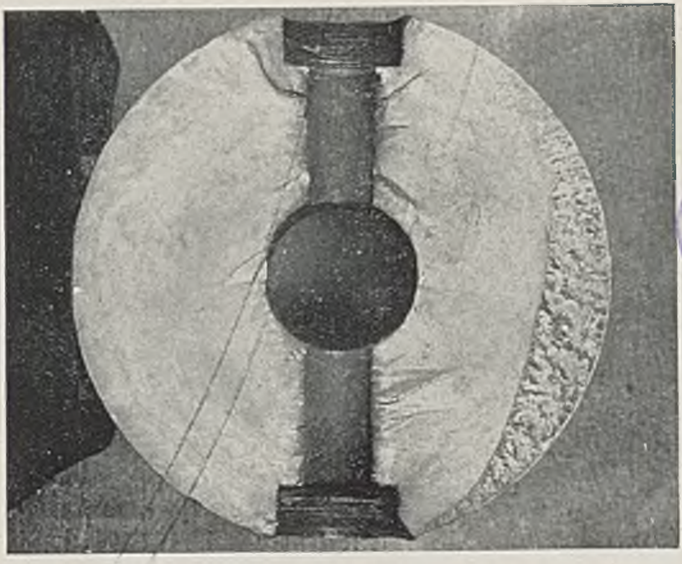


FIG. 5.—Corrosion-Fatigue Failure of a Water-Cooled Piston Rod of a Gas Engine. Service 12 years.

FIG. 6.—Marine Propeller Shaft (14 in. diam.) Failed by Corrosion-Fatigue due to Leakage of Water between Propeller Boss and Shaft Liner. Service 15 months.

FIG. 7.—Ship's Tail Shaft (9 in. diam.) Fractured in Service under Corrosion-Fatigue.

FIG. 8.—Fractured Surface of the Shaft shown in Fig. 7.

Fig. 9.—Fracture of Marine Propeller Shaft (16 in. diam.) Occurring between Two Sections of the Brass Protective Sleeve. Service 3¼ years.

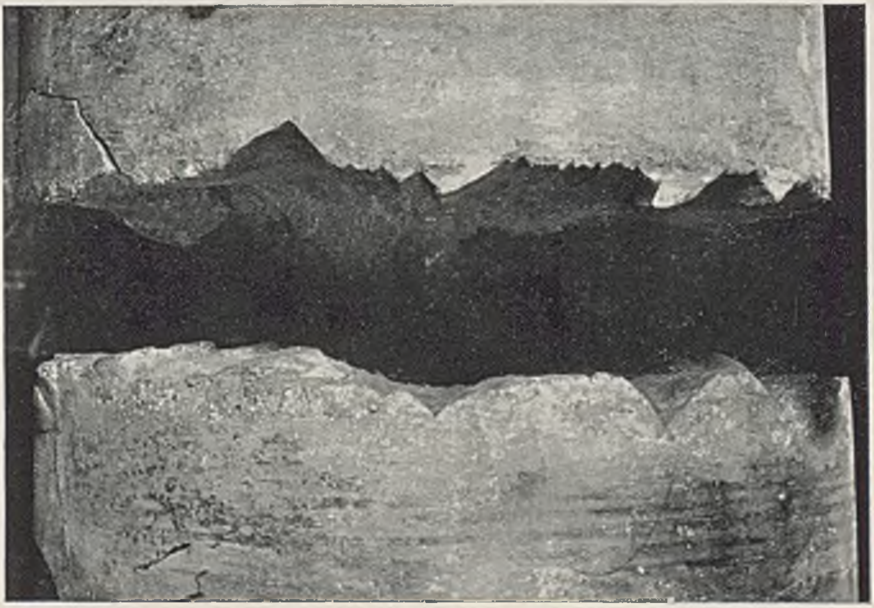


Fig. 10.—Serrated Edge of the Fractured Shaft shown in Fig. 9.

FIG. 11.—Shaft Failure in Tapered Portion of Tail Shaft Originating at Keyway in Boss.

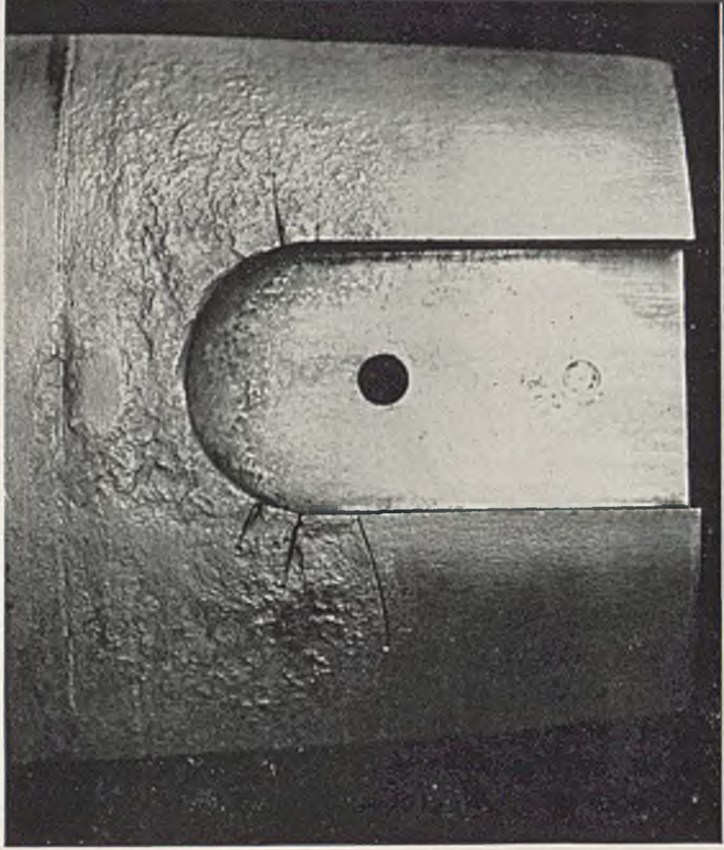


FIG. 12.—Tail-Shaft Failure due to Sea-Water Evading Rubber Sealing Ring.

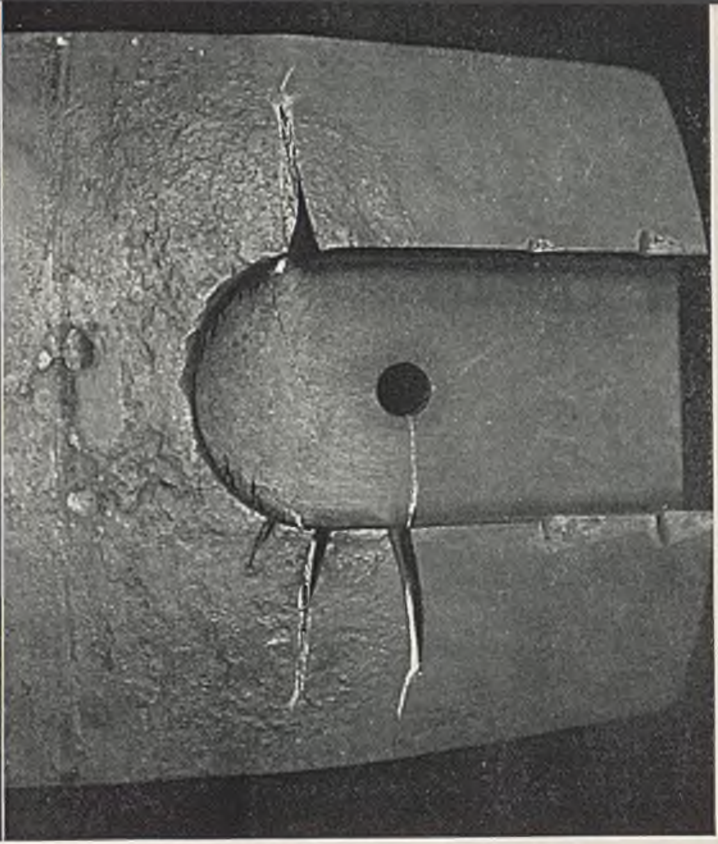


FIG. 13.—Same Shaft as in Fig. 12, but Showing Additional Corrosion-Fatigue Cracks Revealed by Bending Shaft.

PLATE VIII.

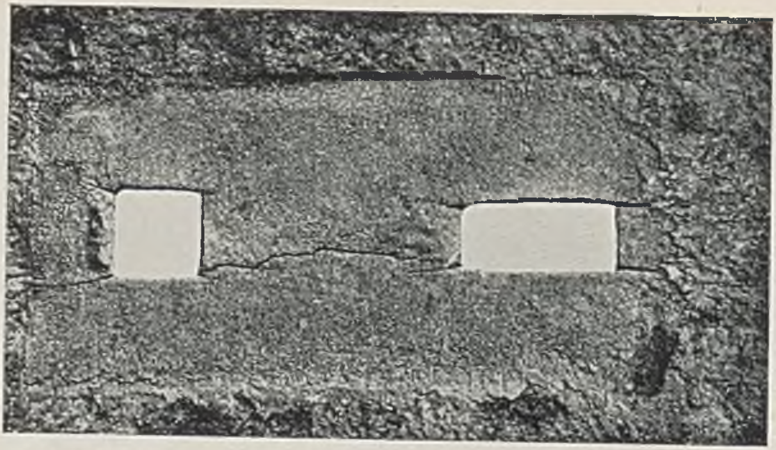


FIG. 14.—Corrosion-Fatigue Cracks in a Steel Railway Sleeper.

FIG. 15.—Corrosion-Fatigue Failure of a Railway Helical Spring.

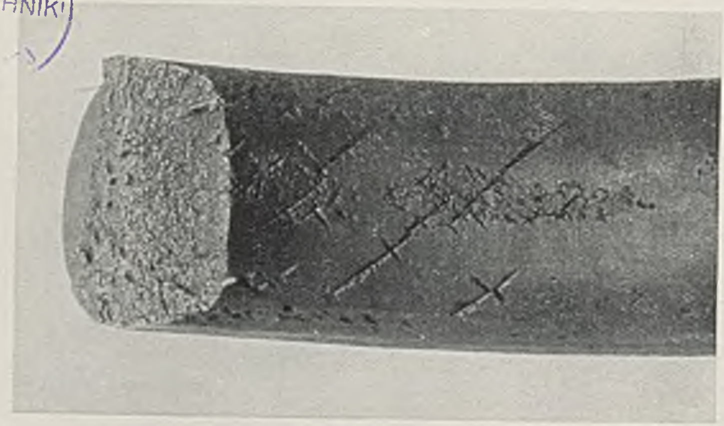


FIG. 16.—Double-Helicoidal Corrosion-Fatigue Cracks in a Spring.

FIG. 17.—Corrosion-Fatigue Failures of Pump Rods in Various Stages of Development.

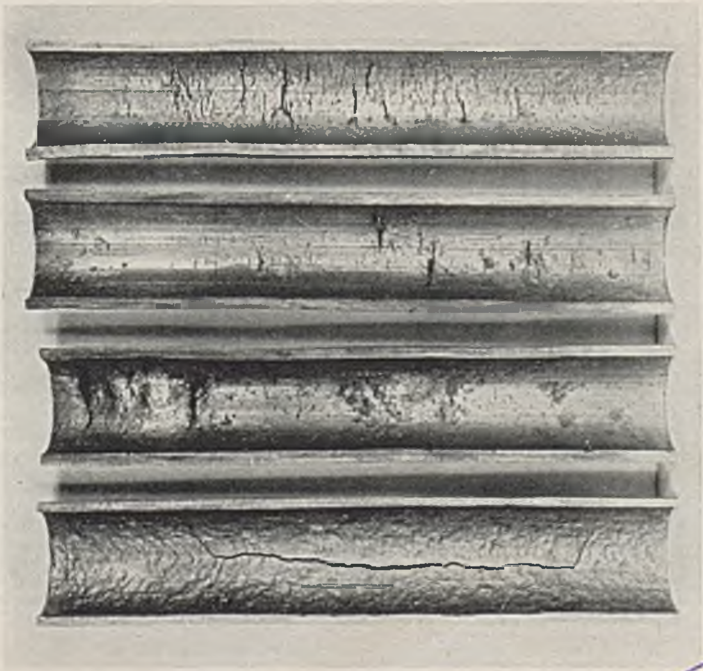


FIG. 18.—Failure of Superheater Tubes due to Corrosion-Fatigue.

FIG. 19.—Lead Pipe Failed in Service while Carrying 70% Sulphuric Acid at 140° C.; Vibration due to Adjacent Motor.

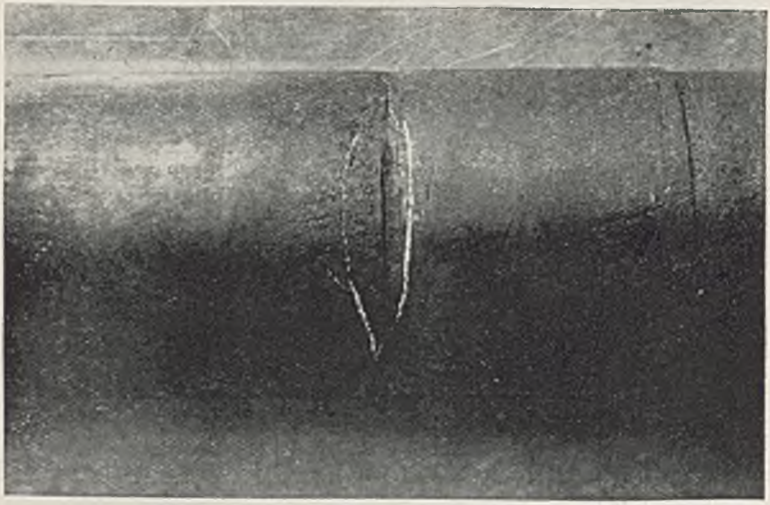


FIG. 20.—Corrosion-Fatigue Failure of an 8 in. diam. Pump Shaft: due to Leakage at a Joint, the Shaft was Subjected to a Drip of River Water.

endurance of the specimens increased, logarithmically, as the range of stress was reduced, but at a stress of ± 2·6 tons/in.^{2}, fracture still occurred after 66,363,000 revolutions. (The fatigue limit in air of this material was ± 17 tons/in.^{2}.)

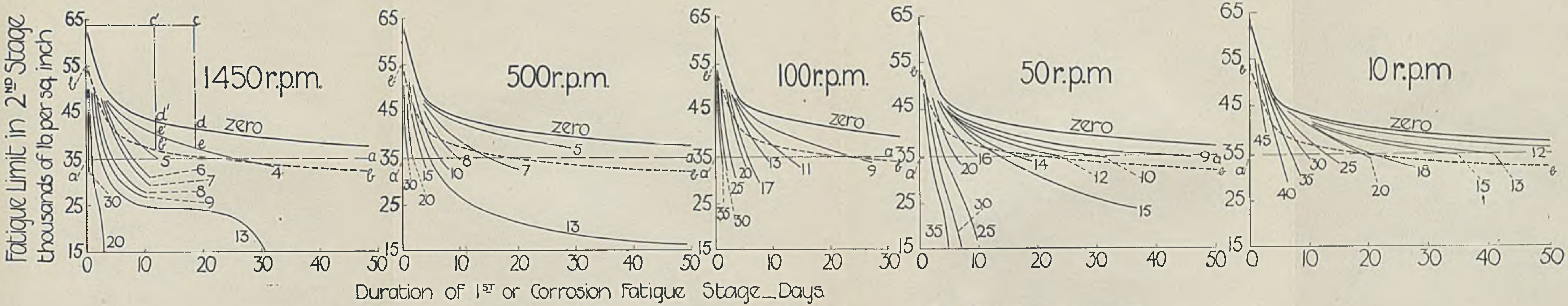
The photographs referred to will indicate the wide range of failures caused by corrosion-fatigue: they also reveal various characteristic appearances of the fractures. In some cases the surfaces exposed to the corrosive agent have suffered damage by general corrosion, but it will be recognized that the loss of strength due to mere reduction of dimensions is of a negligible order compared with the actual damage caused by the formation of sharp pits under corrosion-fatigue conditions. It is unnecessary to discuss in detail the failure of corrosion-fatigue specimens tested in the laboratory. The same general characteristics observed on service failures are exhibited in laboratory specimens, with the difference that in such specimens the surface corrosion is usually much less evident; this is due to the shorter total life of most laboratory specimens owing to the high cyclic speeds usually employed for testing purposes. The actual amount of surface corrosion observed will naturally depend on the test environment and on the metal under test. Ordinary steels tested in tap-water show slight surface rusting: in strongly saline solutions the rusting is, naturally, more pronounced. Materials such as stainless steels and nitrided steels often show no signs whatever of surface rusting, although the fatigue strength has been reduced considerably by subjection to a salt spray. Even where the surface of a specimen becomes heavily coated with corrosion products, examination usually shows that the amount of general surface corrosion has been extremely small and that the diameter of the specimen has not been sensibly reduced; extremely corrodible metals like magnesium alloys are exceptions. It is usual, in failed corrosion-fatigue specimens, as in service fractures, to find that, in addition to the main fracture, a large number of other cracks is present; this is a characteristic not usually observed in ordinary fatigue failure. [Typical examples of laboratory specimens tested in a stream of sea-water, and subjected to alternating bending or torsional stresses, were exhibited at the lecture.]

A further point may justify a word of explanation. To those unacquainted with fatigue phenomena it may appear strange that, if corrosion-fatigue failure is essentially a surface pitting effect, large service failures and small laboratory specimens should exhibit such similar lack of resistance to corrosion-fatigue destruction: in other words, a scale effect might be expected. It must be remembered, however, that the stress concentration due to a sharp pit is controlled primarily by the *shape* of the pit, and not by its *dimensions.* Similarly shaped pits in large and small sections, if of sufficient "sharpness," would all tend to start a progressive fatigue crack, even though it might take longer for *complete* fracture to occur in the larger section. McAdam[33] has, in fact, shown experimentally that the resistance to corrosion-fatigue of specimens of diameters from 0·5 to 2·5 in. is practically independent of the actual diameter, and we may safely infer that no scale effect exists for much greater sizes. To avoid any possible misunderstanding, however, it must be mentioned that severe pitting often results from exposure to the corrosive environment, irrespective of whether cyclic stress is or is not applied. In the case of *very thin* sections, therefore, this pitting due to "stressless corrosion" may reduce the fatigue resistance practically to zero value; hence, such a section would appear to disadvantage when compared with thicker sections, but this is *not* a scale effect in the sense of the above remarks.

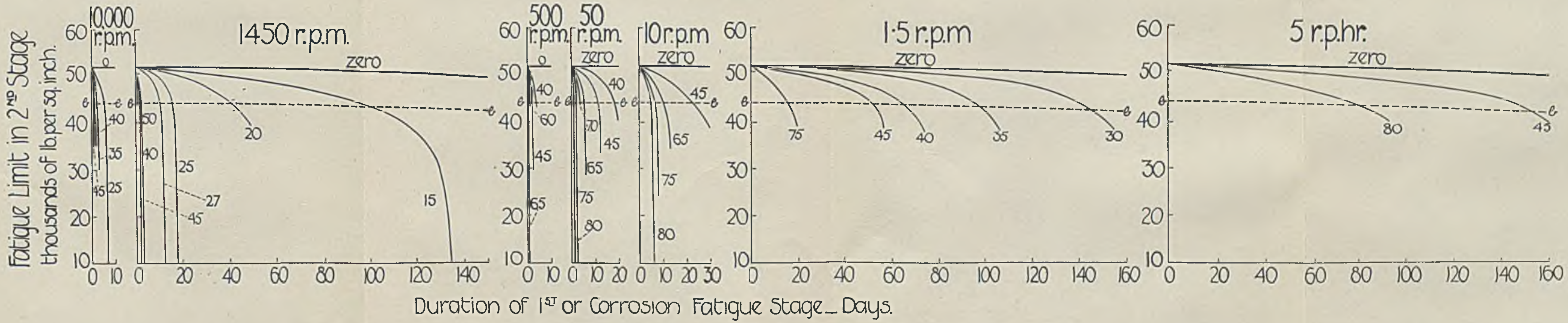
4.—THE INFLUENCE OF CHEMICAL COMPOSITION, HEAT-TREATMENT, AND COLD-WORKING ON RESISTANCE TO CORROSION-FATIGUE.

It has been pointed out in a previous section that because of the many important operative variables—corrosivity of environment, method and speed of test, type of stressing action, &c.—which control the resistance of a metal or an alloy to corrosion-fatigue, it is quite futile to attempt to express this resistance as a simple numerical quantity. If, however, a wide range of materials is investigated, employing some selected set of test conditions, certain valuable broad conclusions can be reached regarding the influence of chemical composition, heat-treatment, and cold-working. (It must *not* be assumed, *a priori*, that these conclusions will apply equally to any other set of conditions for the same materials.) For this purpose, the author has selected some of the comprehensive results obtained by Dr. McAdam; these data were derived from tests made under one such constant set of conditions, in which the stress system employed consisted of cycles of reversed bending stresses (rotating cantilever specimen) applied at a constant frequency of 1450 stress cycles per minute, whilst a stream of water was directed at the specimen throughout the test. The quantity which has been taken to represent the resistance of the metals and alloys to corrosion-fatigue is that ordinate of the corrosion-fatigue S/N curve either at which the curve has become nearly parallel to the N axis or which represents the longest endurance investigated. These values of the corrosion-fatigue limit (N)—where N represents endurances varying between 20 and 100 millions of stress cycles, depending on the group of metals under

Figures adjacent to graphs indicate the semi-range of stress (in thousands of lb/sq. in.) applied during the Corrosion Fatigue Stage.



3·7% NICKEL STEEL — hardened and tempered (Ref. No IW-W-10)



MONEL METAL (Ref. No E.P-8)

FIG. 24.—Results of Two-Stage Tests on Nickel-Steel and Monel Metal.

Each Individual Graph Relates to Constant Stress Range and Constant Cyclic Frequency during Corrosion-Fatigue Stress.

[To face p. 34.

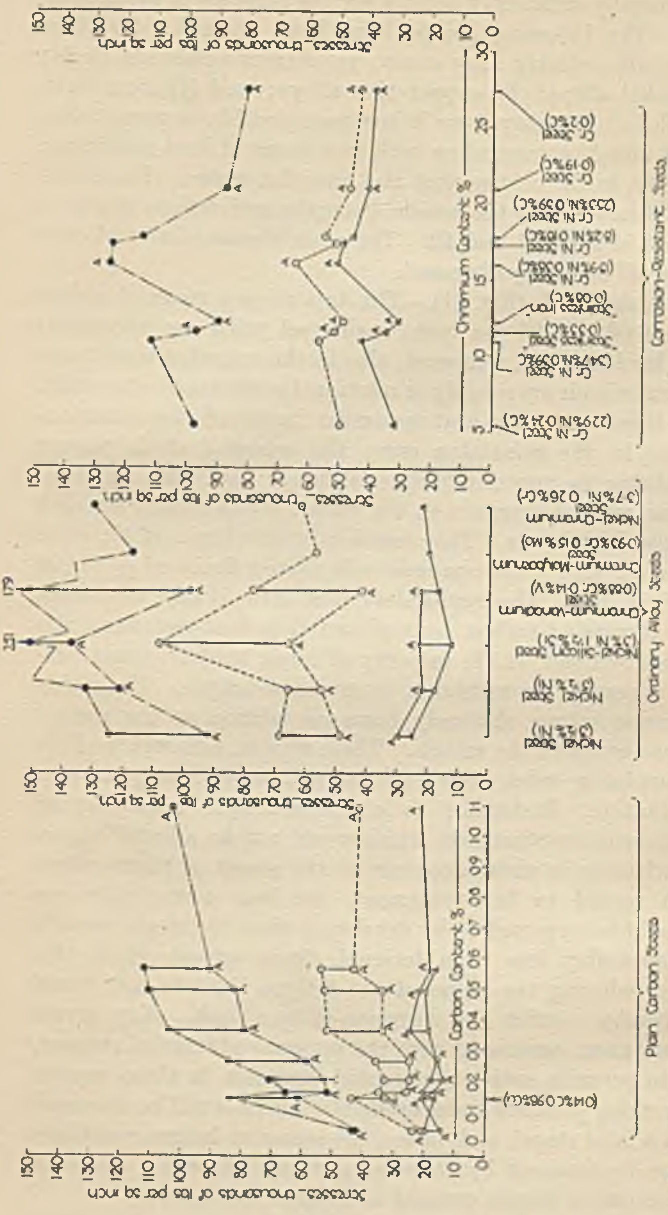

1450rpm
200


1450rpm

test—were generally sufficiently definite for the purposes of the desired comparisons. The following groups have been selected: (*a*) plain carbon steels; (*b*) ordinary alloy steels; (*c*) corrosion-resistant steels; (*d*) copper–nickel alloys; (*e*) copper–zinc alloys; and (*f*) some light aluminium alloys. In many cases it has been possible to present test data for each metal corresponding with two forms of heat-treatment, or, alternatively, in the cold-worked also annealed states. The corrosion-fatigue "limits," also the tensile strengths and fatigue limits in air, are plotted in Figs. 21 and 22. The main characteristics of each series of tests will be briefly discussed.

(a) *Plain carbon steels* (Fig. 21).—The data cover a range of carbon content from 0·03 to 1·09 per cent., each steel (with one exception) being in the hardened and tempered, also in the annealed conditions. The fatigue limits in air are roughly proportional to the tensile strengths, but in only three cases has heat-treatment improved the corrosion-fatigue limit; in the remaining cases the *annealed* steels possess superior resistance to corrosion-fatigue, although hardening and tempering produce marked increases in the values of the tensile strength and the fatigue limit in air. The corrosion-fatigue limits *of the whole range of steels* fall within the comparatively narrow limits of ± 14,000 and ± 24,000 lb./in.^{2}. The results show that little, if any, advantage is gained by increasing carbon content and that heat-treatment also has little effect: in fact, in the majority of cases, hardening and tempering affect *adversely* the resistance to corrosion-fatigue. The resistance to corrosion-fatigue obviously bears no relation to the general mechanical properties of the metals. These results, although perhaps somewhat surprising when first encountered, require only a very simple explanation. Resistance to corrosion-fatigue must depend *primarily* on corrosion-resistance, which would not be affected appreciably by variations in carbon content in the group of plain carbon steels. With regard to heat-treatment, the best corrosion-fatigue resistance would be expected to be developed when the steels are in a condition appreciably free from internal stress, except where this condition, by reducing the value of the fatigue limit in air, would inevitably thereby restrict the corrosion-fatigue limit. Any severe quenching treatment, associated with the presence of internal stresses, would tend to promote active preferential corrosion in those regions where cold-working proceeds under cyclic stresses (this will be discussed more fully at a later stage), and, hence, the corrosion-fatigue resistance would tend to be *decreased* by those very treatments which normally produce an *increase* in tensile strength and fatigue resistance.

Considered in this way, it is not surprising to find that such little



● Denotes Tensile Strength.
⊙ " Fatigue Limit in Air.
△ " Corrosion-Fatigue "Limit" (20×10^6) when Tested in Stream of Fresh (Carbonate) Water at 1450 Stress Cycles per Minute.
A " Annealed; Other Data Relate to the Hardened and Tempered Condition.

FIG. 21.—Influence of Heat-Treatment and Chemical Composition on Resistance to Corrosion-Fatigue (Steels).

variation is found in the corrosion-fatigue limits of the whole range of carbon steels. (Fig. 21 also shows that the addition of 1 per cent. of copper to a 0·15 per cent. carbon steel had no effect on the resistance to corrosion-fatigue; on the other hand, Schulz and Buchholtz [47] report that the corrosion-fatigue limits (2×10^7) of structural steels are definitely improved by small additions of copper.)

(b) *Ordinary alloy steels* (Fig. 21).—Test data for six steels are shown: four of these steels were tested in the annealed as well as in the hardened and tempered condition. The tensile strengths (92,000–251,000 lb./in.^{2}) and air endurance limits (41,000–109,000) vary very widely, yet the corrosion-fatigue limits all fall within the limits of 12,500 and 30,000 lb./in.^{2}; hardening and tempering produce inferior values compared with annealing. Although the corrosion-fatigue resistance of this group is slightly higher, in general, than that of the plain carbon steels, it is apparent that this increase, from a design point of view, is not sufficient to justify the substitution of ordinary alloy steels of much greater cost.

(c) *Corrosion-resistant steels* (Fig. 21).—For convenience, these data have been plotted on a base of chromium content, but attention is also directed to the variation in nickel content. First, considered as a group, it is evident that the resistance to corrosion-fatigue is greatly superior to that of the plain carbon or ordinary alloy steels; the corrosion-fatigue limits vary between 30,000 and 50,000 lb./in.^{2}. It is clear that high chromium content is more effective than high nickel content, the best results being obtained with high contents of both elements.

(d) *Copper–nickel binary alloys* (Fig. 22).—Test data on seven metals enable the whole range, from electrolytic copper to commercially pure nickel, to be broadly surveyed: each metal has been tested in two conditions: (i) cold-working followed by a low-temperature annealing to relieve serious internal stress; (ii) fully annealed. The usual wide variations in tensile strength and fatigue limit in air are recorded. Considering the alloys containing 67 and lower percentages of copper, it will first be noticed that the corrosion-fatigue limits of each alloy in the cold-worked or fully annealed conditions have the same value: also, over this range of composition the corrosion-fatigue limits of all the alloys have nearly the same value (20,500–26,500 lb./in.^{2}); also the fatigue limits in air exceed the corrosion-fatigue limits. Turning to the 79 : 21 copper–nickel alloy, it will be observed that the corrosion-fatigue limit of the cold-worked material is 22,000 lb./in.^{2}, whilst that of the annealed alloy is 18,000 lb./in.^{2}, but in the latter case the fatigue limit in air is also 18,000 lb./in.^{2}. The corrosion-fatigue

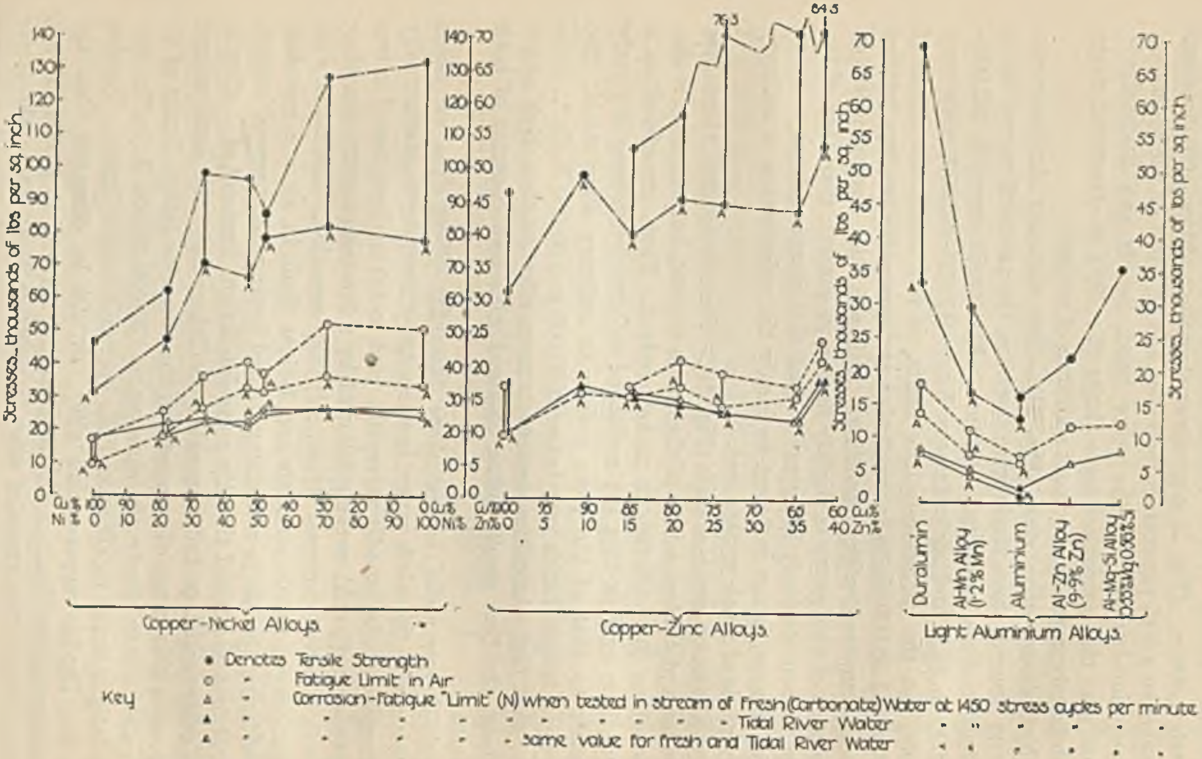


FIG. 22.—Influence of Heat-Treatment and Chemical Composition on Resistance to Corrosion-Fatigue (Non-Ferrous Metals and Alloys). "A" denotes Fully Annealed Condition.

limit of pure copper is, in each condition, slightly *higher* than the fatigue limit in air. From these interesting results it appears reasonable to infer that the alloys covering the whole binary system possess a *practically uniform value* of the corrosion-fatigue limit, *except* in those cases where the value of the limit is *artificially depressed* by the low value of the fatigue limit in air. This probably merely means that the alloys possess nearly uniform corrosion-resistance under the test conditions. McAdam expressed this idea by saying that the group of alloys have an " intrinsic corrosion-fatigue limit." Recent experiments by Gough and Sopwith [14] indicate why the corrosion-fatigue limit of copper may exceed the fatigue limit in air.

(e) *Copper–zinc alloys* (Fig. 22).—In some of these tests the applied stream of water had a saline content equal to about one-sixth that of sea-water, instead of the fresh water previously used. Little difference, however, is recorded in the corrosion-fatigue limits of *these* alloys when tests are made using both waters, and, hence, it may be inferred, *for this group of alloys*, that the waters are equivalent. For each metal the corrosion-fatigue limit is practically independent of heat-treatment: all values fall between the limits of 12,500 and 18,000 lb./in.^{2} (the artificially depressed value of the annealed copper has been referred to previously).

(f) *Some light aluminium alloys* (Fig. 22).—These results again show the small effect of heat-treatment on the corrosion-fatigue limit, and indicate the poor resistance offered by aluminium alloys to corrosion-fatigue.

From detailed consideration of the above data, and of similar data relating to other alloys, emerge the following general conclusions regarding the effect of chemical composition, heat-treatment, and cold-working on the resistance to corrosion-fatigue: with any particular metal or alloy the corrosion-fatigue properties will depend primarily on the resistance of the alloy to corrosion in the particular environment under the conditions of tests. The maximum resistance of the alloy to corrosion-fatigue will be exhibited when the material is in the most favourable condition to resist corrosion. Other forms of heat-treatment and cold-working in general, although causing wide variations in other mechanical properties, will not effect any improvement in the corrosion-fatigue resistance, but may be extremely harmful, especially if internal stresses or discontinuities in the material are set up by the treatment or cold-work. Improvement will result from a change in chemical composition only provided that the change confers increased resistance to corrosion under the particular environment.

5.—INFLUENCE OF STRESS RANGE, TIME, NUMBER OF CYCLES, AND CORROSIVITY OF ENVIRONMENT AS FACTORS IN CORROSION-FATIGUE.

Visual examination of a typical service failure due to corrosion fatigue (see, for example, Figs. 7 and 8 (Plate IV)) reveals three main characteristics: a general surface roughening similar in nature to the effects of stressless corrosion, also deep sharp pits; and emanating from the latter the spreading fatigue cracks which cause the final fracture. The main problem of corrosion-fatigue is the identification and inter-relationship of the various factors which control the formation and propagation of these sharp pits: directly the stress conditions at the base of these pits are sufficient to exceed the fatigue limit of the material, failure will proceed by a spreading crack in a manner which is sufficiently well understood. The process of corrosion-fatigue can conveniently be considered as consisting of two stages: a first or pitting stage, and a second or fatigue stage. In investigating the mechanism of the important first stage, little information of a fundamental type will be gained from the results of complete tests to fracture, such as are exhibited in Fig. 1 (pp. 26–27). We require information concerning the variation in strength of the specimen during the course of the test as fracture is approached, also, of the damage entailed under conditions which do *not* produce complete fracture. The pit formation in question is not that of ordinary corrosion, but of corrosion as influenced by stress and strain conditions, and the factors involved include the following: nature of environment, corrosion-resistance of metal, intensity of applied stress, frequency of stress cycle, number of cycles * of stress, total time,* and temperature of test. With the exception of the effect of temperature—on which no work has yet been published—much fundamental knowledge of the separate effects of the other variables mentioned is now available, owing entirely to the extensive researches of McAdam, who has devised a special and most admirable technique for isolating these effects and demonstrating their inter-relationship; the results of this work are described in ten papers.[32–41] A wide range of ferrous and non-ferrous metals, and four types of environment † have been employed: a stream of carbonate well-water, a stream of saline river-water, a spray of soft water, and a stream of water which approximated to distilled water but was actually taken

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* It is important to note that, as corrosion is involved, " time " and " number of cycles " must be considered as independent variables, and not as merely inter-related by the " frequency " of the stress cycle.

† For analysis of these waters, see following references: 33 (carbonate water, salt water, and soft water), and 41 (condenser water).

from a condenser. In general, it was found that the carbonate water and soft water were about equally damaging in their effects, both being less damaging than the salt water.

The data obtained by McAdam are too voluminous to be adequately summarized in the present lecture, but a few selected experiments will be discussed in order to present certain broad conclusions which can be deduced from his researches.

General Method of Test.

The general scheme of the investigation is to determine the amount of damage sustained under various corrosion-fatigue conditions. Each experiment consists of two stages: first, that in which the required conditions are applied unchanged throughout, and secondly, a test made to determine the *extent* of the damage. In this second stage the fatigue limit in air is determined, the value of which, by comparison with the fatigue limit of new uncorroded specimens, gives a measure of the damage produced during the first stage. Thus in the first or "pitting" stage, specimens, whilst exposed to a water stream or spray, are subjected to a constant stress range, applied at a constant frequency, for a predetermined number of cycles. In the tests made at a constant frequency, each number of cycles will correspond with a certain "corrosion-time," "cycles" and "time" being dependent variables; by making similar first stage tests at *various* frequencies, the influence of these factors as independent variables can be examined. Tests are also made using *zero* stress in the first stage, giving information regarding the effect of stressless corrosion; the specimens are tested while rotating in the water stream, in order that the conditions of relative velocity of the stream and specimens shall be exactly similar to those in which positive stress values are employed.

General Effect of Stress on Damage.

In Fig. 23 (*a*) are shown the results of some selected experiments which indicate the general influence of cyclic stress on damage. During the first stage the following conditions were held constant: frequency of stress cycle (1450 per minute); number of cycles (20×10^6); corrosion time (10 days), and environment (stream of carbonate water in air). The stresses applied during the first stage are plotted against values of the fatigue limit obtained in the second stage. Each graph terminates in a vertical descent at the value of stress which produces fracture at 20×10^6 cycles in the first stage. The slope of a graph at any point is evidently a measure of the rate of damage. The graphs fall into three types: (1) the three carbon and ordinary alloy steels; (2) stainless iron and Duralumin; and (3) "aluminium–bronze." In the first group the rate of damage at first rapidly increases with the stress range, but at some further point commences to diminish; in two cases the graph becomes horizontal before turning abruptly to vertical. The tendency of these graphs to become horizontal has not yet been adequately explained: it may be due to the effect of accumulating corrosion products in retarding the access of the electrolyte to the bottom of the corrosion pit, or to the strengthening of the metal in the corrosion pits by the process of "under-stressing," which

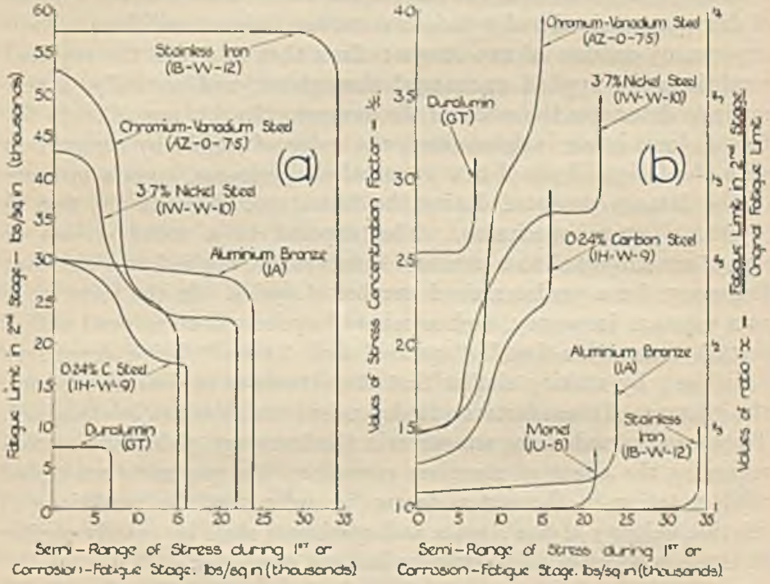

Fig. 23.—General Influence of Cyclic Stress on Damage.

is a well-known characteristic of ordinary fatigue. In the second group, stainless iron and Duralumin, the graphs remain horizontal over a wide variation in stress range, whilst the major part of the graph for "aluminium–bronze" consists of a straight line of gentle slope. Curves of the type shown in Fig. 23 (*a*) have the great disadvantage that they do not disclose the relation between the original fatigue limit of the material and the fatigue limit in the second stage; thus no indication is given of the actual damage sustained under stressless corrosion, and because of this they are apt to be somewhat misleading. This defect can be overcome by re-plotting the results as in Fig. 23 (*b*), in which the scale of abscissæ is unchanged, but the ordinates now represent the value of the ratio (x), obtained by dividing the fatigue limit of the corroded specimens by the original fatigue limit of the metal. Alternatively, we may consider the pits or notches caused by stressless corrosion and cyclic stresses as magnifying the nominal applied stress by a *stress concentration factor*, the value of which is given by the reciprocal of x: it is usually more convenient to employ this latter method. The data of Fig. 23 (*a*) have been replotted in Fig. 23 (*b*), a curve for Monel metal being added. Duralumin (typical of aluminium alloys) is now seen to be damaged as seriously by 20 million cycles of stressless corrosion as by the same number of cycles of stress ranges up to ± 5000 lb./in.^{2} under corrosion-fatigue conditions. Monel metal and stainless iron remain entirely undamaged until the stress range reaches a high value. This may mean that zero or negligible pitting occurs until a limiting stress is reached, or that a protective film is formed which strains elastically until a certain limiting range of strain is superimposed on the specimen and film; once this limit is exceeded, the opposing forces of rupture and repair are in operation, resulting in damage which increases rapidly with further increase in stress range. "Aluminium–bronze" in behaviour approximates closely to the other corrosion-resisting metals. The curves for the three steels show that damage results from stressless corrosion, also, the rate of damage increases very rapidly at first as the stress increases.

Using numerous other types of diagrams, which are really variations of Fig. 23, McAdam demonstrated other characteristic effects of cyclic stress on corrosion pitting, but detailed reference to these is not essential, and we may pass on to the results of the later stages of the investigation.

The Influence of Cyclic Stress, Corrosion–Time, and Number of Cycles on Damage.

In this investigation, each experiment consisted of two stages, a first or corrosion-fatigue stage and a second or fatigue stage. In the first, the rotating specimens were subjected to reversals of bending stress while in contact with a water stream or spray; specimens were thus corroded under various stress ranges, at various cyclic frequencies, and for various times. The fatigue limits of the corroded specimens were then determined. McAdam has investigated a large number of metals and alloys, the characteristics of which can be placed into two general classes, of which nickel–steel and Monel metal are representative. Fig. 24 (Plate XI) shows the results of two-stage tests on these typical metals; the corroding medium was a stream of carbonate water in air. Each individual graph in this figure shows the relationship between total time in the first stage, number of cycles, and the resultant fatigue limit, for a chosen stress and cycle frequency (the base of each diagram can be converted into *cycles* by multiplying the corrosion time by the frequency of test). All graphs for each metal have as common origin the fatigue limit in air. Each graph shows the decrease of fatigue strength, resulting from increase in time or number of cycles in the first stage. The uppermost graph in each group represents the effect of stressless corrosion. The essential difference between the behaviour of the typical metals lies in the shapes of the stressless corrosion graphs. Commencing with a steep slope, the graph for nickel–steel proceeds with a decreasing slope and tends to a horizontal asymptote, although it is certain that, at some stage, the curvature of the graph must be reversed. The slope of the stressless corrosion curve for Monel metal is at first slight, but gradually increases, showing an accelerated rate of damage. The shape of each stress graph is evidently greatly influenced by that of the stressless corrosion curves, demonstrating clearly *that the resistance to damage by corrosion fatigue is controlled largely by the corrosion resistance of the metal.* With increased stress, the initial slopes of the curves also increase and the curve departs to an increasing extent from the stressless corrosion graph. A most significant general characteristic of these curves is that the same general shape holds down to very low stress ranges, showing the very considerable damage which can be caused by small ranges of stress if continued for a sufficiently long time, thus giving further evidence—in addition to that afforded by lengthy endurance tests—that there is grave reason to doubt the existence of a true corrosion-fatigue limit for any range of stress, however small. It has been said that these two groups of graphs are typical: graphs, generally similar to those of the nickel–steel, are obtained with all plain carbon steels, ordinary alloy steels, Duralumin and aluminium alloys, whilst similar graphs to Monel metal are exhibited by corrosion-resistant steels, "aluminium–bronze," and nickel. McAdam has published diagrams,[34–41] similar to those of Fig. 24 (Plate XI), for a number of metals: these contain all the experimental data required by the reader for investigating in detail the behaviour of a particular metal. It will be evident, however, that the general relationship between the influence of the factors involved in corrosion-fatigue and the damage caused cannot be easily revealed by such diagrams. In the tests described, the environment and test temperature were held constant, leaving a minimum of *three* variables, stress range, time, and number of cycles, and to examine their influence a *three-dimensional diagram* must be employed; the surface of such a diagram may, for example, be used to express the relation between the variables and a certain selected (constant) measure of damage. Obviously, an infinite number of such surfaces can be constructed. Of these, two general types—termed " constant total damage " and " constant net damage "—will be found most generally useful.

Constant Total Damage.

A measure of the total damage sustained during a corrosion-fatigue test is given by the amount by which the fatigue limit obtained in the second stage test is inferior to the original fatigue limit in air. Thus, referring to Fig. 24 (Plate XI), the fatigue limit of the nickel–steel is ± 64,000 lb./in.^{2}, and we may choose to investigate the first stage conditions which reduce the fatigue limit to a value, say, of ± 35,000 lb./in.^{2} The necessary data are obtained from the intersections of the individual graphs with the dotted lines *a* . . . *a*, the ordinate value of which is 35,000. These values have been plotted against the three rectangular co-ordinates of stress, time, and cycles, to give the three-dimensional diagram shown in Fig. 25 (Plate XII), the surface of which thus represents the corrosion-fatigue conditions which produce a constant amount of total damage equal to 47 per cent. of the original fatigue limit of the material; this surface is one of " constant total damage."

The diagram has a " time boundary " at a value just exceeding 110 days, which is the time required to produce the stated amount of damage by stressless corrosion alone : thus, *a constant damage surface may also be regarded as representing those combinations of stress and number of cycles which produce the same amount of damage as stressless corrosion, but in a shortened time.* Constant frequency lines, corresponding with speeds of 1450, 500, 100, 50, and 10 cycles per minute, are shown in Fig. 25 (Plate XII). If sections taken along these lines are plotted to logarithmic co-ordinates and to a common base of time, it will be found that a series of parallel straight lines is obtained (except in the region of the time boundary). Further, if the entire diagram is plotted to logarithmic co-ordinates, the constant damage surface (except near the time boundary) is practically a plane. Similar results were obtained with plain carbon and other ordinary alloy steels, leading to the important conclusion *that, for these steels, an exponential relationship* * *exists between the stress, time, and cycles required to produce constant total damage.*

Fig. 25 (Plate XII) also shows that constant total damage may be caused by a certain stress range either due to the application of a large number of cycles at high frequency and small total time or of a small

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* It is improbable that this relationship holds for metals in general.

number of cycles of low frequency occupying much greater time. Now as damage is caused by stressless corrosion, which involves only time, it is clear that the influence of stress on corrosion pitting cannot be studied in terms of *total* damage.

Constant Net Damage.

The total damage caused by corrosion-fatigue, as measured by the reduction in the fatigue limit, is a summation of the damage due to stressless corrosion and the excess or " net " damage due to the cyclic stress. Thus, in Fig. 24 (Plate XI) the vertical intercepts *ce* and *cd* represent the total damage and damage due to stressless corrosion, respectively, whilst the excess or " net " damage due to the cyclic stress is represented by the intercept *de*. A comparison of *de* with similar intercepts, such as *d′e′*, between the same two stress graphs shows that the ratio of net to total damage varies with corrosion time. Comparison of the equivalent graphs for the nickel–steel and Monel metal also shows that the ratio varies considerably from metal to metal, being largely dependent on the relative resistances of the metals to stressless corrosion. To study the effect of *cyclic stress* on damage, therefore, the quantity chosen is a constant percentage reduction of the fatigue limit below that value that would result in the same time from stressless corrosion. The lines *b* . . . *b* in Fig. 24 (Plate XI) represent lines of 15 per cent. constant net damage; *e.g.* the ordinate of *b′* is 85 per cent. of the ordinate of *d′*. McAdam chose this particular value (15 per cent.) of constant net damage as a convenient and useful figure; other values can be studied from diagrams such as Fig. 24.

Inter-relationship of Cyclic Stress, Corrosion–Time, and Number of Cycles in Producing 15 *per cent. Constant Net Damage.*

From Fig. 24 (Plate XI) are abstracted the data represented by the lines *b* . . . *b*. These data can be conveniently represented by the *surface* of a three-dimensional model, the rectangular co-ordinates of which are stress, time, and number of cycles; the vertical axis will be chosen, for purposes of discussion, to represent stress. It is convenient to use logarithmic scales for the " time " and " cycles " axes, as various values of constant cyclic frequency will then be represented by parallel vertical planes. Before considering the general appearance and significance of these three-dimensional models, much can be learnt from the form of the lines of interpenetration of the surface of the model with the vertical planes representing constant cyclic frequencies. Two-dimensional diagrams are obtained of which the co-ordinates are stress and time during the first stage: Fig. 26 gives typical examples plotted to logarithmic co-ordinates. As all the data given in these diagrams relate to a constant amount of net damage (15 per cent.), the base of each diagram also represents the *average rate of net damage*: the appropriate scale is inserted at the top of Fig. 26.

The uppermost series of graphs relate to nickel–steel. Each individual graph is a straight line, and all lines are nearly parallel. McAdam also made tests on a representative selection of steels, including plain carbon steels, copper–steel, various nickel–steels, and chromium–vanadium–steels, some of which were tested in more than one condition of heat-treatment; the experiments thus investigated a wide range of composition and physical properties. When *all* the data were plotted on one diagram, the scatter of experimental results was extremely, and surprisingly, small. The results are expressed by the graphs of Fig. 26 (*b*). The composite graph for each frequency is an extremely close approximation to a straight line, and the various graphs are nearly parallel, the slope increasing slightly with increase in cyclic frequency. From this diagram two main conclusions emerge: (a) *that the influence of stress on corrosion pitting is practically the same for all carbon and ordinary alloy steels*, and (b) *that an exponential relationship obtains between the stress and the average rate of net damage.* The latter can be expressed by an equation of the type

$$R = CS^n$$

where R represents the rate of net damage, S is the semi-range of cyclic stress, C is a constant, and n is the exponent, both C and n depending on the corrosion resistance of the metal to the environment and on the cyclic frequency (n is the cotangent of the slope of the graph, whilst the value of C fixes the position of the graph with regard to the co-ordinate axes).

Graphs for Monel metal are given in Fig. 26 (*c*). Straight lines are again obtained for frequencies up to 500 cycles per minute. At higher speeds, however, the slopes of the curves decrease with decreasing time. Duralumin, "aluminium–bronze," nickel, and stainless iron give groups of curves which are exactly similar in *type* to those of Monel metal. If use is made of these graphs in order to compare the behaviour of different alloys, it is evidently necessary to make comparison at more than one cycle frequency. To illustrate this necessity, graphs for the same representative range of alloys at a low, also at a high frequency, are given in Figs. 26 (*d*) and (*e*). It should be noted that not only the shape and position of the graph for any one metal alter with the frequency, but also the relative positions of the graphs for different metals. At low frequencies, the straight-line relationship

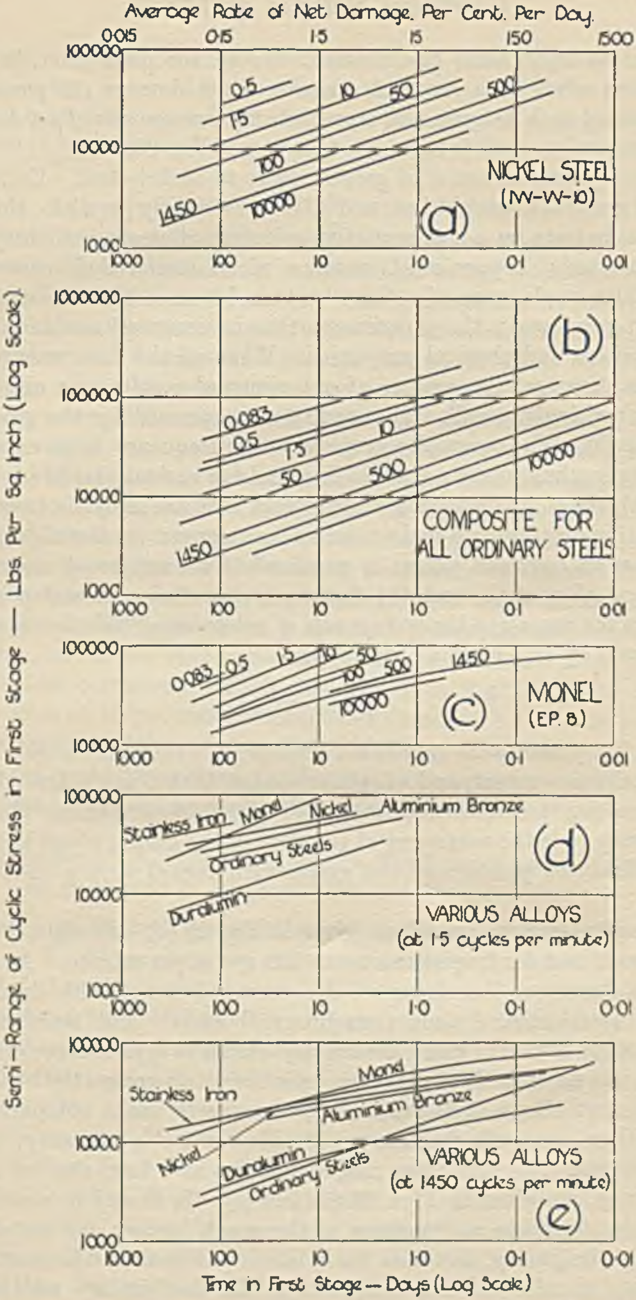

Fig. 26.—Relationship between Stress and Time at Various Constant Cyclic Frequencies. 15% Constant Net Damage under Carbonate Water in all Cases.

Note.—The figures against the graphs indicate the cycle frequency in cycles per minute.

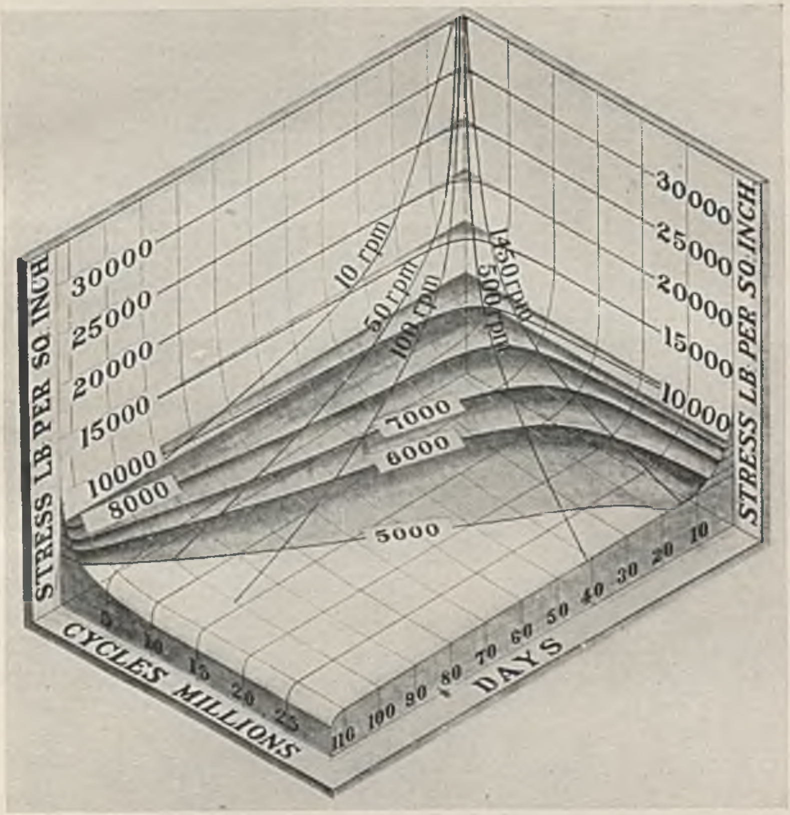

Fig. 25.—Three-Dimensional Diagram showing Corrosion-Fatigue Conditions which Produce a Constant Total Damage of 47% (3·7% Nickel–Steel in Carbonate Water).

[*To face p.* 48.

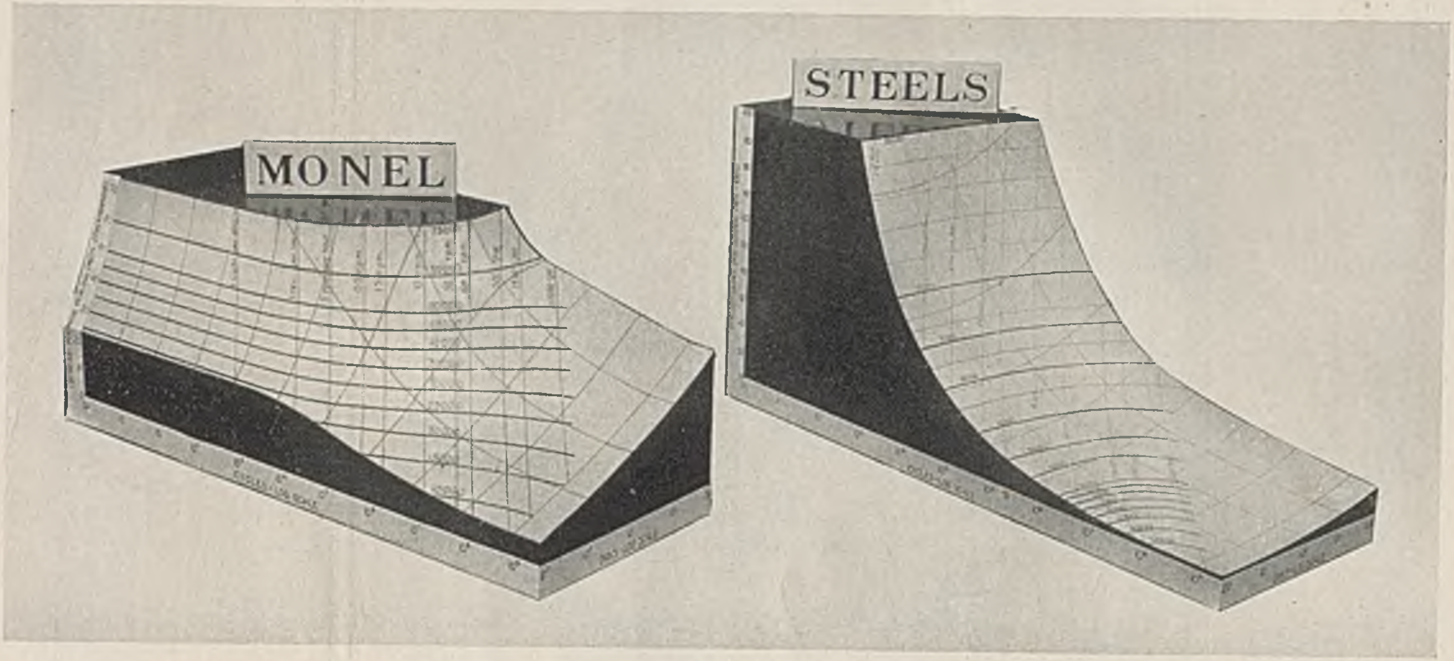

FIG. 29.—Models Representing 15% Constant Net Damage for Steels and Monel Tested in Carbonate Water.

obtains for *most* metals, showing that the rate of net damage varies as a power of the stress (according to an equation of the type $R = CS^n$); McAdam has obtained the following approximate values of the exponent, n: 3·0–4·0 for ordinary steels in carbonate or salt water; also, for carbonate water only, 4·7 (stainless iron), 2·6 (Monel metal), 5·7 (nickel), 4·5 ("aluminium–bronze"), 3·0 (aluminium alloys in general). These values of n should not be used too freely as exact figures, but rather as a general indication of the relative behaviour of the various alloys under the exact stress conditions employed in the tests. It should also be realized that the graphs of Fig. 26 are insensitive to changes of value of the constant C: these graphs represent a range in values of this constant of more than one hundred-fold. On the other hand, the very fact of this wide range of values, obtained with one environment and materials representing a large variation in corrosion-resistance, may mean that the exponential relationship obtained between stress and rate of net damage is a general characteristic for any one metal when exposed to corrosion-fatigue under environments varying widely in degree of corrosivity: further research, however, is needed before this general deduction can be safely made.

Having thus studied the relationship between stress and rate of damage by means of sections taken along constant-frequency lines of the three-dimensional models, the relationships between stress, time, and cycles can be examined using *plan* views of the models. Plans of this type are reproduced in Figs. 27 and 28. In each case two diagrams appear in each figure, because each double diagram reveals the principal characteristics of the *two distinct types* into which may be classed the constant net damage (15 per cent.) diagrams covering all the metals which have yet been completely investigated by McAdam. Each stress line represents a horizontal contour of the surface corresponding with the indicated stress value on the (imaginary) vertical stress scale. It will be convenient, in discussing the diagram, to refer to each stress contour as a "graph." The composite diagram for steels in carbonate water (Fig. 27—full lines) will first be considered. Each graph, over wide variations in stress, and cycle frequencies varying from medium down to the lowest values explored,* approximates to a *horizontal straight* line. With higher frequencies, the slopes of the graphs become more and more steep, tending to approximate to *vertical straight* lines. Thus, the average rate of net damage at low cycle frequencies is nearly proportional to the cycle frequency; as the frequency increases, the

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* It will be understood that only a small amount of data is available relating to tests made at very low frequencies, owing to the testing time involved; the low-frequency end of the diagram cannot be regarded as established to the same degree of accuracy as that relating to medium and high frequencies.

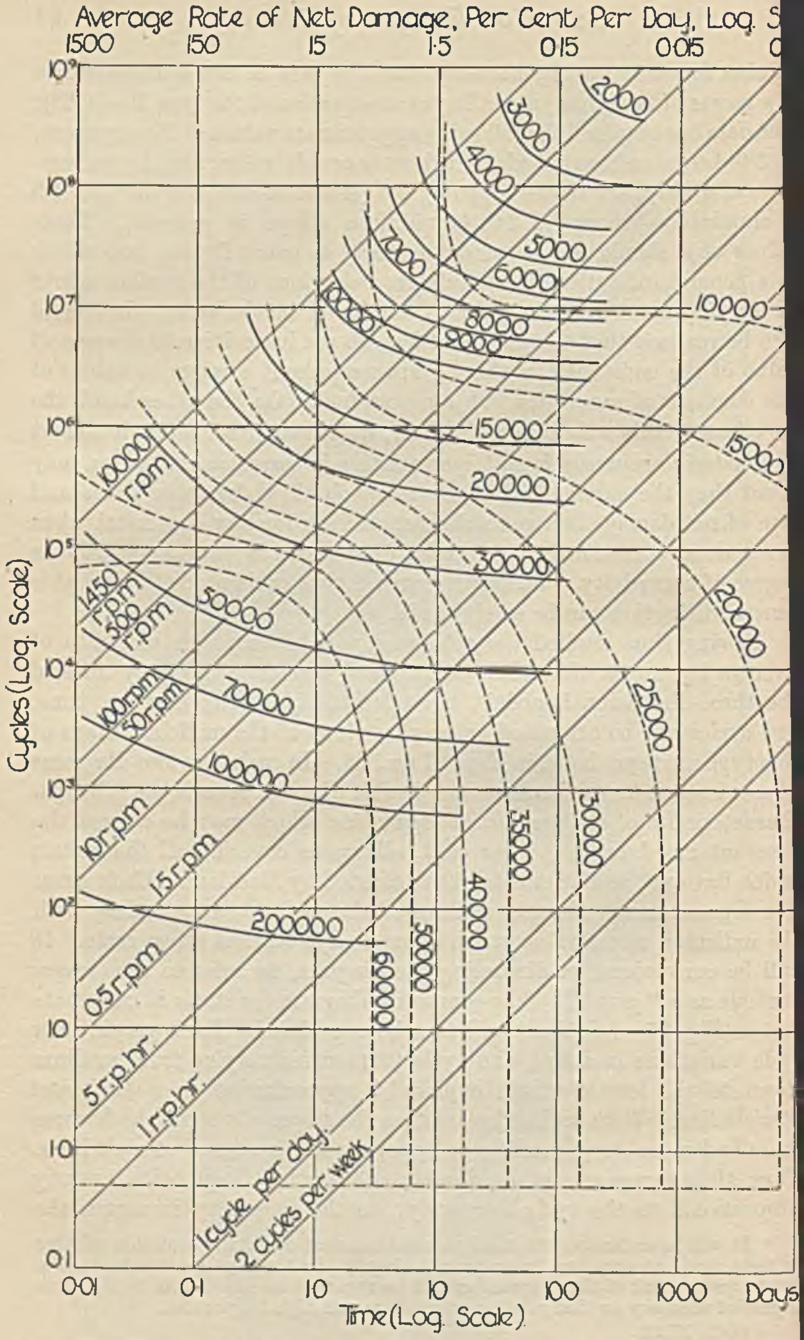

FIG. 27.—Plan of Three-Dimensional Models showing Conditions Producing 15% Constant Net Damage for (*a*) Steels in Stream of Carbonate Water (Full Line Stress Contours), and (*b*) Steels in Stream of Condenser Water (Dotted Line Stress Contours).

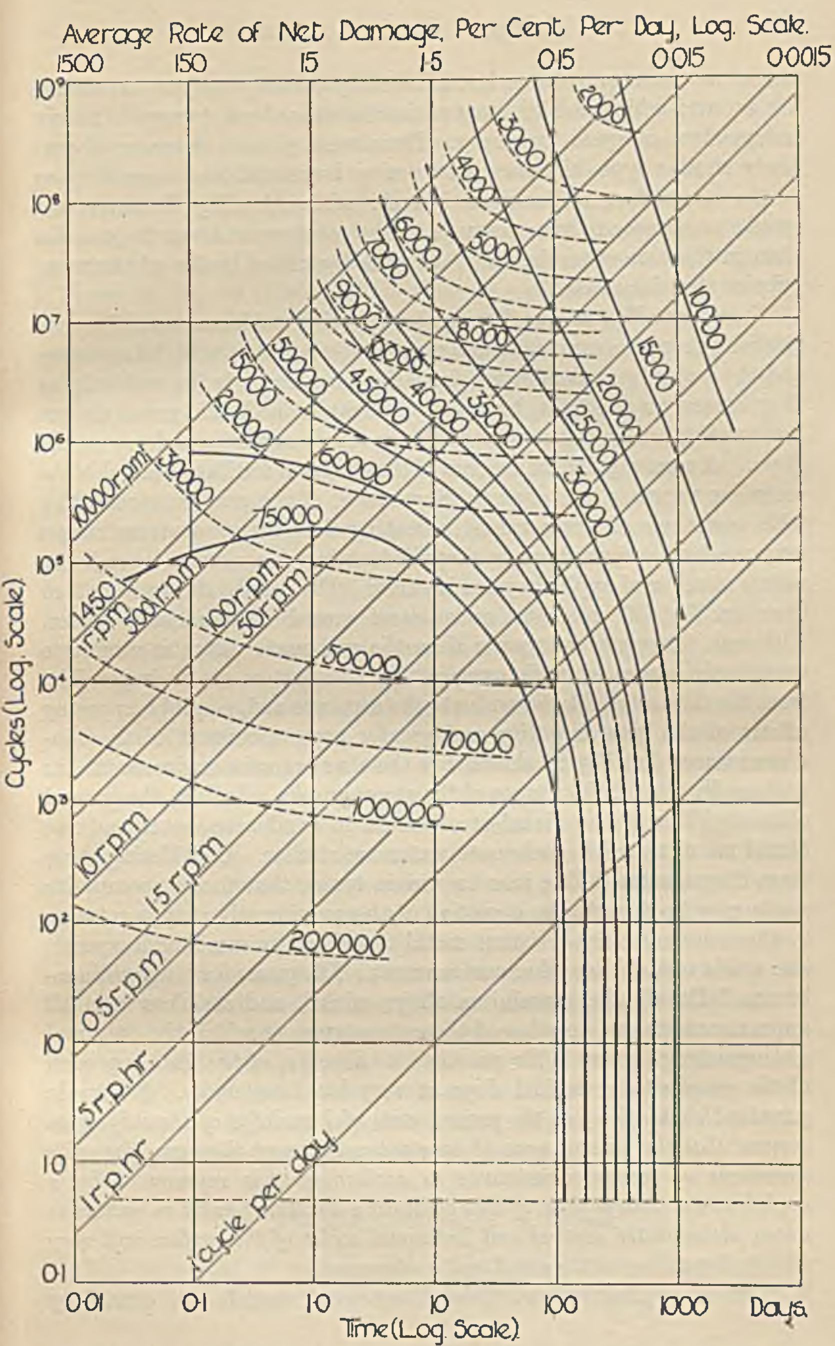

Fig. 28.—Plan of Three-Dimensional Models showing Conditions Producing 15% Constant Net Damage for (*a*) Monel Metal (Full Line Stress Contours), and (*b*) Steels (Dotted Line Stress Contours): all Tested in Stream of Carbonate Water.

rate of net damage becomes less affected by the frequency to an increasing extent; whilst at high frequencies the rate of net damage is nearly independent of cycle frequency. Duralumin gives a diagram of precisely similar type, the curves becoming horizontal and remaining so at the lowest frequencies investigated: with this alloy, however, the graphs commence to turn towards a vertical slope at lower frequencies than in the case of steels. The diagram for nickel is also of the same type as that for steels.

Turning to Fig. 28, the diagram for Monel metal is seen to differ considerably from the composite diagram for steels. At the high-frequency end the majority of the graphs similarly curve towards the vertical; as they extend to the right, however, the graphs for Monel metal do not become horizontal, but reverse their curvature and approach a vertical slope. A most significant feature of the diagram for Monel metal is the crowding together, at very low frequencies, of the graphs representing wide variations of stress value, indicating that very low stress ranges may produce serious damage if applied at low frequencies, even if the actual number of applied cycles is small. The graphs shown in dotted lines on Fig. 27 refer to nickel–steel tested in condenser water. Although this water was purer than the carbonate water, it was more completely saturated with oxygen than the latter. It is impossible, from the data available, to evaluate the separate and, possibly, opposing effects of the greater purity and greater oxygen content of the condenser water, but Fig. 27 shows that the change in the environment has profoundly altered the shapes of the stress graphs. In fact, the general characteristics of the nickel–steel tested in condenser water and the Monel metal tested in carbonate water are similar. Considering these three diagrams as falling into two main types, that for the composite steels may be regarded as a *portion* of the more involved type relating to the more corrosion-resistant metal tested in the same environment, also steels tested in another environment. Diagrams for "aluminium-bronze," Duralumin, aluminium alloys, nickel, and stainless iron, all approximate to one or other of these two types, of which the only real distinguishing feature is the presence, or absence, of the final approach of the graphs to a vertical slope at very low frequencies. *It may be permissible, therefore, in the present state of knowledge of the subject, to assume that the general type of constant net damage diagram, for wide variations of corrosion-resistance to environment, is represented by a surface of the general form of that obtained with Monel metal in carbonate water, although the vertical and horizontal scales of the surface will vary widely, depending on the metal and environment.*

Plan view diagrams of three-dimensional models are extremely useful in studying the influence of stress on corrosion-pitting, but much clearer ideas can be obtained from the solid models themselves. [The following models were available for inspection at the lecture: (1) composite for steels;[41] (2) Monel metal;[41] (3) "aluminium–bronze";[39] (4) Duralumin;[37] (5) stainless iron,[39] and (6) nickel–steel;[41] each related to tests made in carbonate water except model (6), which referred to condenser water.] A general idea of the appearance of these models is shown in Fig. 29 (Plate XIII), which is a photograph of models (1) and (2). Although a section of any model along a plane representing constant frequency is bounded by an approximate straight line (when plotted to logarithmic co-ordinates), yet each stress graph is of such a complex shape that the surface of no model can be represented by a simple mathematical expression. The nearest approach to this ideal is the composite model for steels, a large portion of which is a close approximation to a plane surface. A seventh model, constructed to logarithmic co-ordinates throughout, has been made to show this characteristic, which is equivalent to an exponential relationship not only between stress and time, but also between stress, time, and cycles. *It must be emphasized, however, that this complete relationship is exceptional, and does not apply to metals in general, or even to the entire surface of the composite diagram for ordinary steels.*

In applying the results of the study of net damage to practice, two points are of special interest. Attention may be directed to the serious effect of low stress ranges on corrosion-pitting at low frequencies, even with alloys which are very resistant to stressless corrosion; engineering components which exhibit little visible signs of general corrosion may therefore fail by the formation of local deep and sharp pits. McAdam, after careful study of various boiler failures, concluded that many of these were directly attributable to the effects of corrosion-pitting under stress cycles of small range and extremely low frequency. The second interesting fact is the relative course of the stress graphs in Fig. 27 relating to steels tested in two different environments. Although at medium and high frequencies the stress graphs are generally parallel, they cross at low frequencies. If this actually occurs, it follows that the relative corrosion-fatigue resistances offered by *the same metal* exposed to two different environments of varying corrosivity may be completely altered by a change in cyclic frequency.

6.—CORROSION-FATIGUE IN STEAM.

The behaviour of metals when subjected to alternating stresses in an atmosphere of steam is an aspect of corrosion-fatigue which is of considerable practical importance in connection with steam-power production; it also possesses theoretical interest as demonstrating that the fundamental characteristics of corrosion-fatigue, in steam as in other environments, are controlled by the same primary factors. This aspect of the subject has received some experimental attention by several investigators: the most systematic investigation of which the author is aware is that carried out by Fuller,[8, 9] who determined the endurance properties, in air and in steam under various conditions of temperature and pressure, of materials commonly used in turbine construction. One series of tests was made in steam atmospheres at gauge pressures up to and including 220 lb./in.^{2} (371° C.): in these cases the steam was slightly "wet," and the oxygen content was comparable with that existing in a turbine plant *not* fitted with a de-aerator. The effect of the liquid phase was studied by tests made in an atmosphere of steam and air at 76° C., whilst the importance of the presence of oxygen was studied in tests in which a jet of steam in air was directed at the most highly stressed portion of the specimen. Prior corrosion effects were examined by tests on specimens which were heated for one week in an atmosphere of wet steam and air, and subsequently tested in air, also in steam at each of two pressures, also when exposed to a steam jet in air. The materials used were a 3·5 per cent. nickel–steel (in two forms of heat-treatment), a stainless iron, a steel containing 12·5 per cent. chromium and 0·10 per cent. carbon (in three forms of heat-treatment), various nitrided steels, and on three series of 18 : 8 chromium–nickel austenitic steels each of different carbon content and in nine conditions of heat-treatment. Reversed flexural stresses were employed, at a frequency of 2200 cycles per minute, the corrosion-fatigue limits (N) being determined for values of N varying from 10 to 50 millions of cycles. To present in a concise manner typical results of this investigation, Fig. 30 has been prepared. Referring to this diagram, it will be seen that the resistance of the materials to fatigue, under moderately dry steam up to temperatures of 371° C., decreases with increasing temperature, with the exception of nickel–steel "B" and stainless iron "D," which are scarcely affected. An atmosphere of wet steam and air is more destructive than an atmosphere of steam, but a jet of steam in air is still more destructive, except in the case of nitrided steels, the performances of which under all conditions are remarkably good. Chromium plating of nickel–steel "B" afforded very good protection under the severe conditions of the steam jet. The results of the tests made on previously corroded specimens show that with steam, as with corrosive water, the effects of previous corrosion on the fatigue properties are small as compared with the damage done by simultaneous cyclic stress and corrosion. An extensive series of tests (the results of which are not included in Fig. 30) made on 18 : 8 nickel-chromium steels showed that the best resistance to fatigue in an atmosphere of steam at 60 lb. gauge pressure was obtained when these materials were in the hot-rolled condition.

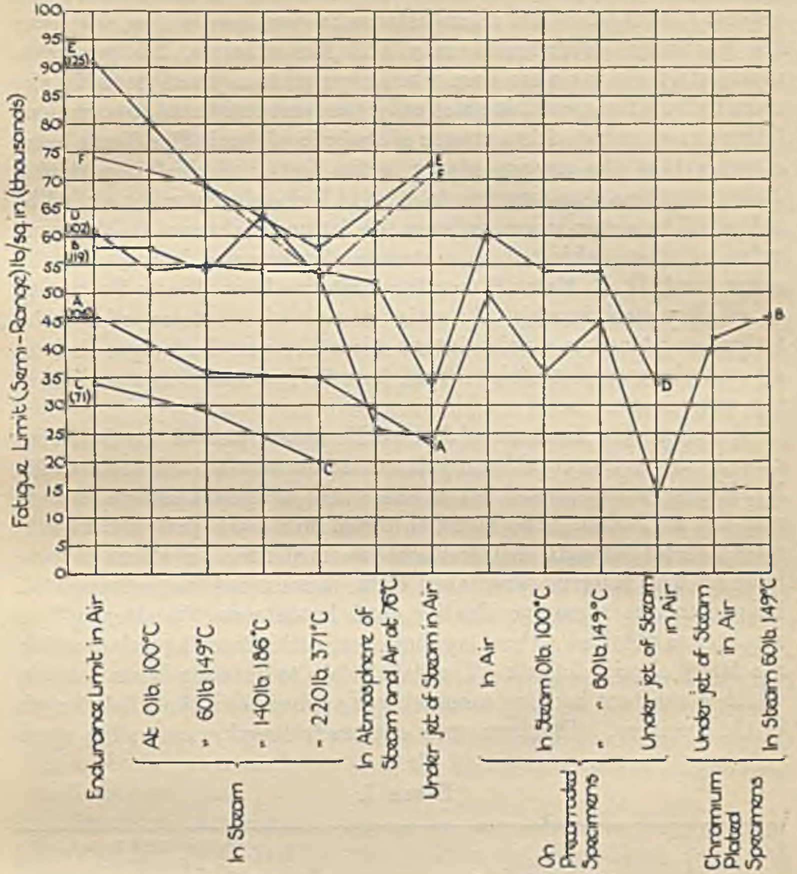

Fig. 30.—Corrosion-Fatigue in Steam.

Curves A and B relate to 3·5% Nickel-Steel (0·35% C).
,, C ,, D ,, Stainless Iron (12·5% Cr; 0·1% C).
Curve E relates to Nitrided Steel (0·36% C).
,, F ,, ,, ,, (0·18% C).
Note.—The figures in parentheses indicate tensile strength.

The results demonstrate the practical importance of using pure dry steam in turbines and the advantages obtaining from the use of suitable water treatment and thorough de-aeration; they bring out clearly the destructive effects produced by the presence of liquid water and of oxygen in steam. The results direct attention to the general factors which are of importance in corrosion-fatigue, whatever the particular environment may be. For example, 3·5 per cent. nickel–steel and stainless iron, when exposed to a jet of steam in air, as in Fuller's tests, exhibit practically the same resistance to corrosion-fatigue as when tested in a stream of water in air, as in McAdam's tests, showing that the oxygen supply is the factor of chief importance. Fuller mentions that exposure to a jet of high-velocity moist air, while subjected to cyclic stress, reduces the fatigue resistance to the same value as when subjected to a stream of tap water in air. On the other hand, H. F. Moore[42] mentions tests made at Illinois University on an alloy steel, in which the action of a jet of wet steam reduced the fatigue resistance to a value intermediate between the fatigue limit in air and the corrosion-fatigue limit (2×10^7) obtained in a stream of tap-water in air.

Owing to the kindness of Dr. E. Honegger, and of the firm concerned, the author is able to refer to some unpublished tests which Dr. Honegger has carried out at the works of Messrs. Brown, Boveri and Co. at Baden. The material tested was 3–3·5 per cent. nickel–steel (tensile strength 85,000–92,000 lb./in.^{2}) used for steam turbine blades. The material was taken from various batches, although all bought to the same specification, and hence some "scattering" of results was obtained; these lay, however, within limiting values which are fairly clearly defined. The data relate to rotating beam tests in which a constant bending moment was applied over the whole length of the specimen. The tests were extremely lengthy, extending up to

TABLE I.

Condition.	Fatigue Limit lb./in.^{2}. (2×10^8)	
	Limits.	Average.
In air	46,000–40,000	43,000
In air (chromium-plated)		
In hot water at 100° C.		
In air; specimen covered with film of oil .		
In atmosphere of dry saturated steam at 100° C.	34,000–26,000	30,000
In atmosphere of dry saturated steam at 100° C. (chromium plated)	32,000–23,000	27,500
In water stream	23,000–18,000	20,500
In water stream (chromium plated) . .	25,000	25,000

200 millions of stress reversals, at which stage the S/N curves had all become nearly parallel to the N axis. The results obtained are given in Table I.

A film of oil or chromium plating has not affected the fatigue limit in air, whilst the hot-water test shows that the "temperature" effect of the steam can be neglected. The corrosion-fatigue limit (2×10^8) in steam has a value intermediate between that of the fatigue limit in air and the corrosion-fatigue limit (2×10^8) in water. Little, if any, improvement was afforded by chromium plating in the steam or water tests: this, however, may have been caused by faults (discontinuities, internal stresses, &c.) in the actual coating employed. Fig. 31 (Plate XIV) is of interest: all three specimens of the nickel–steel tested by Dr. Honegger were bent cold after lengthy fatigue tests. Specimen 1 remained unbroken after 30,180,000 cycles of ± 45,000 lb./in.^{2}, tested in air. No cracks are visible on the surface after bending. Specimen 2 was subjected, in the water stream, to 47,880,000 cycles of ± 14,200 lb./in.^{2} and removed from the machine. The surface was rusted, but a careful examination failed to reveal any signs of cracking. The specimen was then bent, and the photograph shows the profuse system of cracks which appeared. Although the specimen had been tested at a range of stress which was considerably less than the corrosion-fatigue limit (2×10^8), a large number of fine cracks had been initiated during the corrosion-fatigue stage which opened up under the subsequent bending action. Given a sufficiently lengthy number of reversals, this specimen would probably have failed ultimately under corrosion-fatigue. Specimen 3 shows the appearance, after subsequent bending, of a chromium-plated specimen which had withstood 48,260,000 cycles of ± 17,000 lb./in.^{2} in the water stream: very faint signs of cracking are revealed, although the range of applied cyclic stress was much lower than the apparent corrosion-fatigue limit for these conditions.

The above experiments appear to the author to indicate that, provided the broad facts of the problem are appreciated, failure by corrosion-fatigue should not be a source of anxiety in connection with turbine plant that has been carefully designed and is properly maintained.

7.—CORROSION ACCELERATORS AND INHIBITORS.

Laboratory researches into corrosion-fatigue usually involve experiments in which the uniformity of the environment is carefully controlled and maintained within close limits. It has previously been shown that the resistance of a metal to corrosion-fatigue depends much more on the corrodibility of that metal in relation to its particular environment than on the physical and mechanical properties of the metal. Hence, it is impossible to assign to a metal for all conditions any such definite property as a "corrosion-fatigue limit," even if S/N curves did become parallel to the N axis. The dangers of attempting to translate laboratory results into practice have been emphasized and the important influence of such factors as cyclic frequency and time has been discussed. It might, however, be assumed that if these factors were maintained constant in relation to the same metal and environment, reproducible results would normally follow: such an assumption, however, is generally unwarranted and dangerous. It is true that, under laboratory conditions, good repeat results of corrosion-fatigue tests are usually obtained, but this is due to the fact that not only are the *main* conditions of test exactly similar, but also because small *local* differences are reduced to a minimum. It is essential to recognize that small local variations in the environment or condition of the surface of the metal may produce effects which are far greater in magnitude than those resulting in circumstances from which such local variations are absent, although the general or average conditions of corrosion and stress remain unchanged. Local variations of concentration of the corrosive agent or of the oxygen supply in the environment assume great importance, also non-uniformity in the surface condition of the metal itself. Thus, a discontinuous coating of protective material is generally more harmful than if the coating had been entirely omitted. Local variations producing destructive effects may be termed *corrosion accelerators.* Again, although in the future considerable reliance may be placed on protective coatings to reduce corrosion-fatigue, many cases occur where the use of corrosion inhibitors offer considerable advantages. A study of the characteristics of corrosion accelerators and inhibitors is thus of great importance in corrosion-fatigue phenomena, and in this connection the valuable researches of Speller, McCorkle, and Mumma [49, 50] will repay detailed study.

Their experiments were made in a rotating-beam testing machine, operating at 1800 r.p.m.; all solutions were maintained completely saturated with oxygen, and the stressed portion of the specimen was entirely surrounded by a stream of the solution. Fig. 34 shows the results obtained with a normalized 0·35 per cent. carbon steel. Curve *a* is the air endurance curve; curve *b* relates to corrosion-fatigue tests made in synthetic tap water (25 p.p.m. sodium chloride + 25 p.p.m. sodium sulphate). Curve *c* shows the effect of adding to the tap water 200 p.p.m. of sodium dichromate as a corrosion inhibitor. Not only has the sodium dichromate prevented lowering of the fatigue limit, but the *S*/*N* curve has been moved bodily to the right, due to the cooling effect of the stream: curve *c* is probably closer than curve *a* to the true form of the endurance curve (in the absence of all corrosion) for this material. A number of specimens were painted at the centre with a narrow band of paint which was inert to the steel, and these were tested in the same solution (tap water plus inhibitor) as that used for the experiments of curve *c*. The results are expressed by curve *d*. The position of curve *d*, intermediate between *b* and *c*, shows that some degree of protection has been afforded, but the failure to inhibit corrosion-fatigue is possibly due to differential aeration or a surface tension effect making the stressed metal more anodic at the edge of the paint band, and thus breaking down the protective film of the inhibitor at that section. In order to produce more severe localization of corrosion conditions, specimens having a tightly fitting narrow

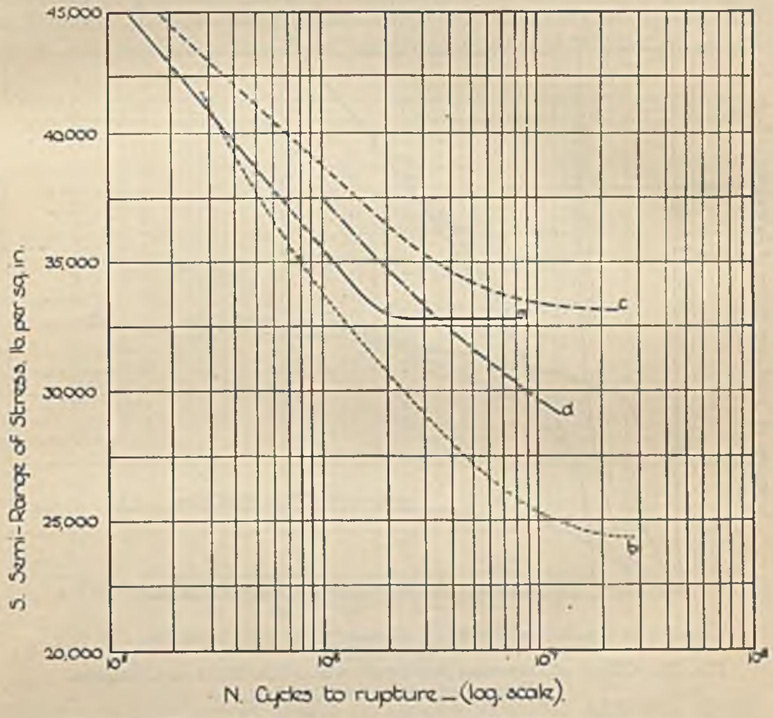

FIG. 34.—Effect of Corrosion Accelerators and Inhibitors on Corrosion-Fatigue of 0·35% Carbon Steel.

rubber washer instead of the paint band were tested in the same solution. The protective effect of the inhibitor was completely broken down, the results falling either on or to the *left* of the curve *b* : fracture always occurred at the edge of the washer, and the position of the fracture could be altered at will by moving the washer along the specimen. Tests made on 0·42 per cent. carbon steel similarly showed the increased destructive effect of a local corrosion accelerator, the fitting of a rubber ring to specimens tested in synthetic tap water resulting in considerably reduced endurances to fracture. Generally similar results were obtained from tests on stainless iron (chromium 18·5, carbon 0·07 per cent.). The endurance limit for this material was ± 45,000 lb./in.^{2}, but when tested in synthetic tap water, under conditions of general corrosion fatigue, the ordinate to the *S*/*N* curve at 10^7 reversals was ± 38,000 lb./in.^{2}, whilst when rubber washers were fitted, the whole curve was displaced downwards, the corresponding ordinate being ± 36,000 lb./in.^{2}. Fig. 35 gives the results of a series of tests on 0·42 per cent. carbon steel made to determine the comparative usefulness of additions, to salt solutions of various concentrations, of different

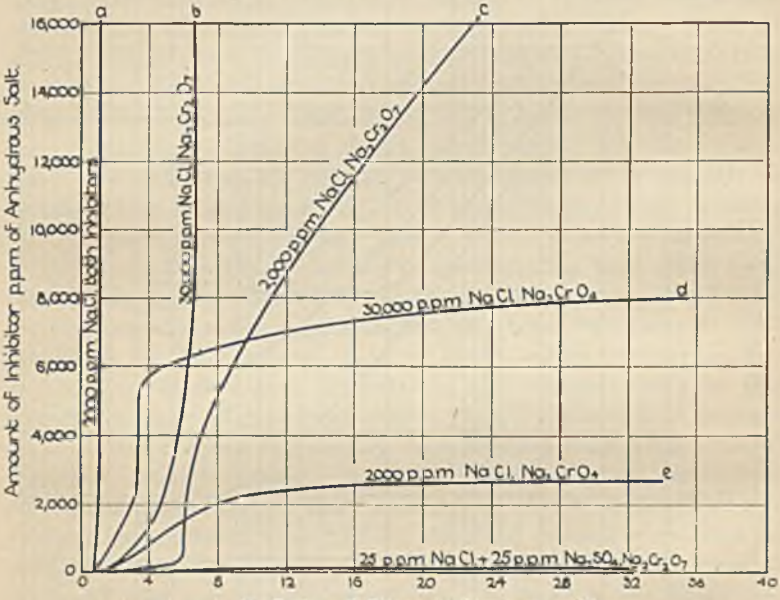

FIG. 35.—Effect of Corrosion Accelerators and Inhibitors on Corrosion-Fatigue of 0·42% Carbon Steel.

amounts of two well-known inhibitors (sodium chromate and dichromate) in lessening the damage caused by general and local corrosion-fatigue. All specimens were tested at the same range of stress, ± 34,000 lb./in.² (which is ± 2000 lb./in.² below the air endurance limit; see Fig. 36). This value was chosen in order to eliminate thermal effects and to preserve all the tests under corrosion-fatigue conditions. A study of these curves discloses the following results: general corrosion-fatigue in mild salt solution was overcome by the addition of small additions of the *dichromate* inhibitor (curve *f*), but very large additions could not prevent failure in solutions of 2000 and 30,000 p.p.m. of sodium chloride (curves *b* and *c*); whilst sufficient additions of the *chromate* to these strong solutions were effective (curves *d* and *e*). When, however, a corrosion accelerator in the form of a tightly fitting rubber washer was fitted to the specimens, very large additions of *either* inhibitor were equally ineffective in preventing local corrosion-fatigue. It may be mentioned that, as compared with the protection afforded under stressless corrosion conditions, both inhibitors show enormously reduced usefulness under corrosion-fatigue.

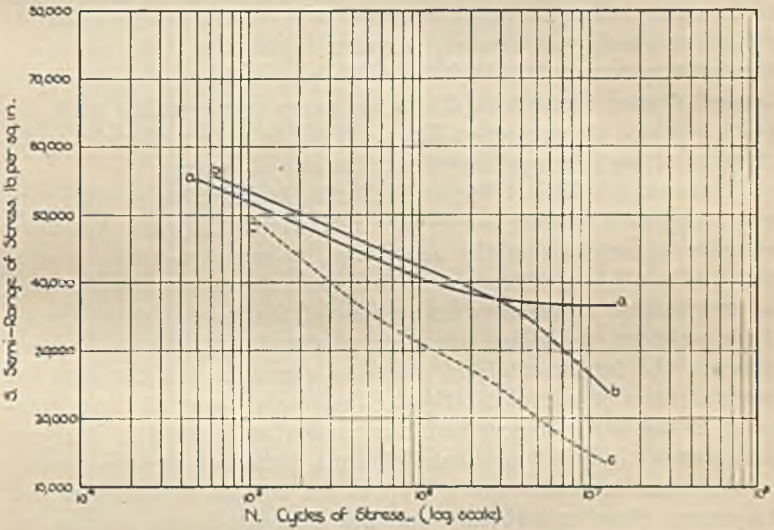

FIG. 36.—Effect of Corrosion Inhibitor on Corrosion-Fatigue of 0·42% Carbon Steel.

A very interesting example of the complex actions which occur in solutions containing inhibitors is shown in Fig. 36: these tests were also made on the 0·42 per cent. carbon steel. Curve *aa* is the air endurance curve, *cc* represents general corrosion-fatigue in a strong salt solution (30,000 p.p.m.), whilst curve *bb* shows the effect of the addition of 2500 p.p.m. of the dichromate inhibitor. Although the addition of inhibitor is insufficient to prevent corrosion-fatigue, it confers endurances greater than those obtained in tests made in air when the nominal stress ranges exceed the air endurance limit. This increased performance was not due to the absence of corrosion: copious corrosion products were observed, and the surfaces of the specimens were covered with small pits. The shape of the curve probably indicates that the inhibitor had retarded the process of pit formation to such an extent that the cooling effect of the stream was effective in displacing the curve bodily to the right until sufficiently low stresses were reached at which thermal effects were mainly eliminated. Another explanation is the decreasing film-building power of the inhibitor as the pits at the most strained part became deeper, the sudden dip in the curve corresponding with the point at which the protective film could not be re-formed under cyclic stress resulting in a rapid increase in the rate of damage.

These experiments of Speller, McCorkle, and Mumma provide very interesting data relating to corrosion inhibitors. They are even more valuable in emphasizing the importance, in corrosion-fatigue phenomena, of small *local* differences of conditions the effects of which may be much more destructive than those of the general environment. Their publication directed attention to the direct link which exists between the fundamentals of stressless corrosion and the essential characteristics of corrosion-fatigue. Previously, many of those interested in the latter subject had been somewhat inclined to interpret the results entirely in " mechanical " terms, giving consideration mainly to the stress concentrations set up at the bottom of corrosion pits. Important these undoubtedly are, but corrosion-fatigue phenomena are incomprehensible until the problem is considered from the aspect of the formation and stability, repair, penetration by diffusion, or breakdown, of surface films. Also the essential differences between stressless corrosion and corrosion-fatigue are difficult to reconcile until the effect of cyclic strain on the film is considered.

8.—The Importance of Oxygen as a Factor in Fatigue.

" Corrosion-fatigue " and " fatigue " are terms usually applied to distinguish between two groups of phenomena which are often regarded as essentially different in nature although possessing many features in common. Yet, although this division is useful and generally practicable, it cannot be justified on any scientific grounds, as will become apparent if attempts are made to prepare discriminative definitions. Much too careless a use is made of the type of "definition," such as, for example, "that corrosion-fatigue is in operation when a metal is exposed to an agent of a corrosive nature and subjected simultaneously to alternating stresses, resulting in destructive effects greater than those obtained when either action is operating alone." Many experiments are on record the results of which are incomprehensible when considered in this way. Again, if the term "fatigue" is to be restricted to the fracture of metals under alternating stresses in an environment entirely devoid of corrosive substances, it becomes open to doubt if many real fatigue tests have ever been made; certainly the usual type of test made in air cannot be placed definitely in this class, as air must be considered as of a corrosive nature, however mild. A useful insight into the importance of this aspect of the subject will be obtained if some critical consideration is given to various unrelated experimental results selected from the literature.

A number of experiments was made by Haigh[17] to determine whether, in typical rolled and extruded brasses, fatigue was accelerated by the presence of various corrosive fluids in contact with the metal during test. For this purpose, a pad of cotton, moistened with corrosive and exposed to the atmosphere, was tied round the mid-section of the specimen and moistened from time to time. It was found that ammonia reduced the fatigue strengths of annealed Muntz metal ($\alpha + \beta$) and Naval brass ($\alpha + -$) by 15 per cent. and 17 per cent., respectively, but dilute hydrochloric acid did not affect the fatigue strength of the Naval brass, and a similar result was found with phosphor–bronze (α) tested in contact with ammonia, hydrochloric acid, and sea-water. In fact, the endurances of specimens moistened with hydrochloric acid were generally greater than those of dry specimens tested in air under the same ranges of stress. With regard to the absence of marked attack, it should be pointed out that Haigh's tests rarely extended to more than three million stress cycles, and were insufficiently lengthy to show up the full effects of combined corrosion and fatigue; also, the increased endurances recorded might be partly due to the cooling effects produced by the wet pad. However, the observations induced Haigh to remark that "the atmosphere, as well as chemical reagents, may act chemically upon the metal." These early experiments were somewhat inconclusive, although possessing definite historical interest. The points raised received no further attention until 1926, when experiments made by Lehmann,[23] in Professor C. F. Jenkin's laboratory at Oxford, gave results some of which appeared to be incompatible with the view that simultaneous chemical action and alternating stress produced accelerated destructive effects. With the express object of producing marked corrosive action, hot aqueous solutions of considerable concentrations were employed. The tests were made in a specially designed vertical fatigue machine of the Wöhler type: a tube enclosed the specimen, the aqueous solution entirely filling the space between the specimen and tube; the solution was heated by a steam jacket surrounding the tube. Tests made on a normalized 0·33 per cent. carbon steel gave the curious results shown in Table II.

TABLE II.

Condition of Test.	Temperature, ° C.	Endurance Limit (10^7 cycles), lb./in.^{2}.
In air	17	±41,000
In air (after immersing in sulphuric acid for 2 hrs., washing and drying)	17	±37,600
In distilled water	96	±38,800
In sodium nitrate solution * (2 parts H_2O : 1 part $NaNO_3$)	96	±39,100
In sodium chloride solution (3 parts H_2O : 1 part NaCl)	96	±41,200
In ammonium chloride solution (3 parts H_2O : 1 part NH_4Cl)	96	±32,500

* Lehmann records that the specimens were slightly pitted, the pits increasing in number along the specimen with increase in stress, whilst an unstressed specimen exhibited an even spacing of pits. This is an interesting example of the effect of cyclic stress on corrosion pitting.

With the exception of the tests in ammonium chloride solution, little or no reduction in fatigue resistance resulted from substituting a strong salt solution, at 96° C., for air as the environment. These results were surprising, and raised considerable discussion; one obvious explanation was that the mild attack produced was due to the general absence of air from the hot " corroding " solution. Further tests to explore this point were made by Binnie,[4] using the same steel. He found that a salt spray (1 part sodium chloride to 4 parts of water) in air produced very destructive results, also that the same effect was obtained when the solution was allowed to drip slowly on to the specimen. When an atmosphere of commercial hydrogen was substituted for air, little improvement was recorded in the resistance to salt drip, but when similar tests were made in an atmosphere of much purer hydrogen, marked improvement resulted. Results of a similar nature were obtained from tests made on 0·9 per cent. carbon steel.

The appearance of the specimen surfaces was also informative. With the salt drip in air the surfaces rapidly blackened, whilst in the

TABLE III.

Condition of Test.	Endurance Limit (10^7 cycles), lb./in.^{2}.	
	0·33% Carbon Steel.	0·9% Carbon Steel.
In air	±41,000	±38,100
Salt solution dripping through air . . .	±20,600	±16,800
Salt solution dripping through commercial hydrogen	±21,000	±20,400
Salt solution dripping through purified hydrogen .	±26,400	...

hydrogen tests a very slight darkening could be detected only after several millions of stress cycles. It appears probable, therefore, that in absolutely pure hydrogen specimens would remain bright throughout the test. The types of fracture were also extremely interesting. With a salt drip in air, fracture was not confined to one plane, but a number of cracks appeared, leading to a fracture of serrated appearance. Under a salt drip through purified hydrogen, however, the resulting fracture was indistinguishable from that of an ordinary fatigue fracture in air. The results show the improvement effected by the substitution of hydrogen for air, and while they can only indicate that further improvement would be effected if *every* trace of oxygen could be eliminated, they do assist to explain Lehmann's results. Similar conclusions are reached from the tests of Fuller[8, 9] made in atmospheres of steam of varying oxygen contents, to which previous reference has been made.

Some tests by McAdam,[29] published in 1927, are also relevant. Electrolytic copper in the hot-rolled (fully annealed) and cold-worked (low annealed) conditions, also fully annealed 78 : 21 nickel–copper alloy, were tested in air and under corrosion-fatigue conditions (*a*) in a stream of fresh (carbonate) water, and (*b*) in a stream of river water having a saline content about one-sixth that of sea-water; these tests extended from 20 to 80 millions of stress cycles. For each of the three materials mentioned, the S/N graphs of the fresh- and salt-water tests were practically coincident, each falling slightly, but definitely, above and to the right of the corresponding graph for tests made in air. That the first part of the corrosion-fatigue graphs lay above the air curve is not at all surprising: this feature is often observed in similar tests, and is due to the cooling effect of the water stream. The problem is to explain why these graphs *remained* in the same relative positions after they had become practically parallel to the N axis. Chemical action was undoubtedly in operation, for the surfaces of the specimens tested in water became heavily coated with corrosion products. The fact that the S/N graphs for the corrosion-fatigue conditions were nearly, if not quite, asymptotic to a limiting value of S, suggests that a state of equilibrium had been established, probably due to protective film formation, or to the arrest of further damage owing to the shielding effects of the corrosion products, but, even so, corrosion-pitting must previously have been in operation, and while the effects of such pitting on the fatigue resistance of the corroded specimens may have been so small as to be inappreciable, one cannot reasonably consider that the corrosive attack could have produced *increased* fatigue strength. McAdam made some experiments to examine the possibility that the ordinary tests in air gave unduly *low* results owing to *atmospheric oxidation.* He tested, in air, specimens of copper covered with various protective coatings—mixtures of vaseline and rubber, also vaseline and paraffin, Japan drier, and a mixture of shellac and lacquer—but found that the endurances obtained lay on or near the ordinary fatigue graph, from which he concluded that the ordinary fatigue graph had *not* been influenced by atmospheric corrosion. He then suggested that these materials possessed an " intrinsic corrosion-fatigue limit " which could not be developed in ordinary fatigue tests owing to the physical limitations of the materials. A much simpler explanation is now available.

In the first place, the tests of McAdam on coated specimens *cannot* be accepted as proving that atmospheric corrosion had no effect on the endurance limit of his alloys; the coatings were probably permeable to air. Recently it has been shown [14] that the substitution as environment of a good vacuum for air can result in an increase of 13 per cent. in the fatigue limit of copper. The author would suggest, therefore, that the real fatigue limits of McAdam's alloys in the absence of all corrosive influences were appreciably higher than those obtained from his endurance tests in air. Under corrosion-fatigue conditions, using fresh and salt water, corrosion at first took place, resulting in pitting followed by the attainment of a state of equilibrium. Stress concentrations due to the pitting were in operation, reducing the fatigue limits to values which, whilst lower than the real fatigue limits of these alloys, were yet slightly higher than the values normally obtained in air. This explanation, which is entirely compatible with our usual experience of corrosion-fatigue phenomena, is sufficient to explain satisfactorily the results of McAdam's experiments.

Some experiments on lead and lead-alloys made by Haigh and Jones,[19] and published in 1930, form the next link in the chain. The behaviour of lead under fatigue is particularly interesting as the normal path of the fatigue fracture is intercrystalline, this material being peculiar * in this respect. That the intercrystalline failure of the lead sheathing of cables is directly attributable to fatigue was satisfactorily demonstrated by Townsend [52] in 1927, and independently confirmed by Beckinsale and Waterhouse [2] in 1928. In discussing the tests of Haigh and Jones on lead alloys, it is necessary to remark that even the tests made in air were insufficiently lengthy to indicate the existence of a definite limiting range of stress; probably experiments extending to many hundreds of millions of stress cycles are required to determine whether the S/N curves for these alloys become parallel to the N axis, therefore, the results can be discussed only with reference to the *shape and position* of the endurance curves. Comparative tests on lead were carried out on samples in air and on other samples immersed in a bath of oil. A specimen tested in air at a range of stress of ± 0·25 ton/in.^{2} fractured after 5·6 millions of stress cycles. A similar specimen tested while immersed in oil remained unbroken after 11·7 million cycles of the same range of stress and after further cycles of stress up to and including a range of ± 0·45 ton/in.^{2}. Similar results were obtained with lead alloys containing small proportions of tin and cadmium, also of bismuth. When the unbroken specimens were bent cold after the fatigue tests, the presence of a large number of cracks was observed. Thus it is clear that the substitution of oil for air as the ambient condition had displaced the S/N curve away from the stress axis: fatigue had been "delayed," but not prevented. The results were reasonably interpreted by the authors as indicating that the oil bath had delayed the rate at which air reached the surface of the test-piece, thus suggesting that atmospheric oxygen was a factor entering into the ordinary process of fatigue of lead alloys. A layer of grease was found to be less effective in delaying fatigue than a bath of oil. In order to adopt *chemical* means of removing air from the surface of the test-piece, the authors made other tests in which samples of lead alloys were tested while immersed in a bath of acid, so that any acid attack set in operation would liberate nascent hydrogen which would combine with any oxygen present. Acetic acid was chosen, as this was known to attack lead, provoking intercrystalline failure. Specimens of lead tested in the acid bath remained unbroken after 8·5 million cycles of ± 0·35 ton/in.^{2}, although the specimens were deeply corroded in the process; subsequent cold-bending tests failed to show up any cracks. Other tests in which the specimen surface was

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* As the author pointed out in discussing this paper by Haigh and Jones, fatigue tests made at air temperature on a metal such as lead, which possesses a low melting point, probably should be considered as equivalent to tests made at *very high* temperatures on other alloys of relatively much higher melting points: hence intercrystalline fatigue fractures *may* not be really exceptional.

merely *moistened* with a trickle of acetic acid gave endurances which were no greater than those obtained in tests conducted on dry specimens in air.

These tests of Haigh and Jones are undoubtedly important. They suggest strongly (1) that oxygen is a factor in the normal process of the fatigue of lead and some lead alloys, (2) that as the available oxygen supply to the specimen surfaces is reduced, the endurance of the specimens is improved, (3) that the beneficial effect produced on the fatigue resistance by reducing oxygen more than outweighs the destructive effects brought about by roughening the surface of the specimen by acid corrosion: but the authors' claim that, in the tests made in a bath of acetic acid, the chemical action had " successfully eliminated oxygen *and* fatigue," cannot be accepted as having been established by the data presented. Very much more lengthy endurances and a much wider range of stress cycles must be investigated before such a significant claim can be logically advanced. The present author would suggest that a rational interpretation of these experiments is that they have shown definitely that, in fatigue tests on some lead alloys, the decrease of oxygen in the environment has resulted in a displacement of the S/N curve away from the S axis and probably also away from the N axis, but to extents that were not determined. Considered in this way, the results are entirely consistent with the experiments of Haigh,[17] Lehmann,[23] McAdam,[29] and Binnie,[4] to which reference has been made.

Some very curious and apparently contradictory results, obtained quite independently, thus become intelligible and consistent if we *assume* that atmospheric oxygen is a factor in ordinary fatigue tests, but the results themselves offer evidence only of an *indirect* nature on this point. Tests made *in vacuo* or in atmospheres of inert gases were obviously required to give *direct* evidence; such tests are in progress at the National Physical Laboratory, and some results are now available. Gough and Sopwith [14] have determined the fatigue limits, under reversed direct stresses, of a range of materials tested (*a*) in air, and (*b*) in a partial vacuum in which the air pressure was not greater than 10^{-3} mm. of mercury.

The fatigue limits marked thus * in Table IV represent average values, as some " scatter " of results was obtained; the effect of the partial vacuum was, therefore, not clearly established. From the other tests it is evident that the atmosphere definitely affects the fatigue resistance. The effect on steels is but slight, as a 5 per cent. increase in fatigue limit *in vacuo* is the maximum recorded. The magnesium alloy appears to be unaffected by the change of environment. Copper and brass, however, show increases of no less than 14 per cent. and 26 per cent., respectively, the latter being a really remarkable improvement.

TABLE IV.

Material.	Fatigue Limits, tons/in.².		Ratio. Fatigue Limit in Vacuum/Fatigue Limit in Air.
	In Air.	In Partial Vacuum.	
0·5% Carbon steel (cold-rolled) .	±21¾*	±22½	1·03
Stainless steel (Cr 15, C 0·12%) .	±22	±22¼	1·01
Stainless steel (Cr 18, Ni 8, C 0·1%)	±24¾*	±24¼	0·98
Stainless steel (Cr 17, Ni 1, C 0·25%)	±28¼	±28¼	1·00
Duralumin	± 7¾*	± 8¼	1·06
Magnesium alloy (Al 2·5%) .	± 5½	± 5½	1·00
0·13% Carbon steel . . .	±13·0	±13·7	1·05
Copper (99·96%) annealed . .	± 4·3	± 4·9	1·14
Brass (70 : 30) annealed . .	± 7·2	± 9·1	1·26

It is possible that the use of higher degrees of *vacua* may reveal even greater increases in the fatigue limits of the same materials, also, other materials may be even more sensitive to atmospheric corrosion. Lead is a metal which should also be tested *in vacuo*, but these few tests already reported afford the necessary amount of direct experimental evidence which was needed to enable us to reconcile the results of Lehmann, McAdam, Binnie, and Haigh and Jones. In future, the fatigue resistance of a metal as determined *in vacuo* should be regarded as the real standard of comparison; if any other environment is used, the fatigue resistance may be equal to, or less than, this optimum value, but it is reasonable to suppose that—apart from temperature effects—it cannot be greater, although in certain circumstances the value obtained may exceed the endurance limit when tested in air. Should the environment be such as to permit of chemical attack in the presence of an adequate supply of oxygen, then the mechanical and physical properties of the film formed will decide entirely whether a temporary or a progressive destructive effect is set in operation. That oxygen *must* be the factor of primary importance in the combined process of corrosion and fatigue follows from the definition of corrosion, and it is curious that the various unrelated experiments dealt with in this section have been often regarded as "mysterious"; actually no mystery existed—all that was required was direct experimental evidence that oxygen is a factor in fatigue. This evidence has now been obtained.

Assuming that the *maximum* possible fatigue resistance of an alloy is determined when tested *in vacuo*, it may be of interest, from a design point of view, to consider the test conditions which would determine the *minimum* fatigue resistance of the same alloy when exposed simultaneously to cyclic stress and to a particular corrosive solution. Our present experience would suggest that this liquid should be *sprayed* on to the surface, thus making available an excess of oxygen. To these conditions should be added some local shielding factor, so that a portion of the surface would be completely screened from oxygen while a neighbouring portion was fully exposed, or to bring surface tension effects into operation; for this purpose, a tightly fitting rubber ring, such as used by Speller, McCorkle, and Mumma,[49] would probably be suitable. Under such test conditions, favourable both to severe general and local corrosion, very destructive corrosion-fatigue effects might reasonably be expected to develop. It is suggested, therefore, that a laboratory test, on the lines indicated, might be useful to obtain comparative data; these data should be of greater value than those obtained under corrosion-fatigue conditions in which " general " corrosion only is in operation.

9.—CORROSION-FATIGUE PHENOMENA AS EXHIBITED BY CHANGES OF MICROSTRUCTURE.

When one recalls the valuable additions that have been made by the aid of the metallurgical microscope to the knowledge and understanding of the mechanism of the deformation and fracture of metals, it is somewhat surprising to find that such limited attention has hitherto been given to the changes in microstructure occurring during corrosion-fatigue. It is, however, a fact that no systematic study has yet been made in this direction: as a result, little information exists on such fundamental points as (1) the actual point of initiation of a corrosion-fatigue crack; whether it is situated at a crystal boundary, or on the site of previous slip bands, or at local corrosion pits bearing no distinct relation to these special positions; (2) the general course of a crack, whether intercrystalline or transcrystalline, and (3) whether the existence of a " corrosion-fatigue limit " receives support from visual observations.

Systematic researches are in progress on these aspects in at least one laboratory at the present time, although the results are not yet fully available; a certain amount of valuable information, however, can be gained by careful examination of certain published results and of unpublished photographs and data which various correspondents have been good enough to place at the author's disposal.

To show the broad characteristics of corrosion-fatigue cracks, reference may be made to the failure of the piston rod of a Diesel engine which has been previously referred to (see Figs. 2 and 3 (Plates I and II)), the microstructure of which has been examined by the author and his colleague, Dr. C. H. M. Jenkin. The piston rod, of 0·36 per cent. carbon steel, was hollow-bored for water-cooling, and failure occurred owing primarily to the stresses due to cyclical thermal changes in conjunction with the corrosive attack of the circulating water: the rod fractured by circumferential cracks perpendicular to the axis of the rod. In Fig. 2 (Plate I) some of these cracks are visible on the inner surface of the rod in various stages of development. Fig. 4 (Plate II) is a composite photomicrograph of one of the smaller of these cracks. At the "mouth" of the crack a considerable degree of corrosion has occurred; the width of the corrosion pit decreases as the depth increases, and ends in a very fine crack which is indistinguishable from an ordinary fatigue crack and which penetrates for a considerable distance into the metal. Examination, under high magnification, of this crack showed that it did not follow the grain boundaries of the ferrite or the pearlite areas but passed through these without discrimination. No precise information can be gained from a fracture of this sort of the location of the initiation of the damage. The appearance of this crack is quite typical, however, and illustrates admirably the general mechanism of the corrosion-fatigue process whereby a surface effect of conjoint corrosion and stress produces a pit which penetrates into the material to a depth at which the "notch" effect is sufficient to start a fatigue crack which then spreads in the usual manner. As the photomicrographs now to be discussed have been taken mostly from specimens tested in the laboratory, Figs. 37 and 38 (Plate XV) will give preliminary assurance on an important point. Fig. 37 shows a section through the wall of a steel (18 : 8 : 1 chromium–nickel–tungsten) tube used, in service, to convey boiling ammonium sulphate which passed through the tube at a sufficiently high velocity to cause vibration of the tubes: failure has occurred by corrosion-fatigue. Fig. 38 shows a corrosion-fatigue failure of a laboratory test specimen of 18 : 8 : 1 chromium–nickel–tungsten steel which fractured after $11{\cdot}167 \times 10^6$ cycles of $\pm 8{\cdot}3$ tons/in.^{2} whilst subjected to a drip of (neutral) ammonium sulphate liquor, at 50° C. throughout the test. The essential features of the failure are the same in both cases, although the roughening of the surface of the service tube is more pronounced owing to the shorter time occupied by the laboratory test. These, and many similar examples, also comparisons of the appearance of the fractures show clearly that corrosion-fatigue failures in service and in the laboratory exhibit essentially similar characteristics, and, hence, the experience gained by study of the latter can be used, with confidence, in interpreting the cause of the former.

With the exception of lead,[2, 52] the author is not aware of any other metal in which the normal course of ordinary fatigue failure in air follows the crystal boundaries. In view, however, of the marked tendencies of certain metals and alloys to fail along the boundaries when exposed to corrosive influences, it would not be surprising to find that these would also fail in a similar manner under corrosion-fatigue conditions. Corrosion-fatigue cracks of this nature, however, appear to be extremely rare. Fig. 19 (Plate X) shows the failure of a lead (chemically pure) pipe used for carrying 70 per cent. sulphuric acid at 140° C.; failure was due to the combined effects of corrosion and alternating stress, the latter being caused by vibration of the pipe due to an adjacent motor. Intercrystalline cracks are clearly visible, but in this case it should be remembered that this metal would probably have failed in an exactly similar manner had corrosive influences been absent.

Duralumin is an alloy well known to be prone to develop intercrystalline cracking under corrosive conditions, and in view of the number of corrosion-fatigue tests that have been carried out on Duralumin, surprisingly little is known of the method of failure under these conditions; some informative tests, however, have been made on Duralumin sheet by Rawdon.[45] In these tests, specimens were subjected to reversed flexure at 75 cycles per minute. At intervals of 15 minutes, the specimens were immersed for 1 minute in a normal solution of sodium chloride (5·5 per cent. by weight) to which had been added an amount of commercial hydrogen peroxide solution equal to 0·1 of the total volume. Under these severe conditions, the Duralumin failed by intercrystalline cracks, but this was also the method of failure under conditions of stressless corrosion, or of corrosion while subjected to static tensile stress. The above examples are the only recorded cases, to the author's knowledge, of intercrystalline failure under corrosion-fatigue conditions. R. R. Moore[44] made some tests on Duralumin tubes to determine the effect of corrosion embrittlement on the *normal fatigue resistance.* For this purpose, one set of specimens was subjected to salt spray (20 per cent. sodium chloride) for a total of 40 hrs., applied intermittently during a period of 5 days; a second set for 120 hrs., during a period of 10 days. The fatigue limits of the corroded specimens were then determined in air. It was found that the endurance limit (2×10^8) of both batches had about the same value ($\pm$ 11,000 lb./in.^{2}) representing a decrease of 39 per cent. from the endurance limit (± 18,000 lb./in.^{2}) of the uncorroded material. Photomicrographs[44] of the tubes after corrosion, and before the fatigue tests, showed that marked intercrystalline attack had resulted. (The maximum depth of the attack was less than 0·001 in. This is interesting in view of the large resulting effect—39 per cent. reduction—on the endurance limit.) These experiments, being of the "prior-corrosion" type, offer no real evidence on the course of fracture during corrosion-fatigue; they show, however, that if intercrystalline failure *were* to occur, marked destructive effects might result. Schulz and Buchholtz[47] have published photomicrographs of the paths of corrosion-fatigue cracks in structural steels, and remark that they "are principally transcrystalline, and only in a few cases follow the grain boundaries"; some further photomicrographs which Professor E. H. Schulz has kindly sent to the author can be similarly described. McAdam has remarked, on various occasions, on the course of corrosion-fatigue cracks, but in somewhat contradictory terms, and it does not appear that he has yet found opportunities for a thorough investigation of this aspect of the subject. In discussing his 1926 paper[27] he said, "Whether or not corrosion-fatigue cracks originate in the metallic inclusions or pores in the metal, their chief progress is probably along intercrystalline boundaries. Preliminary investigation of ingot-iron indicates that for this material corrosion-fatigue failure is at least partly intercrystalline," and "Microscopic examination of failed corrosion-fatigue specimens of a variety of steels has not revealed any purely intercrystalline fracture. In its path from one inclusion to another, however, a crack sometimes deviates and for a short distance follows intercrystalline boundaries. It is possible that at lower cycle frequency the higher ratio of corrosion to fatigue may increase the tendency towards intercrystalline fracture." In a later paper,[30] in discussing the great effect of stressless corrosion on aluminium alloys he said, "Intercrystalline corrosion has been frequently found in Duralumin that has been under slow cyclic stress. In Duralumin that has been under rapid cyclic stress, purely intercrystalline cracks have not yet been found." Fig. 32 (Plate XIV) shows a photograph, by Inglis and Lake,[21] of a corrosion-fatigue fracture of a mild steel specimen, fatigued while exposed to a drip of tidal river water; the fracture is predominantly transcrystalline.

Chromium–nickel austenitic steel (18 : 8 : 1 chromium–nickel–tungsten) when heated in the range 500°–900° C. (and especially at 650° C.), followed by slow cooling, is known to be prone to disintegration in an intercrystalline manner when subjected to corrosive attack: the cause is stated to be the precipitation of a carbide. If intercrystalline failure occurs under corrosion-fatigue, this alloy, when in the improperly heat-treated form, should provide an excellent example. But Fig. 33 (Plate XIV) shows a specimen [21] of 18 : 8 : 1 chromium–nickel–tungsten steel cooled in air after heating to 650° C. for 1 hr., and broken under reversed bending stresses while subjected to a drip of tidal river water. The fracture is entirely transcrystalline. Striking evidence that the actual resistance to corrosion-fatigue is not adversely affected by the susceptibility of the boundaries to ordinary corrosion is given by some tests of Fuller [9] on three batches of 18 : 8 chromium–nickel austenitic steel made in an atmosphere of wet steam (at 60 lb./in.^{2} pressure). The "corrosion-fatigue limits" obtained, on a 10^7 cycles basis, were as shown in Table V.

TABLE V.

Carbon Content. Per cent.	Form of Heat-Treatment and Corrosion-Fatigue Limits (10^7 cycles).			
	Hot-Rolled. (1)	Held at 650° C. for 6 hrs.: Air-Cooled. (2)	Held at 650° C. for 500 hrs.: Air-Cooled. (3)	Held at 1150° C. for 1 hr.: Water-Quenched. (4)
0·06	±46,000	±45,000	±34,000	±24,000
0·08	±51,000	±51,000	±21,000	±21,000
0·15	±56,000	±46,000	±40,000	±34,000

As treatments (2) and (3) are known to produce a considerably decreased resistance to corrosion at the crystal boundaries, whilst treatment (4) should produce a satisfactory condition, it is clear that the boundary conditions did not determine the resistance to corrosion-fatigue; hence it is reasonable to infer that the course of the corrosion-fatigue fractures was not intercrystalline. Rosenhain and Murphy [46] subjected bars of mild steel to repeated bending while in contact with mildly corrosive liquids. Each bending operation involved considerable plastic strain and the maximum number of bends to failure was extremely small, whilst varying times elapsed between successive bends, hence the tests bear little resemblance to the usual form of corrosion-fatigue test: probably the significant factors at work were stressless corrosion of severely deformed metal, and the influence of subsequent strain on the protective film and the corrosion products. However, the interesting observation was made that the fractures were mainly transcrystalline, no sign of intercrystalline cracking being detected.

The available evidence therefore shows clearly that the *paths* of corrosion-fatigue cracks are essentially transcrystalline. It still remains a possibility that the surface *origin* of the crack is intercrystalline. The only published evidence on this point is due to Ludwik,[24] whose photographs are reproduced as Figs. 39 and 40 (Plate XVI). These fractures were obtained under corrosion-fatigue conditions employing reversed bending stresses and sea-water. In Fig. 39 it is clearly shown that the crack, in its path, avoids crystal boundaries, passing from crystal to crystal in a direction at right angles to the boundaries, thus behaving exactly in the same manner as the normal fatigue crack. The photograph also shows, in an unmistakable manner, that the intersection of the crack with the surface is well removed from the crystal boundary: it offers no positive evidence regarding the position of the origin of the crack with relation to the boundaries. Fig. 40, however, affords indisputable evidence on this fundamental point, for the photograph has been taken at a stage when the whole of the crack, seen in the middle of the field, is confined to one crystal grain: this is therefore a definite case of a corrosion-fatigue crack which *cannot* have started at a boundary. Also, assuming that the crack started at the free surface—and the varying width clearly indicates this origin—the course is such as to reduce approach to the boundary to a minimum. It should be noted that both the specimens referred to in Figs. 39 and 40 were tested under truly corrosion-fatigue conditions. The aluminium specimen fractured after 10^7 cycles of $\pm$ 4270 lb./in.^{2} followed by $1{\cdot}5 \times 10^6$ cycles of $\pm$ 5690 lb./in.^{2}: the soft iron specimen broke after $6{\cdot}9 \times 10^6$ cycles of $\pm$ 17,000 lb./in.^{2}. The endurance limits, in air, of these materials were, respectively, $\pm$ 8530 lb./in.^{2} and $\pm$ 24,200 lb./in.^{2}.

It has been suggested by several writers that the increased destruction produced when a corrosive environment is present during a fatigue test is due to the change over from the transcrystalline type of failure associated with fatigue in air to the intercrystalline cracking often produced by corrosion. As this explanation—if it were true—would be of great importance in interpreting corrosion-fatigue phenomena, the actual experimental evidence available has been reviewed above at some length: the author suggests that it can be accepted that intercrystalline failure is so extremely rare in corrosion-fatigue as to be regarded as an exceptional occurrence. Thus evidence obtained from changes in microstructure also confirms the view that the essential mechanism of corrosion-fatigue consists of a preliminary process of surface pitting, under the combined influences of corrosion and stress, leading to the initiation of a crack, the subsequent propagation of which through the metal is determined largely by stress concentration effects of the shape of the crack when under cyclic stresses. The cause of the "pitting" may be due, among other causes, to local corrosive attack, removal of inclusions, presence of impurities, cold-worked material, or internal stress. As corrosion is usually regarded essentially as a surface effect in its initial stages, it would appear unreasonable to suggest that the first stages of corrosion-fatigue can occur at any other position than at the metal surface, and every photomicrograph that the author has seen confirms this view. Haigh, however, suggests that the initiation of corrosion-fatigue is *not* at the free surface, and his views merit a frank discussion.

In the first place, Haigh[18] suggests that fatigue failure, under all conditions, is a fracture of the metal caused by triple tensile stress (hydrostatic tension). As such stress conditions cannot be set up at a free surface, it is assumed to occur at some depth *below* the surface. This particular stress system is stated to result from contractions in volume accompanying phase change (from crystalline to amorphous) resulting from the applied stresses. At the region of triple tensile stress brittle fracture occurs; between this region and the outer surface exists a "marginal zone" which is supposed to be relatively immune from fatigue and which often deforms by shear in ductile materials; according to Haigh, plastic deformation by shear is not the cause of fatigue failure, but is a process rather tending to prevent such failure. In support of this general theory of fatigue, Haigh attaches importance to a small "lip," of the cup and cone type, which is sometimes observed on the edge of fatigue fractures. He also states that there exist definite differences in discoloration of the marginal zone and the inner fracture, the discoloration being greatest at the inner edge of the zone where the assumed triple tensile stress condition has been set up. Haigh also believes that the behaviour of a fatigue specimen in the stages immediately preceding fracture is such as to lend support to the view that internal cracking has occurred before surface cracks are rendered visible. In applying the above general theory to failure by corrosion-fatigue, Haigh suggests that the chemical reagent diffuses through the outer layer of metal and reaches the region where a state of triple tensile stress is in existence. This conception is perhaps most concisely stated in the paper by Haigh and Jones[19] in the following words: "The reductions of fatigue strength often observed when water or other reagents act upon the surfaces of test-pieces during the continuance of fatigue tests are attributed only in a small degree to superficial actions, such as corrosion or notching, and chiefly to diffusion into the metal of foreign substances that provoke chemical or physical change under cyclic stress." The present author would merely comment that in the very numerous microscopical examinations of the surface and sections of specimens (excluding such especial cases, of course, as case-hardened and nitrided steels) subjected to fatigue and corrosion-fatigue which have been made by himself and his colleagues at the National Physical

Laboratory, no observation has ever yet been made which suggested that the origin of the fractures was at any point other than at the free surface. It is considered that the photomicrographs referred to above afford exceptionally strong, if not incontrovertible, evidence that initial damage occurs at the surface. Haigh and Jones mention some lead test-pieces the surface of which, after subjection to fatigue stresses when immersed in oil, appeared to be free from cracks: when these test-pieces were subsequently severely deformed by bending, a large number of shallow cracks became visible. They express the opinion that these "shallow cracks broke through the surface from the interior." In Fig. 31 (Plate XIV) the middle specimen, of 3·5 per cent. nickel steel, has been subjected to 47·9 millions of stress cycles of ± 14,200 lb./in.^{2} in a water stream (the *S/N* curve under these conditions is practically horizontal at a value of ± 20,500 lb./in.^{2} after 200 *millions of cycles*). The surface of the specimen was apparently undamaged, no signs of cracking being visible. When, however, the specimen was bent cold, the profusion of cracks shown in the photograph became visible. The tests were made by Dr. E. Honegger, who reasonably assumes that very small surface corrosion-fatigue cracks had been opened out and rendered visible by the deformation of the specimen: general agreement will, the present author suggests, be expressed with this view. Conclusive evidence on the point at issue might be looked for in a *section* through a specimen which has emerged unfractured from an extremely lengthy corrosion-fatigue history under a range of stress far removed from the fatigue limit in air: if cracks were present in such a specimen, some would probably be in the very earliest stages of development. The author is indebted to Professor P. Ludwik for some hitherto unpublished photomicrographs which, it is suggested, afford the required decisive evidence: these are reproduced as Figs. 41 and 42 (Plate XVII). They refer to a section of a specimen of hardened and tempered chromium–nickel steel which withstood, without fracturing, *five hundred million* cycles of ± 18,500 lb./in.^{2} under corrosion-fatigue in tap water. These cracks have attained a *maximum* depth of 0·004 in. only, and were quite invisible on the surface. It is practically certain, however, that these would have been rendered visible had the specimen subsequently been greatly deformed by cold bending; the specimen would have assumed a similar appearance to that of the bent specimens of Haigh and of Honegger. The most careful examination of these cracks fails to suggest any reason for assuming that their origin is anywhere but at the surface of the specimen, and the evidence presented by these photographs and by Fig. 40 (Plate XVI) appears to render superfluous further comment on the

" internal " crack hypothesis. Incidentally, photographs which have been discussed lend considerable visual support to the view that no such property as a true " corrosion-fatigue limit " really exists : the extreme sharpness of the cracks is such that fracture would probably have resulted at some stage had the test been continued for a sufficiently lengthy number of cycles.

There is no doubt that further metallographic study of corrosion-fatigue will add greatly to our knowledge of the finer aspects of corrosion-fatigue phenomena. At the National Physical Laboratory we have commenced with single crystals and specimens consisting of a few large crystals : this type of specimen possesses the special advantage that by the combined use of X-ray, microscopical, and mechanical methods, the observed effects can be related directly to the crystalline structure of the metal and to the applied stressing system. To eliminate altogether the crystalline boundary, a test [13] was made on a single crystal of aluminium tested under alternating torsion at a low frequency, 400 cycles per minute, whilst immersed in a slow stream of ordinary tap water. Throughout the experiment a uniform range of cyclical stress was employed the value of which was less than that required to produce fracture in air, but was sufficient to produce deformation by slip of amounts varying round the specimen according to the known stress distribution based on the X-ray analysis. (Single crystals offer unique opportunities for metallographic study, as the plastic deformation follows established laws : by comparing the behaviour of different parts of the specimen, deductions can be made from one specimen equivalent to those obtained from a *number* of ordinary specimens.) The specimen fractured after 24×10^6 stress cycles, the microstructure being observed at intermediate stages. The main characteristics observed were threefold : a general pitting attack, a local attack, and preferential corrosion on the site of slip bands. The general pitting attack consisted in the formation of a large number of tiny corrosion pits at all parts of the surface, their measured initial " density " being, approximately, 10^6 pits/in.^{2}. As the test proceeded, these pits increased in size, and some combined with neighbouring pits to form small holes. The stress concentration effects due to the presence of these holes did not, in the total time occupied by the actual test (1000 hrs.), become sufficiently great to produce accelerated fatigue : no fatigue cracks radiated from these holes, although it is possible—had not the specimen fractured from other causes—that fatigue failure might have ensued due to pit formation and growth. Fig. 43 (Plate XVIII) shows the typical appearance of these pits after $14{\cdot}6 \times 10^6$ stress cycles. The " local attack " consisted of several large corrosion pits, which may have been due to the removal of inclusions, but the exact cause of which is unknown. As "stress-raisers" their effect exceeded that of the general pitting attack and might easily have led to fracture, but it was preferential corrosion on the site of previously formed slip bands which was almost entirely responsible for the fracture of the specimen. Due to this cause were developed a large number (40–50 at least) of very long cracks, and a countless number of small cracks. The most marked preferential corrosion and cracking had occurred at the most severely cold-worked regions, *i.e.* regions of greatest plastic deformation by slip. Fig. 44 (Plate XVIII) shows the typical appearance—in its early stages—of the selective corrosion attack and the initiation of cracks along the slip bands. The experiment brought out very clearly the marked accelerated corrosion-fatigue which can be set in operation in cold-worked material, and this knowledge is of very great assistance in interpreting some characteristics of the corrosion-fatigue of metallic aggregates. It offers an explanation why cold-working, although raising the normal fatigue resistance of a metal, renders the material particularly liable to fracture by corrosion-fatigue. In some cases, as has been seen, the resistance to corrosion-fatigue of a metal in the cold-worked state is sometimes equal to, and sometimes inferior to, that of the fully annealed or normalized condition. Again, certain forms of heat-treatment involve the setting up of severe internal stresses, although increased tensile strength and fatigue resistance is obtained. In the case of an air-hardened steel, for example, the presence of severe stresses is shown by the curved form throughout of the tensile stress–strain curve. When such a steel is subjected to repetitions of a range of stress less than the air fatigue limit, it has been shown that a state of elasticity is eventually attained, but that the specimen develops permanent set in the process due to the occurrence of slip at regions of high internal stress. When such a steel is tested under corrosion-fatigue conditions, this cold-working due to the cyclic stress will also be in operation, and the single crystal experiment may indicate why marked destructive effects result. It is not surprising, therefore, to find that the benefits normally associated with some types of heat-treatment tend to disappear under corrosion-fatigue, especially when it is remembered that such heat-treatment confers no increased resistance to ordinary corrosion. The importance of this aspect in spring materials, for example, is shown clearly in the following test results (Table VI) of McAdam.[31]

It appears probable that selective corrosion-fatigue in areas of cold-worked material may be an extremely important factor in the process of destruction. It is also probable that cold-worked material, being "notch-sensitive," facilitates the more rapid propagation of a corrosion-

TABLE VI.—*Tests on Chromium–Vanadium Spring Steel*

(C 0·46, Cr 0·88, V 0·14%.)

Heat-Treatment.	Tensile Strength, lb./in.^{2}.	Fatigue Limit in Air, lb./in.^{2}.	Corrosion-Fatigue Limit in Tap Water (20 × 10^6 cycles), lb./in.^{2}.
Annealed	97,800	±42,000	±22,000
Oil quenched: tempered at 540° C.	146,800	±69,000	±16,000
Oil quenched: tempered at 400° C.	179,300	±78,000	±16,000

fatigue crack. German investigators find some degree of correlation between "notch-sensitivity" and resistance to corrosion-fatigue. There is a curious fact which appears previously to have escaped attention. We can safely accept the view that corrosion-fatigue cracks are initiated at "pits," but why should these pits be so widely spaced? For example, McAdam has published some photomicrographs[27] of the surface (unetched) of some of his fractured specimens: the cracks definitely start at pits, but the pits are spaced apart at distances of 0·003 in. and upwards. Again, Fig. 45 (Plate XIX) shows the appearance of the surface of a steel specimen fractured under reversed bending stresses while exposed to a jet of wet steam. The process of failure is seen in three stages: pitting, joining up of pits, and crack formation at pits leading to one large crack the course of which deviates to include a number of pits, but here again the distance between pits must be large compared with the crystal size. It may be that *each* crystal is actually attacked, the laws of probability deciding that only certain individual crystals exhibit marked attack. On the other hand, the author has found that when a specimen is subjected to cyclic stresses which are much less than the proportional limit of the material (as judged from a tensile stress–strain diagram), an examination of the microstructure shows that slip bands are visible in a large number of individual crystals, with large areas of intervening crystals quite free from evidences of cold-work, probably owing to differential orientation. It may be that the isolated pitting that is evidently the chief cause of corrosion-fatigue failure may correspond with the positions of these deformed crystals, at which preferential corrosion-fatigue may originate. At present this is offered only as a possible explanation: no doubt, future work on changes in microstructure will afford definite information on these and other very interesting points.

There is one feature of failure under corrosion-fatigue which has an important bearing on pitting. When specimens of *ductile* materials

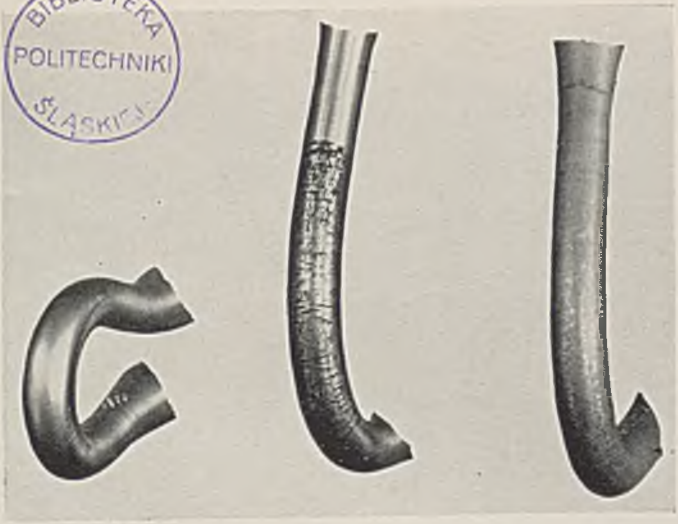

FIG. 31.—Nickel-Steel Specimens Bent Cold after Lengthy Fatigue Tests.
(1) 30 × 10^6 cycles of ± 45,000 lb./in.^{2}, Tested in Air.
(2) 48 × 10^6 ,, ± 14,200 ,, ,, Water Stream.
(3) 48 × 10^6 ,, ± 17,000 ,, ,, ,, ,,
(Chromium Plated Specimen.)

IG. 32.—Fracture of Mild Steel Specimen after 441,000 Cycles of ± 16·2 tons/in.^{2} while Exposed to a Drip of Tidal River Water. × 300.

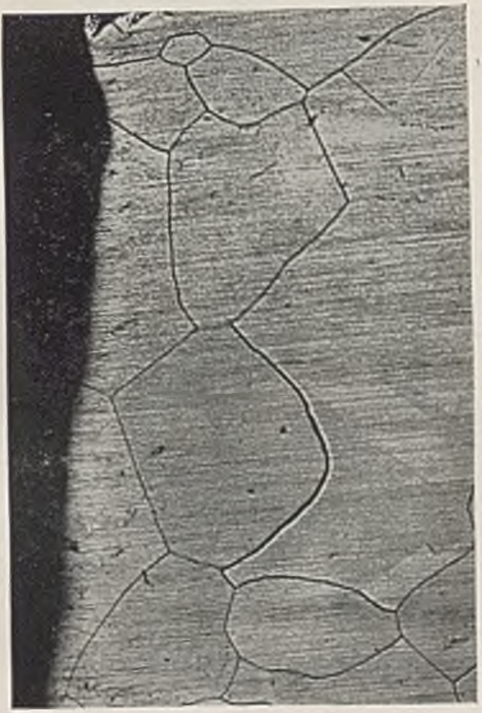

FIG. 33.—Fracture of 18 : 8 : 1 Cr–Ni–W Steel (Previously Heated at 650° C. for 1 hr.) after 6·75 × 10^6 Cycles of ± 10·1 tons/in.^{2}, while Exposed to a Drip of Tidal River Water. × 100.

FIG. 37.—Steel Tube (18 : 8 : 1 Cr–Ni–W) Failed in Service, by Corrosion-Fatigue, while Conveying a High-Velocity Stream of Boiling Ammonium Sulphate Liquor: the Tube was in a State of Vibration. × 100.

FIG. 38.—Laboratory Specimen of 18 : 8 : 1 Cr–Ni–W Austenitic Steel. Failed after 11,167,000 Cycles of ± 8·3 tons/in.^{2} while Subjected to a Drip of Ammonium Sulphate Liquor (50° C.) throughout Test. × 100.

FIG. 39.—Transcrystalline Corrosion-Fatigue (Sea-Water) Fracture of Aluminium (99% Pure). × 20.

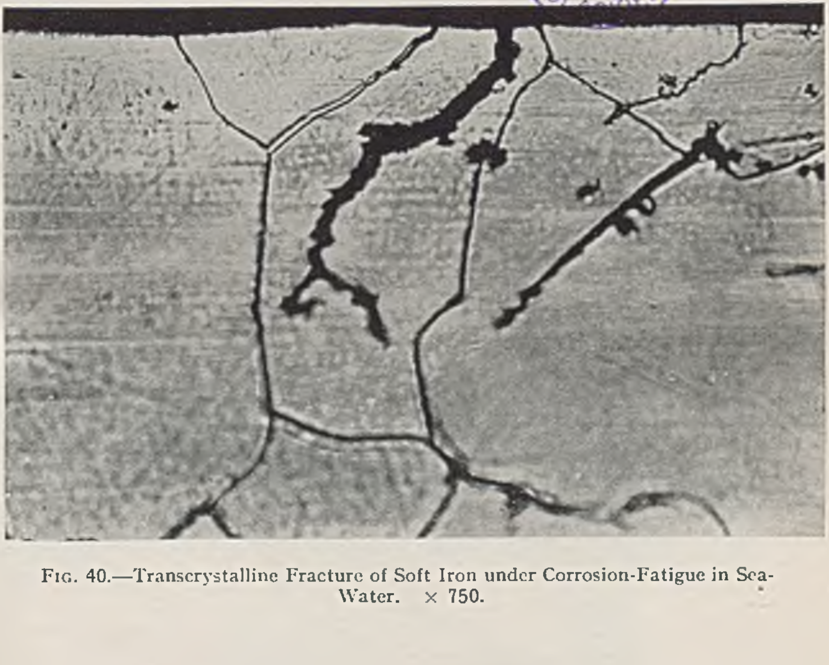

FIG. 40.—Transcrystalline Fracture of Soft Iron under Corrosion-Fatigue in Sea-Water. × 750.

FIG. 41.—Cracks in Chromium–Nickel Steel after 5 × 10^8 Cycles of ± 18,500 lb./in.^{2} in Tap Water. Polished but Un-etched. × 150.

FIG. 42.—As Fig. 41, but after Etching. × 150.

PLATE XVIII.

FIG. 43.—Typical Pitting on a Single Crystal of Aluminium after 14·6 × 10^6 Cycles of Corrosion-Fatigue in Tap Water. × 100.

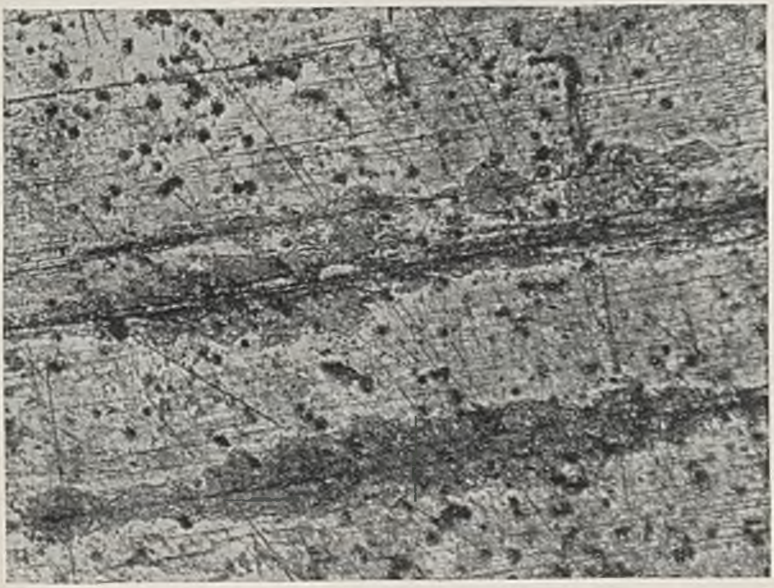

FIG. 44.—Corrosion-Fatigue of a Single Crystal of Aluminium, showing Selective Corrosive Attack and Initiation of Cracks along Slip Bands. × 100.

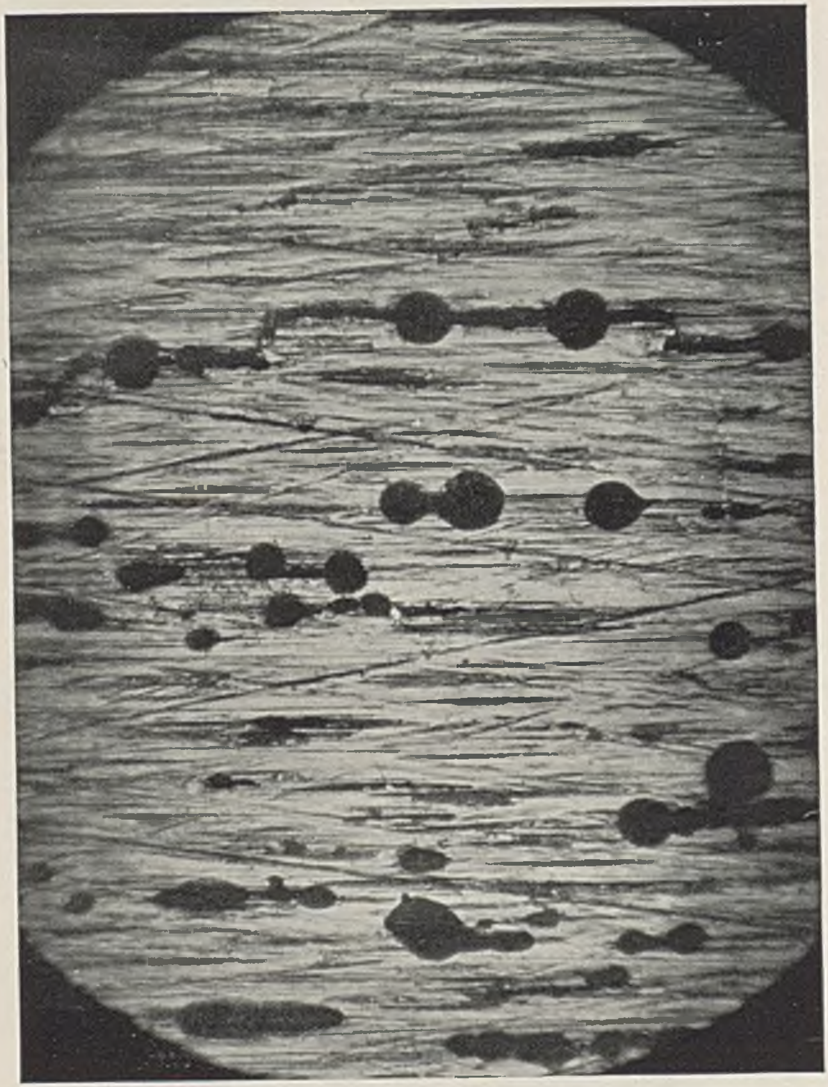

FIG. 45.—Corrosion-Fatigue Fracture, under Jet of Wet Steam, of Specimen of 0·5% Carbon Steel. × 115.

are fractured by alternating torsional stresses under ordinary fatigue conditions, the fracture usually follows the planes of maximum shear; *i.e.* the fractures are generally parallel or perpendicular to the axis. In service, however, shafts often fail by a spiral fracture, although usually some discontinuity, such as an oil hole, is seen to be the origin of the helicoidal fracture. This problem was solved mathematically, and demonstrated experimentally, by Southwell and Gough,[48] who showed that the presence of a small spherical flaw has the effect of raising the stress on the helicoidal planes to 2·7 times their original value; hence failure tends to be initiated on these planes in preference to the planes normally subjected to maximum shear. It was also shown experimentally that a material which fractured normally would fracture helicoidally if a small surface flaw was inserted, whilst a harder material which usually fractured helicoidally still fractured in the same way if a flaw was inserted. If the applied shear stresses are *repeated* in one direction only, the stress concentration tends to produce fracture along one spiral path: if the stresses are alternating, a double fracture (on both spiral paths) is produced. McAdam has published [33] photomicrographs of corrosion-fatigue cracks produced by alternating torsional stresses: these are X-shaped, the cracks being mutually perpendicular and inclined at 45° to the axis. Fig. 7 (Plate IV) shows a ship's tail shaft which has failed by corrosion-fatigue. One branch of the spiral fracture would be formed in going "ahead"; the addition of the perpendicular second branch is probably explained by the damage done during "astern" manœuvring: the author has seen other examples where the shaft exhibits cracks following only one helicoidal path, due to "ahead" steaming. Professor P. Ludwik has also sent to the author laboratory specimens that have failed under alternating-torsion corrosion-fatigue and exhibiting helicoidal fractures. To describe helicoidal fractures as "characteristic" of torsional corrosion-fatigue is not correct, as they can occur under ordinary fatigue, but the important point has hitherto been missed that this type of fracture is in strict accordance with theory *provided a surface flaw is present.* We have now ample evidence that the required flaws are produced by pitting, and the evidence obtained from the microscope of the importance of the latter in corrosion-fatigue failure as the origin of the spreading crack thus receives confirmation from the somewhat unexpected quarter of the mathematical theory of elasticity.

10.—THE MECHANISM OF CORROSION-FATIGUE.

The time has not yet arrived at which attempts to formulate a *theory* of the failure of metals by corrosion-fatigue can hope to meet with success. The complex laws governing corrosion phenomena do not appear to be thoroughly understood; similarly, a fundamental theory of fatigue has yet to be evolved. Nevertheless, by availing ourselves of those interpretations of the characteristics of corrosion and fatigue which have obtained general acceptance, it is possible to deduce a useful working conception of the combined process. A typical case of corrosion-fatigue will be discussed—namely, a specimen subjected to a constant range of applied loading (less in magnitude than that required to produce fracture when the test is made *in vacuo*) while simultaneously exposed to a stream of liquid of a corrosive nature (say, a neutral salt solution), saturated with oxygen.

The history of the specimen can first be divided into two main periods. During the first stage of corrosion-fatigue damage is done to the specimen, resulting in a condition (by pitting, crack formation, wastage, &c.) such that if the corrosive environment is removed altogether, fracture due to the cyclic stresses will result ultimately by the process of a spreading crack or cracks. Thus what will be termed the second stage of the history is essentially a "fatigue" stage, in which failure proceeds according to the general laws of fatigue, the most important characteristic feature of which is the *propagation* under the applied cyclic stresses of a crack or flaw by stress concentration effects the magnitude of which is controlled, primarily, by the shape of the flaw or crack and the physical properties of the material under test. These characteristics of failure by a spreading crack have received much detailed study,[10, 11] using the metallurgical microscope; they are well understood and require no comment. In discussing the first stage—during which the effects of corrosion and cyclic stress are in operation—it will be helpful to consider separately the effect of the maximum stress of the cycle (as a static stress), and then consider how this effect is modified by the range of *strain* associated with the cyclic stresses.

The type of corrosion-fatigue in which we are primarily interested—namely, industrial metals and alloys in nearly neutral solutions—essentially requires the presence of oxygen. While the simple process of direct chemical union of the oxygen with the metal cannot be altogether excluded, the general effect of such an action is relatively small. The much greater order of damage usually sustained in corrosion-fatigue, also the nature of the damage (by a process of deep local burrowing), indicate unmistakably that a process of electrochemical corrosion is in operation. A characteristic of this type of corrosion is a lack of uniformity * in conditions, either internal or external to the

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* In some cases in service, failure by corrosion-fatigue can be ascribed to the junction of dissimilar metals: such junctions are, however, rare in laboratory tests.

metal. Some of the well-known causes of non-uniformity in metals may be mentioned: in duplex and more heterogeneous alloys, electrochemical action may be set up between differing phases; ($\alpha + \beta$) brasses form an example. Usually, however, due to the close proximity of the phases, the action is small and of a temporary nature only. Thus in steel, which in the normalized condition consists primarily of ferrite and cementite, although the rate of corrosion attack by *dilute acids* increases with the carbon content, a similar relation is not usually observed in corrosion by neutral salt solutions in the presence of oxygen. Nevertheless, it is interesting to note, in passing, that, from the corrosion aspect, an increase in carbon content—which is usually accompanied by increased tensile and fatigue strength—would not be expected to confer increased, but rather decreased, resistance to corrosion-fatigue; immersion tests on ferrous alloys show that for the same general class of steel, variation of composition and heat-treatment does not greatly affect the resistance to corrosive attack. In cold-worked metals a varying degree of permanent deformation, and hence of crystal break-up and residual internal stress, will exist from crystal to crystal; electrochemical couples will be set in operation, the more severely deformed crystals or portions of crystals being anodic in character and suffering preferential corrosion. This suggests that cold-working a metal would reduce its resistance to corrosion-fatigue, and experience shows that although the fatigue strength is raised by the cold-working, the corrosion fatigue strength is usually not greater, and is often less, than that of the metal in the annealed state. Other causes of non-uniformity are the presence of impurities and surface inclusions. With regard to impurities, provided they are distributed uniformly throughout the metal, their effects as corrosion accelerators are small. Foreign inclusions occasionally exercise an electrochemical effect, but in corrosion-fatigue a much greater effect often results if the inclusions become removed mechanically, thus creating large pits. Another possible cause of non-uniformity is the stress gradient which may exist in the specimen, especially in those of the beam type. Such a difference in stress should produce electrochemical action, but the available evidence indicates that the presence of such stress—provided the metal remains elastic—has remarkably little effect in accelerating corrosion. In fact, the author concludes that stress, as such, plays a very small part in the first stage of corrosion-fatigue, and that it is extremely unlikely that corrosion is accelerated by stress. (The effect of cyclic *strain* on the surface protective film and on the corrosion-products is an entirely distinct process, which has purposely been excluded from this stage of the discussion.) *From the foregoing we conclude that the various causes of* *non-uniformity within the metal are capable of setting up electrochemical actions, but of such a small order as are not likely to produce the gross damage often observed in corrosion-fatigue. We also deduce that corrosion is not likely to be accelerated by the presence of elastic strain.*

Having discussed these possible factors, one arrives at the conclusion that the marked destructive effects in corrosion-fatigue are probably governed by two primary factors: (*a*) unequal distribution of oxygen, and (*b*) behaviour of protective films. It will be realized that the essential problem of corrosion-fatigue is to explain why such severe *local* damage is caused while the general wastage of the specimen is often inappreciable. Visual and microscopical evidence shows that failure usually occurs by a process of deep "burrowing" into the metal of sharp crevices, and it is important to find an adequate explanation of the mechanism of this burrowing. Possibly, the differential aeration theory of Aston [1] and Evans [7] and the knowledge of the properties of protective films made available by the brilliant work of Bengough, Vernon, and Evans, when considered in relation to known fatigue phenomena, may supply the required explanation.

The differential aeration theory developed by Aston and Evans is well known; it will be sufficient to mention its application to the present problem. Broadly, with the metals and the electrolytes with which we are mainly concerned, if two adjacent portions of a metallic surface, in contact with an electrolyte, are exposed to unequal degrees of oxygen supply, electrochemical corrosion is stated to take place at the shielded area, which becomes anodic, with the formation of a soluble metallic salt at this area, the production of an alkali at the aerated (cathodic) portion, and the precipitation of an insoluble hydroxide where the products of the cathodic and anodic areas meet. Thus corrosion may persist in places to which oxygen has least access. If a small corrosion hole or pit is formed, the rate of corrosion is merely governed by the rate of access of oxygen to the surrounding surface, and a very pronounced rate of burrowing may result, unless other conditions intervene. Corrosion products, if discontinuous or porous to oxygen, may also set up differential local corrosion.

The ideas of the "Evans" school of thought on fundamental corrosion phenomena therefore offer a plausible explanation of the essential problem of corrosion-fatigue, *i.e.* the tendency of the pits to *continue* burrowing into the solid body of the metal. This explanation is based on the assumption that the amount of oxygen available at the base of the pit is less than that at the surface of the metal. Views which conflict entirely with this theory have, however, been advanced by Bengough [3] and his collaborators. Their experiments indicate that corrosion proceeds at a rate *directly proportional* to the available oxygen supply, provided that the concentration of anions is sufficient and no protective films are formed. It seems to the author that the application of these essentially different theories to the problem of the corrosion-fatigue pit may be summarized as follows: according to Evans, oxygen cannot penetrate readily to the base of the pit, where preferential corrosion comes into operation by differential aeration; the pit therefore tends to deepen. According to Bengough, the surface of the metal surrounding the pit is less susceptible to corrosion, is probably covered by a wholly or partly protective film, and the oxygen in its neighbourhood becomes available to the pit; the corrosion products offer negligible resistance to the passage of oxygen to the base of the pit, and corrosion proceeds. The intensive fundamental research on corrosion which is now in progress will, no doubt, speedily establish which theory is correct; in the meantime, it is regarded by the author as a happy chance that both offer an explanation of our particular problem.

Existing theories of corrosion thus adequately account for the particularly destructive type of penetration which is observed in corrosion-fatigue, and if it can be explained why penetration *continues* to operate, the observed final failure becomes inevitable. But the same mechanism of corrosion obtains during static corrosion, where the action ceases after a time in some cases, and, in others, continues at a much slower rate. How, then, is the much more rapid action which occurs under corrosion-fatigue to be explained? In the first place, knowledge of fatigue phenomena enables us to say with certainty that once a certain shape of discontinuity of surface has been formed by corrosion or other means, then the mechanical stress concentrations induced become much more effective in producing failure under the action of applied alternating stresses than when static stresses only are in operation; for example, it is well known that the presence of a V-shaped discontinuity may produce an actual *increase* in tensile strength, whilst the same shape will result in a considerable *decrease* in fatigue strength. Further, the decreased fatigue resistance is largely independent of the actual dimensions of the discontinuity, and is controlled mainly by its shape. These facts are incontrovertible, and stress concentration effects also enter largely into corrosion-fatigue phenomena, but they are inadequate to account for the vastly increased velocity of corrosion under corrosion-fatigue conditions. *The author considers that this increased velocity is largely due to the effect of the cyclic strains on the porosity and rupture of the (wholly or weakly) protective films that tend to form under corrosion conditions. The thickness of the film is so small that its strength cannot enter into the problem; its range of strain will be* *determined entirely by the severity of the stresses induced in the metal and by the stress–strain relations of the latter. Should the nature of the metal with respect to its environment be such that a flexible, adherent, and continuous protective film is normally formed, then the degree of protection afforded under corrosion-fatigue would appear to depend on the effect of the cyclic strains imposed on the film on its permeability and freedom from rupture.* Another view is offered by McAdam, who considers that the corrodibility of the metal is directly increased by the cyclic stresses, although he does not exclude altogether from consideration the effect on the film. In discussing the experimental fact that stressless corrosion does not produce such a lowered resistance to fatigue as simultaneous corrosion and cyclic stress, he says [30] that this "seems to indicate that the effective solution pressure is higher in a specimen under cyclic stress than in a specimen not under stress. This increase in effective solution pressure may be due in part to continual removal of a protective film. Probably, however, there is an actual increase in the solution pressure due to the effect of cyclic stress superimposed on the electrochemical stress." Evans [6] has discussed the application of his views on "static" corrosion to the problem of corrosion-fatigue as follows: "If no external stress is applied, corrosion starts at certain points where (either owing to surface defects, or inclusions, or internal stresses) the invisible primary oxide film is weak or discontinuous; such points are anodic towards the parts where the primary film is in good repair and the insoluble secondary products (such as rust) shield these points from oxygen, which might otherwise repair the primary film; thus, anodic attack continues at these points, burrowing down into the metal and producing pits: the further down the pit burrows, the better is oxygen excluded, and at first sight the action should become quicker as it burrows deeper. This acceleration in the rate of destruction is actually realized as McAdam's curves show. Monel metal and stainless steel are materials which readily build a very obstructive primary film, and even a trace of oxygen (such as may enter the pits in the initial stages) would consequently interfere perceptibly with the rate of deepening, but in ordinary steel and Duralumin, another factor comes in. The rapidly formed secondary corrosion products (which must be clearly distinguished from the primary oxide film) occupy a bigger volume than the metal destroyed, and therefore congestion is likely to occur in the pits, tending either (1) to disrupt the metal, (2) to force out the corrosion product, or (3) to clog the pit and bring the burrowing to a standstill. Which of these three things will occur will depend on the strength of the metal, the plasticity of the secondary corrosion product, and the expansion involved in the corrosion, but it is quite clear that if the first prevails, the weakening will continue at a continually increasing speed, and if the third prevails it will diminish with time. Thus it is not surprising to find an accelerated weakening with some materials and a retarded weakening with others.

"If now we superimpose alternating stresses, clearly we aid the disruption, assist the expulsion, and diminish the clogging, hence, metals like steel, in which the rate of weakening falls off considerably with time in stressless corrosion, show more persistent weakening if cyclic stresses are applied. Qualitatively, this idea explains most of the results (of corrosion-fatigue), but when we note the extraordinary effects of increasing stress and frequency, it appears likely that the alternations must be doing something more than what has been suggested above. The clogging and development of pressure by secondary products is a slow process; it seems unlikely that an increase of frequency could make so marked a difference in the rate of weakening unless the function of the cyclic stress is also to prevent some other more rapid process. Actually we know of such a process, namely, the partial repair of the primary film by the small amount of oxygen which will penetrate even into pits; if the alternating stresses are fast enough they will break this skin more rapidly than it can be repaired, and since the metal at the anodic part is then maintained in a completely 'active' condition, the 'solution pressure' will be 'not the solution pressure of stressless corrosion but an enhanced solution pressure due to the cyclic stress.' * This is probably the main reason for the rapid weakening at high frequencies and high stresses. The fact that the building up of the primary film is a process enormously quicker than the clogging with secondary corrosion products is proved by independent researches. The work of Speller, McCorkle, and Mumma [49, 50] shows that chromates, which are known to keep the film in repair in stressless corrosion, prevent the setting in of corrosion-fatigue, whilst chlorides, which militate against their action in stressless corrosion, also do so when the corrosion is accompanied by cyclic stresses. There appears little doubt that damage to the primary film—as well as opposition to clogging by secondary products—must be considered. Alternating stresses keep cracking the film continually and thus accelerate corrosion, which in turn produces stress concentration, and thus the two factors (alternating stress and corrosion) cause more damage when they act together than separately."

These remarks of Evans are quoted to indicate the views on corrosion-fatigue held by one specialist on corrosion phenomena. The author finds it difficult to accept some of the suggested effects of the

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* This is quoting from McAdam.

insoluble secondary products. The degree of protection afforded by these products appears to be a subject of contention among experts on corrosion. Again, in spite of the change in volume accompanying the formation of the products, it seems improbable that the forces involved are sufficient to " disrupt " the metal: also, the use of the term " plasticity " appears to be unsuitable. One point raised by Evans has received some actual experimental attention. It will be noted that he suggests that the "frequency" effect of corrosion-fatigue can be explained by assuming that at high frequencies the film is broken faster than it can be repaired. The general effect to which he referred can be stated thus:—using a constant stress, and at a series of decreasing frequencies, the number of cycles to *fracture* decreases but the total time increases. Speller, McCorkle, and Mumma,[49] in discussing this interesting experimental fact, argued that if it is true that, provided the frequency of the alternating stresses is sufficiently great, the protective film is broken faster than it can be repaired, then conversely, an inhibitor which did not give protection at a certain speed might do so at a slower speed. To test this conclusion, they made tests on specimens of a steel at a constant range of stress (*a*) in a saline solution, and (*b*) in the same saline solution to which sufficient inhibitor had been added to afford partial protection; they obtained the results shown in Table VII.

TABLE VII.

Condition of Test.	Test Frequency Cycles per Minute.	Number of Cycles to Failure.	Time, Hours.	Cycle Ratio.	Time Ratio.
Tests made in distilled water carrying 2000 p.p.m. sodium chloride.	1790	1,078,000	10·0	1·00	1·00
	558	539,100	16·1	0·50	1·60
	189	373,500	32·9	0·35	3·28
Tests made in distilled water carrying 2000 p.p.m. sodium chloride plus 4000 p.p.m. sodium dichromate.	1790	6,889,700	64	1·00	1·00
	558	3,635,200	109	0·53	1·69
	189	2,187,800	193	0·32	3·01

In both series of tests the number of cycles to failure decreases and the time increases with decrease in cyclic frequency. The significant feature is the constancy of ratios of time and cycles in both cases: if it were true that slower speeds tend to promote film-building, this constancy would not be expected. These experiments suggest that the " frequency " effect in corrosion-fatigue is not due to the relative rates of film rupture and repair, but to an increasing effect of velocity on the *permeability* of the film; an increased rate of agitation produces greater porosity. Much more research is needed, however, before the facts are thoroughly understood.

To sum up the present section of this lecture, it may be said that the principal phenomena produced under corrosion-fatigue conditions become comprehensible immediately it is recognized that the main problem is one of corrosion and that the same primary factors are involved. In both groups of phenomena, protection against damage depends essentially on the formation and behaviour of a protective film, also internal or external conditions which tend to set up electrochemical effects will exert considerable influence in disturbing these films. Partial or complete protection can be afforded either by increasing the corrosion resistance of the metal by suitable chemical composition or by passifying the metal in relation to its environment, bearing in mind, however, that local conditions tending to increase corrosion effects may be more damaging than general corrosion. *The author considers that it is very doubtful whether stress, as such, is an important factor in corrosion-fatigue.* It becomes clear why a series of alloys—such as the plain carbon steels—does not exhibit widely different resistances to corrosion fatigue, if the chemical constituent, the proportion of which is varied within the range, does not influence appreciably their corrosion resistance. Similarly, the effects of heat-treatment and cold-work will be very small when compared with their influence on the resistance to static and normal fatigue stresses. It is also made clear how the marked destruction observed in corrosion-fatigue does not proceed from a general " wastage " of area of the specimen, but from a particularly dangerous form of surface discontinuity, which is peculiarly adapted to promote fracture under alternating stresses by the process of a spreading crack, but there is no relation between the amount of local or total damage under stressless corrosion and corrosion-fatigue, nor would this be expected. The cause of this difference, however, is at once understood when consideration is given to the effect of the *cyclic strains* on the corrosion-products and particularly on the protective oxide film. Very thin stable films are generally flexible, whilst thicker and less resistant films break more easily under stress; the marked resistance to corrosion-fatigue of high-chromium steels and the passifying influence of chromate inhibitors form excellent examples. That corrosion-fatigue strength depends much more on the nature and properties of the film formed than on the primary resistance of the metal to corrosion is demonstrated clearly by such metals as the stainless steels: these steels are *not* intrinsically passive.

Thus, we conclude that the mechanism of the failure of metals when exposed to the simultaneous actions of corrosive environment and alternating stresses can be reduced to an ordered sequence of chemical and physical events which are explicable, even in the present admittedly incomplete state of knowledge of the subject, by the established facts of corrosion and of fatigue, thus affording sufficient justification for the use of the term " corrosion-fatigue of metals."

ACKNOWLEDGMENTS.

In preparing the present lecture, the author has derived considerable assistance from letters, photographs, test-data, and examples of actual fractures relating to corrosion-fatigue, which he has received from valued personal friends and correspondents; to such an extent has generous assistance been offered that the task of selection for reproduction purposes has been an extremely difficult one.

Special indebtedness is recorded to the following: To Professor F. Bacon, of Swansea (Fig. 45); to Messrs. Brown, Boveri & Co., of Baden; to Dr. S. F. Dorey, of Lloyd's Register of Shipping (Figs. 2, 3, 7, and 8); to Mr. T. S. Fuller, of the General Electric Company, Schenectady; to Professor B. P. Haigh, of the Royal Naval College, Greenwich; to Professor E. Honegger, of Zürich (Fig. 31); to Dr. N. P. Inglis, of Imperial Chemical Industries (Figs. 19, 20, 32, 33, 37, and 38); to Professor P. Ludwik of Vienna (Figs. 39, 40, 41, and 42); to Mr. R. A. Macgregor, of the Darlington Forge, Ltd. (Figs. 5, 12, and 13); to Dr. D. J. McAdam, of the Bureau of Standards, Washington (Figs. 6, 9, 10, and 11); to Professor H. F. Moore of Illinois University; to Mr. R. R. Moore of the Wright Aeronautical Corporation, Paterson, N.J.; to Dr. F. N. Speller, of the National Tube Co., Pittsburg (Figs. 17 and 18); to Professor E. H. Schulz, of Dortmund (Figs. 14, 15, and 16); to Mr. F. W. Thorne, of the Royal Naval College, Greenwich; also to the United States Shipping Board (for permission to publish Figs. 6 and 9 to 11 inclusive). Also to the author's colleagues, Mr. H. V. Pollard, for considerable assistance in the preparation of the three-dimensional models and diagrams, and to Mr. H. Bowler for the very skilful construction of these models.

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ATMOSPHERIC ACTION AS A FACTOR IN FATIGUE OF METALS.*

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Synopsis.

A review of the literature of corrosion-fatigue reveals many apparent inconsistencies, but a closer examination indicates that such is not the case if it can be shown directly that atmospheric corrosion enters, to a varied extent, into the mechanism of fatigue as exhibited during the usual type of fatigue test in which the surface of the specimen is exposed freely to the atmosphere. In order to obtain this direct evidence, a lengthy series of comparative tests has been made in air and in a partial vacuum, on a range of ferrous and non-ferrous metals and alloys. The results show definitely that the fatigue strength is, in general, improved by the substitution of a vacuum for air as the ambient condition. Various metals are affected to various extents, the maximum improvement obtained, in the tests, representing an increase of 26 per cent. in the case of 70 : 30 brass.

Introduction.

Attention was first publicly directed to the subject of "corrosion-fatigue" of metals in a paper by Haigh § published in 1917. Nothing further was published until 1926, when important papers by McAdam ‖ and by Lehmann ¶ appeared. These 1926 papers aroused great interest, and the subject of "corrosion-fatigue" has since been the object of vigorous research at various laboratories both in America and Europe; the literature of the subject is now voluminous, largely owing to the valuable work of McAdam. In general, the researches referred to have been concerned with the destructive effects of stress and corrosive agents when acting conjointly, and in assessing these effects the

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§ B. P. Haigh, "Experiments on the Fatigue of Brasses," *J. Inst. Metals*, 1917, **18**, 55.

‖ D. J. McAdam, Jr., "Stress–Strain Cycle Relationship and Corrosion–Fatigue of Metals," *Proc. Amer. Soc. Test. Mat.*, 1926, **26**, (II), 224.

¶ G. D. Lehmann, "The Variation in the Fatigue Strength of Metals when Tested in the Presence of Various Liquids," *Aeronaut. Res. Cttee. R. & M.*, No. 1054, 1926.

endurance limit in air has been used as a basis of comparison, but a number of experiments, carried out by various experimenters, have indicated that the endurance limit in air is not necessarily a scientific basis of comparison; in other words, in ordinary fatigue tests some other factor than stress may be operative to some extent, yet unknown. Some significant observations on this aspect may be recalled.

In the paper published by Haigh in 1917, it is recorded that the endurances of brass specimens moistened with hydrochloric acid were generally greater than those of dry specimens under the same ranges of stress, also that no appreciable acceleration of fatigue in phosphor-bronze was produced by any of the corrosive reagents employed; these observations led Haigh to surmise that "the atmosphere, as well as fluid reagents, may act chemically upon the metal." Much more positive indications were obtained by Lehmann,* who studied the endurance limits of two steels tested in air and hot water, and in hot aqueous solutions of sodium nitrate, sodium chloride, and ammonium chloride. The most significant of Lehmann's results in the present connection is that the fatigue limit of 0·33 per cent. carbon steel when tested in a strong aqueous solution of sodium chloride at 96° C. was 6·5 per cent. greater than that obtained when tested in distilled water at the same temperature (96° C.). An equally significant result was obtained by McAdam † in 1927, when investigating the resistance to corrosion-fatigue of the copper–nickel binary system of alloys. In tests on electrolytic copper (purity 99·996 per cent.) the S/N curves representing specimens tested in water spray lay above the corresponding curves representing tests in air: this was not, however, due to absence of chemical attack in the water tests, as the surfaces of the specimens became heavily coated with films of corrosion products. McAdam considered it possible that the protective action of these films might account for the increased fatigue resistance, although this implied that the S/N graph obtained in air was depressed owing to atmospheric oxidation of the copper. (He did not consider this to be *probable*, as all specimens tested in air were covered with a film of mineral oil.) However, to examine the possibility, a series of tests was made, in air, on specimens covered by various protective coatings: a mixture of vaseline and rubber, a mixture of vaseline and paraffin, a mixture of shellac and lacquer, and Japan drier. It was found that the endurances of the coated specimens all fell on, or near, the S/N curve for uncoated specimens tested in air, from which McAdam concluded "that the ordinary fatigue graph has not been influenced by atmospheric corrosion,"

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* *Loc. cit.*

† D. J. McAdam, Jr., "Corrosion-Fatigue of Non-Ferrous Metals," *Proc. Amer. Soc. Test. Mat.*, 1927, **27**, (II), 102.

and ascribed the elevation of the *S/N* graph, for the tests in water, to the cooling effect of the water, also to "the intrinsic corrosion-fatigue limit" of the metal exceeding the endurance limit in air. A fair comment is that McAdam's conclusion was not justified, as he had no evidence that his oil film or protective coatings afforded complete protection from the atmosphere.

Some extremely interesting results were reported by Binnie,* in 1929. The fatigue strength, in air, of a medium carbon steel was reduced by 50 per cent., when a strong solution of common salt was allowed to drip, in air, on to the specimen. When the salt drip, however, was applied in an atmosphere of specially purified hydrogen, the "corrosion-fatigue" limit was definitely raised, and only very slight signs of corrosion were visible on the surfaces of the specimens. Work by Haigh and Jones on the effect of the atmosphere on the fatigue of lead and lead alloys was published † in 1930. Endurance tests were made on these alloys in air, in a bath of oil, under a coating of grease, and immersed in—also moistened with—acetic acid. It was shown that fatigue in lead was "delayed" by immersion in an oil bath (the *S/N* curve had been displaced along the *N* axis), although the tests were not sufficiently lengthy to show if an increase in the fatigue limit had occurred. A layer of grease did not "delay" fatigue to the same extent as immersion in an oil bath. Samples tested while immersed in acetic acid showed a definite further increase in resistance to fatigue in spite of the fact that severe surface corrosion of the specimen took place. Samples merely moistened with acetic acid showed no improvement in fatigue strength as compared with samples tested in air. The investigators considered these results supported a theory that fatigue is a conjoint chemical and mechanical process operating below the free surface of the metal, and that the chemical effect is due to oxygen diffused through the metal from the atmosphere; they did not state their views on the possibility of fatigue action if *all* oxygen were excluded: these would have been interesting in respect to their theory and the results obtained in the present experiments.

The above brief summary is sufficient to bring out two points of interest. First, the usually adopted classification is much too arbitrary by which endurance tests made in air are referred to as "fatigue tests," whilst endurance tests in which other contact substances are employed are broadly termed "corrosion-fatigue" tests, even though the contact-substance may normally be of a corrosive nature. Secondly, although

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* A. M. Binnie, "The Influence of Oxygen on Corrosion-Fatigue," *Aeronaut. Res. Cttee. R. & M.*, No. 1244, 1929.

† B. P. Haigh and B. M. Jones, "Atmospheric Action in Relation to Fatigue in Lead," *J. Inst. Metals*, 1930, **43**, 271.

the evidence available—before the present report—was of an indirect or circumstantial nature only, yet it was sufficient to suggest that the presence of the atmosphere in the usual fatigue test might be exercising some influence on the resistance of metals to cyclic stress. Accordingly, when in 1928 a programme of research on corrosion fatigue was drawn up—this programme to be carried out as a joint investigation at the National Physical Laboratory and the Royal Aircraft Establishment under the general supervision of the Aeronautical Research Committee—tests *in vacuo*, also in atmospheres of active and inert gases, were included.

The present report deals with the results of tests made, using direct and flexural stresses, on a range of materials tested in air, *in vacuo*, and in air when coated with lanoline grease. The tests form part of a research in which the resistance to corrosion-fatigue (when exposed to salt-spray) of commercial aircraft materials is being determined, and the present tests were made, in the first place, on these commercial materials. The results indicated that the atmosphere did exert some influence on the fatigue strength, but the quantitative effect was rather obscured by the lack of uniformity of the materials. Further comparative tests were therefore made on four materials—mild steel, annealed copper, annealed brass, and cupro-nickel—which previous experience had shown to be very uniform in mechanical properties. In each case, the effect of the grease coating is negligible, but substitution of a vacuum for atmospheric conditions produced the following definitely established improvements in fatigue limits: 5 per cent., 13 per cent., and 26 per cent. for mild steel, annealed copper, and annealed brass, respectively. The influence of the atmosphere in ordinary fatigue tests has thus, for the first time, been definitely established, and this is of considerable importance in widening our understanding of corrosion-fatigue phenomena; it also opens up various fields of possible future enquiry. The fatigue limit in air can no longer be taken as a standard, and it appears desirable to investigate the comparative fatigue strength in air and *in vacuo*, of a representative range of sound metals and alloys. Again, as the above summary shows, the substitution of other contact substances for air has sometimes been found to improve the fatigue resistance: experiments made with a range of such contact substances to determine if the fatigue strength *in vacuo* represents the maximum value would be very informative. A further aspect worthy of consideration is the possible effect of a still higher vacuum than that employed in the present tests; a series of comparative tests should be made in order to investigate this interesting point.

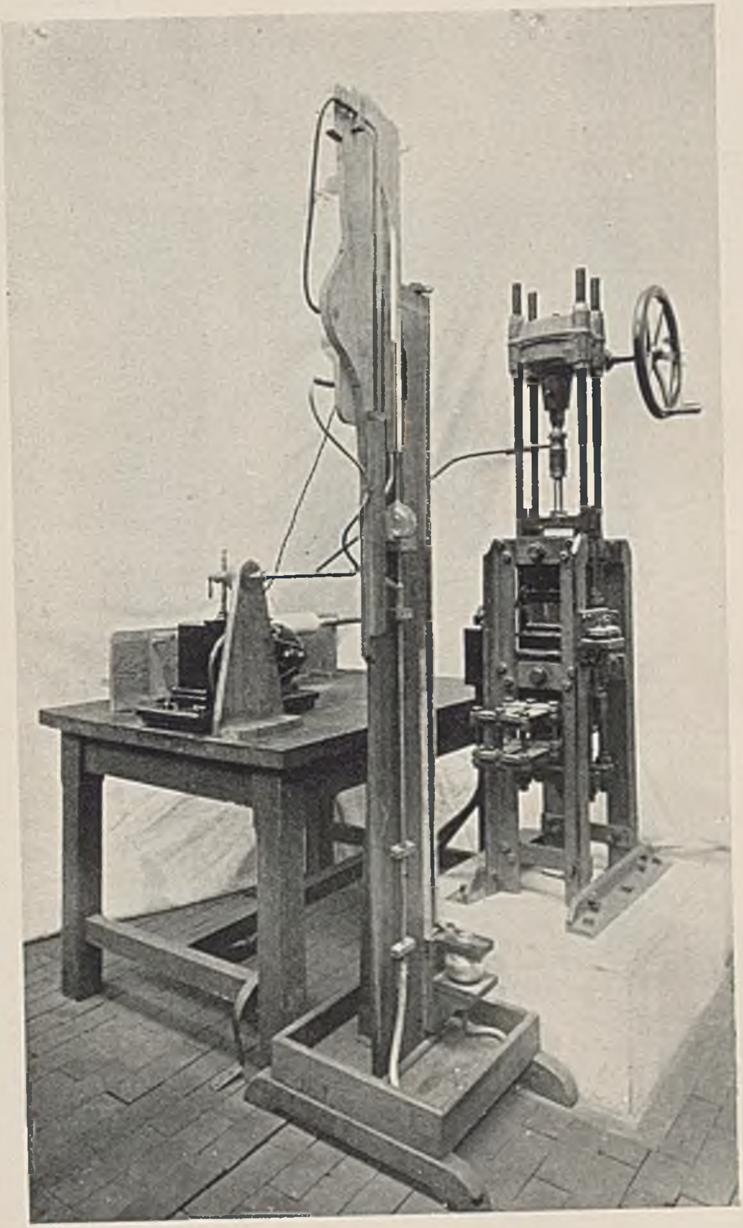

FIG. 2.

[To face p. 96.

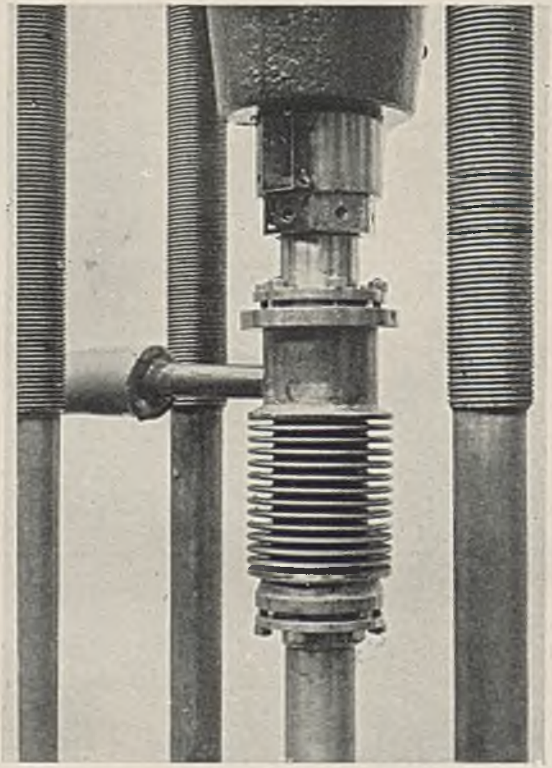

Fig. 3.

DESCRIPTION OF APPARATUS AND SPECIMENS.

The rotating bending tests were carried out in machines of the Wöhler type operating at 2200 stress cycles per minute. All tests with the exception of those made on the 0·5 per cent. carbon steel, were carried out using cantilever type specimens of the form shown in Fig. 1*a*, the diameter " d " of the test portion being 0·375 in. for the steels, 0·4 in. for Duralumin, and 0·35 in. for the magnesium alloy. In the case of the 0·5 per cent. carbon steel, which was very considerably cold-worked, it was considered desirable to apply a uniform bending moment over the test-portion. This was obtained by applying two equal and opposite vertical loads as shown in Fig. 1*b*. The fatigue resistances were determined by means of the usual endurance tests on a basis of ten million stress cycles for the steels and fifty million stress cycles for the non-ferrous materials. In all cases, cycles of reversed stress, alternating between equal positive and negative values, were applied.

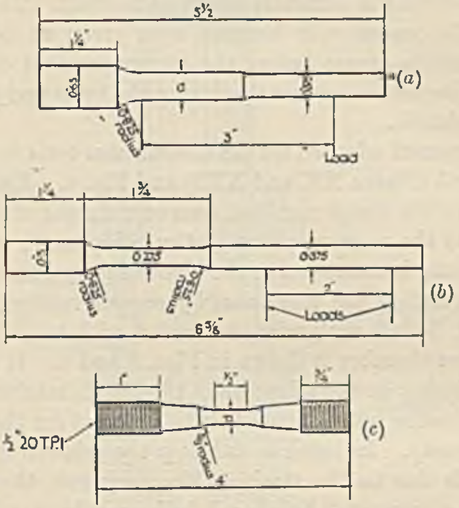

FIG. 1.—Types of Test-Piece Used.
(*a*) Rotating Cantilever Test-Piece.
(*b*) Rotating Beam Test-Piece.
(*c*) Direct-Stress Test-Piece.

The direct stress tests were carried out using three " Haigh " electro-magnetic testing machines. These were carefully calibrated before the commencement of, and at intervals during the progress of the research, and were found to give results in good agreement with each other. The type of specimen used is shown in Fig. 1c, the diameter " d " being chosen according to the fatigue strength of the material, and being usually 0·17 in. for steel and 0·25 in. for non-ferrous metals. Endurance tests were carried out on a basis of ten million stress cycles for the steels, and twenty or thirty millions for the non-ferrous materials.

As the effect of the atmosphere was one of the factors on which information was sought, special precautions were taken to ensure uniform conditions of surface. Immediately after the final machining operation, each specimen was thickly coated with lanoline grease. Specimens to be tested while exposed to ordinary atmospheric conditions were carefully cleaned with acetone, to remove the grease, immediately before the commencement of the test. The specimens to be tested while coated with lanoline were given an additional thick coating of lanoline grease before the commencement of the test, the coating being inspected frequently during the tests and renewed where considered desirable.

The arrangement adopted for the direct stress tests *in vacuo* is shown in Figs. 2 and 3 (Plates XX and XXI) and Fig. 4. Fig. 2 shows the general layout; the Haigh machine, seen on the right of the photograph, is connected to the vacuum pump (" Cenco Hyvac ") on the adjacent table. This pump is connected to the McLeod gauge, and to the vacuum chamber surrounding the specimen, by copper tubing, with joints of rubber tubing, bound with wire and sealed with sealing-wax varnish.

The vacuum chamber is shown in Figs. 3 and 4. It consists of two brass glands fitting on the adaptors of the Haigh machine, the top one having an extension into which a tube is soldered for the connection to the vacuum pump. In order to take up the relative motion between the two glands due to the strain of the specimen, these glands were connected by a piece of " Sylphon " bellows tubing, soldered at each end to one of the glands. The glands were packed with rubber rings about $\frac{1}{8}$ in. square. In the early tests arrangements were made whereby paraffin wax was poured round the joints and allowed to solidify in order to seal the joints. This was, however, found to be unnecessary, it being possible without this precaution to keep the pressure down to between 0·0005 and 0·001 mm. of mercury (about one-millionth part of one atmosphere) throughout the test. The pump was run continuously for the whole duration of each test, and gave an excellent performance throughout the tests.

Owing to atmospheric pressure acting on the outside of the vacuum chamber, specimens tested *in vacuo* were subjected to a steady compression of about 20 lb. in addition to the alternating load. This compression has a negligible effect on the fatigue resistance of the materials investigated.

MATERIALS USED IN THE RESEARCH.

Particulars of the composition, heat-treatment, and static strength properties of the materials are as stated in Tables I and II. The materials themselves should be regarded as consisting of two groups. The first group includes the 0·5 per cent. carbon steel, three steels of the

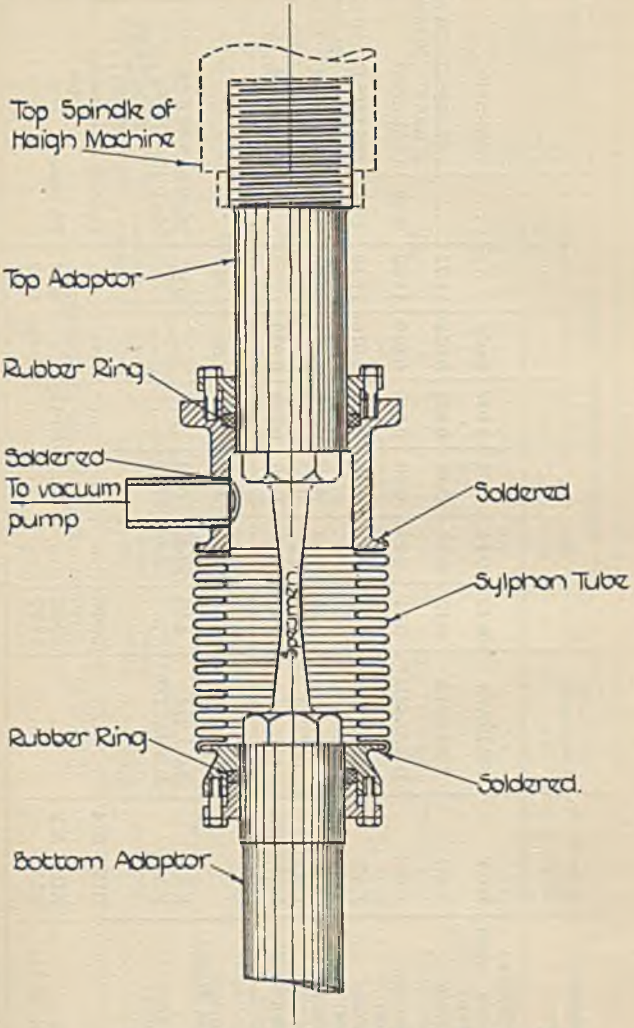

FIG. 4.—Vacuum Chamber for Direct Stress Tests *in Vacuo*.

TABLE I.—*Chemical Composition and Heat-Treatment of Materials.*

Description.	Reference No.	Material to Specification.	Chemical Composition. Per cent.							Heat-Treatment.	
			C.	Si.	Mn.	S.	P.	Cr.	Ni.		
Ferrous Metals:											
0·5% Carbon steel (cold-drawn)	EOY	B.S.I.5W3	0·48	0·11	0·64	0·032	0·034	...	...	Cold-rolled.	
15% Chromium-steel	FAO	B.S.I.S61A	0·12	0·28	0·24	0·022	0·018	14·75	...	OH 950° C. 30 minutes. T 650° C. 30 minutes. WQ.	
18/8 Chromium-nickel-steel	EWZ	D.T.D.43H *	0·11	0·28	0·26	0·010	0·010	18·32	8·23	Cold-rolled.	
17/1 Chromium-nickel-steel	FAP	B.S.I.S80A	0·25	0·52	0·68	0·012	0·016	17·10	1·16	OH 950° C. 30 minutes. T 630° C. 20 minutes. WQ.	
Nickel-chromium steel	S7B	...	0·36	0·29	0·50	0·020	0·023	0·60	3·42	OH 830° C. 15 minutes. T 500° C. WQ.	
0·13% Carbon steel	FQI/GDL	...	0·13	0·18	0·70	0·042	0·046	...	...	Hot-rolled.	
			Cu.	Al.	Mg.	Zn.	Ni.	Fe.			Heat-Treatment.
Non-Ferrous Metals:											
Duralumin	EXA	B.S.I.3L1	4·25	(93·43)	0·64	...	...	0·82		Mn 0·64. Si 0·22.	As rolled.
Magnesium alloy	EXB	D.T.D.127*	...	2·46	(97·15)	...	...	...		Mn 0·13. Pb Sn Fe Si Cu Ni 0·26	,,
Copper	BIF 3 & 4	...	(99·96)	...	...	...	tr.	tr.		O_2 0·04. Pb and As trace	Annealed.
70 : 30 Brass	BIF 1 & 2	...	69·85	...	...	(30·11)	...	0·04		Pb trace	,,
80 : 20 Cupro-nickel	BIX	...	78·92	...	...	...	20·61	0·19		...	...

Figures in parentheses obtained by difference. OH = oil hardened; T = tempered; WQ = water quenched. * Air Ministry.

TABLE II.—*Mechanical Properties of Materials.*

Description.	Reference No.	Ultimate Tensile Strength. Tons/in.².	Yield-Stress. Tons/in.².	Limit of Proportionality. Tons/in.².	0·1% Proof Stress. Tons/in.².	0·5% Proof Stress. Tons/in.².	Young's Modulus E. 10^6 lb./in.².	Elongation on $4\sqrt{\text{Area}}$. %.	Reduction of Area. %.	Brinell Hardness Number.
Ferrous Metals :										
0·5% Carbon steel (cold-drawn)	EOY	63·2	none	none	...	...	29·4	12·0	39·0	280–301
15% Chromium-steel	FAO	43·3	37·9	...	...	...	...	32·0	66·0	218–221
18/8 Chromium-nickel-steel	EWZ	66·3	(41·2)	19·1	...	...	31·1	52·0	36·0	242–255
17/1 Chromium-nickel-steel	FAP	54·5	41·1	...	...	...	...	22·3	53·3	274–284
Nickel-chromium steel	S7B	...	...	...	...	...	...	...	...	409–442
0·13% Carbon steel	FQI/GDL	28·0	21·3	...	...	...	29·6	43·5	...	...
Non-Ferrous Metals :										
Duralumin	EXA	28·2	none	17·4	19·3	19·6	10·7	15·0	23·9	106–117
Magnesium alloy	EXB	16·4	,,	4·8	9·7	11·2	6·0	20·2	44·4	59–61
Copper	BIF 3 & 4	14·4	,,	0·8	...	...	15·9	59·0	74·0	...
70 : 30 Brass	BIF 1 & 2	19·8	,,	2·4	...	...	16·2	84·0	85·0	...
80 : 20 Cupro-nickel	BIX	22·5	,,	2·6	...	...	20·2	44·0	68·0	...

"stainless" type, Duralumin, and the magnesium alloy. These six materials were received from the Royal Aircraft Establishment and tested in the condition as received at the National Physical Laboratory: they may be regarded as representative commercial materials as used in aircraft construction: where the materials were supplied by the makers to a specification, a reference is made in Table I. The second batch of materials—consisting of 0·13 per cent. carbon steel, annealed copper, annealed 70:30 brass, and 80:20 cupro-nickel—were tested subsequently; these materials are very uniform, and are issued by the Aeronautical Research Committee to investigators for use in researches on fatigue. This second batch will be referred to as "Research Materials." In addition, tests were made on the hardened and tempered nickel-chromium steel to afford information of the relative fatigue strengths in air and partial vacuum of a high-tensile steel.

RESULTS OF FATIGUE TESTS ON AIRCRAFT MATERIALS.

(a) *Rotating Beam Tests.*

All the results obtained are plotted, semi-logarithmically, in Fig. 5, in the form of S/N curves. In some cases, a considerable "scatter" of results was observed, and the plotted results are most appropriately considered as lying between two curves of maximum and minimum values. These envelopes are indicated on Fig. 5, and the limiting values of the fatigue ranges obtained in this way are summarized in Table III. It should be mentioned, however, in this connection, that—except where materials of unusually great uniformity are under examination—when a large number of test-pieces are used in fatigue determinations, it is quite common experience to find that the results are most fairly expressed as lying between two such limits rather than by a very closely-defined single value. The present results cannot be said to exhibit an unusual degree of lack of uniformity for commercial materials.

The main interest in the results lies in a comparison of the results contained in columns B and C of Table III. It will be seen that only small and irregular differences in fatigue strength exist between the average value of the fatigue limits obtained using acetone-cleaned specimens tested in air, and specimens of the same materials tested when covered with a coating of lanoline; the effect of the latter coating on the fatigue resistance may, therefore, be regarded as negligible. This result is in accordance with the work of previous investigators and indicates that—even if the atmosphere exerts an influence on the fatigue limit—the lanoline coating is not impervious to air.

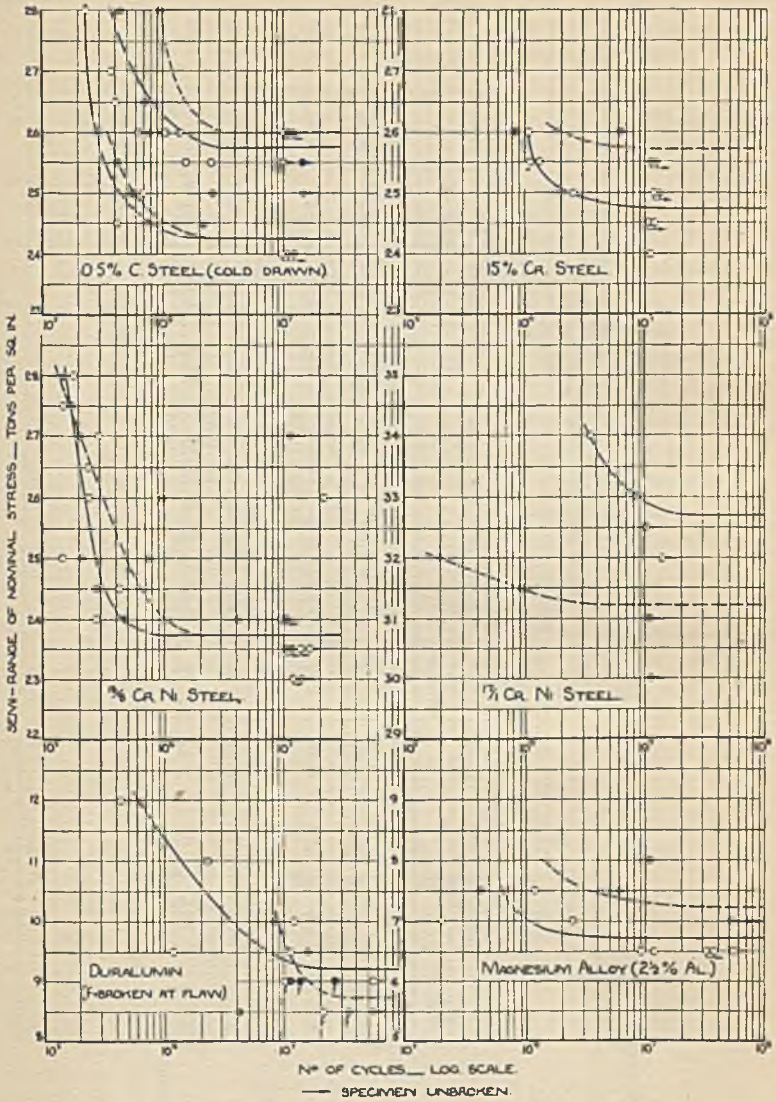

Fig. 5.—Results of Rotating Beam Fatigue Tests.

○——— Tests in Air on Dry, Cleaned Specimens.
●- - - - Tests in Air on Specimens Coated with Lanoline Grease.

TABLE III.—*Summary of Results of Fatigue Tests (Reversed Stresses) on Representative Commercial Aircraft Materials.*

Material.		*Col. A.* Ultimate Tensile Strength. Tons/in.².	Fatigue Limit: Semi-range of Stress (Tons/in.²).										
			Rotating Bending Tests.				Direct Stress Tests.						
Description.	Test Mark.		*Col. B.* In Air.	Ratio $\frac{B}{A}$.	*Col. C.* In Lanoline.	Ratio $\frac{C}{A}$.	*Col. D.* In Air.	Ratio $\frac{D}{A}$.	*Col. E.* In Lanoline.	Ratio $\frac{E}{A}$.	*Col. F.* *In Vacuo.*	Ratio $\frac{F}{A}$.	Ratio $\frac{F\text{ (average)}}{D\text{ (average)}}$
0·5% Carbon steel (cold-drawn)	EOY	63	24¼–25¾	0·39–0·41	24¼–26	0·39–0·41	20¾–22¾	0·33–0·36	21½–22¼	0·34–0·35	22¼–22¾	0·35–0·36	1·03
15% Chromium-steel	FAO	43	24¾	0·57	25¾	0·60	21¾–22¼	0·51–0·52	21¾–22¼	0·51–0·52	22¼	0·49	1·01
18/8 Chromium-nickel-steel	EWZ	66	23¾	0·36	23¾	0·36	24¼–25½	0·37–0·39	24¼	0·37	24¼	0·37	0·98
17/1 Chromium-nickel-steel	FAP	54½	32¾	0·60	31¼	0·57	28¼–28½	0·52	28¼–29	0·52–0·53	28¼	0·52	1·00
Duralumin	EXA	28	9¼	0·33	8¾	0·31	6¾–9	0·24–0·32	6–8	0·21–0·29	8¼	0·29	1·05
Magnesium alloy (2·5% aluminium)	EXB	16½	6¾	0·41	7¼	0·44	5¼–6	0·32–0·36	5¼–6	0·32–0·36	5¼–6	0·32–0·36	1·00

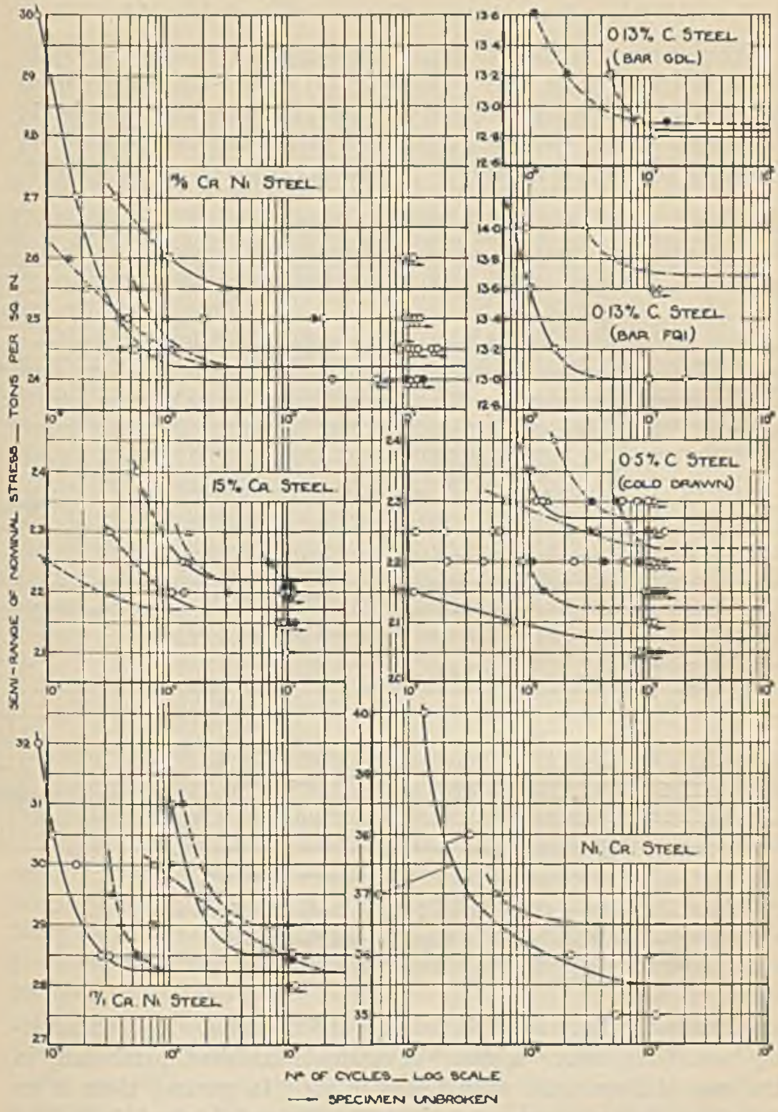

FIG. 6.—Results of Direct Stress Fatigue Tests (Ferrous Metals).

○——— Tests in Air on Dry, Cleaned Specimens.
●- - - - Tests in Air on Specimens Coated with Lanoline Grease.
△-·-·-· Tests *in Vacuo.*

(b) *Direct Stress Fatigue Tests on Aircraft Materials.*

These tests were made to exhibit the comparative fatigue strengths of the materials under three conditions: (*a*) acetone-cleaned specimens tested in air, (*b*) specimens coated with lanoline grease and tested in air, (*c*) acetone-cleaned specimens tested in a partial vacuum (pressure not exceeding 10^{-3} mm. of mercury). The results of the tests are expressed, graphically, in Figs. 6 and 7, in the form of *S/N* curves. As in the rotating beam tests, some " scatter " of results is exhibited, particularly in the case of Duralumin when tested in air. In general, there is an indication that much more consistent results are obtained during the vacuum tests than in the other two series: to some extent, however, this may be due merely to the smaller number of specimens used in the former.

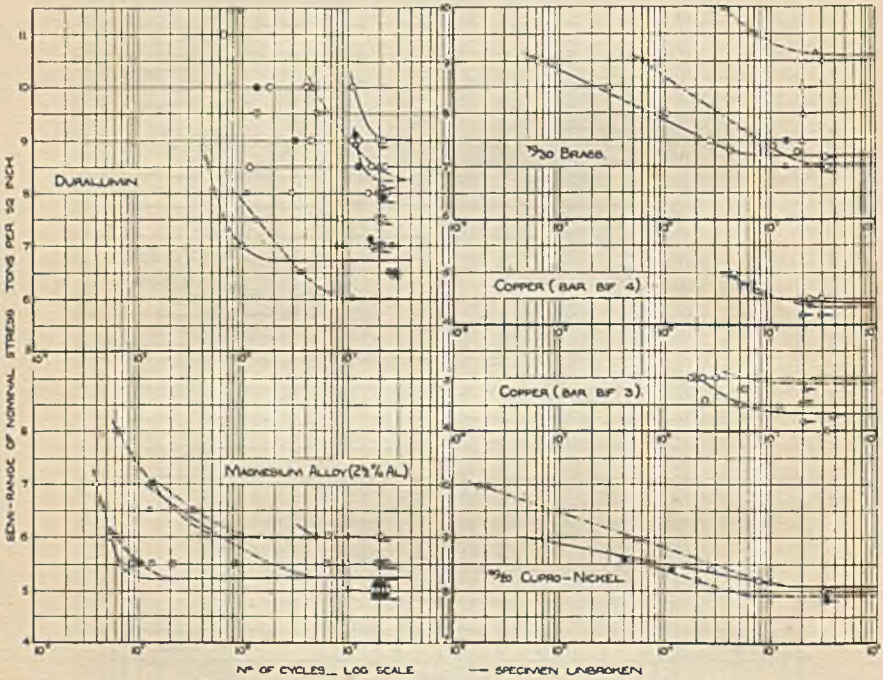

FIG. 7.—Results of Direct Stress Fatigue Tests (Non-Ferrous Metals).

○——— Tests in Air on Dry, Cleaned Specimens.
●- - - - Tests in Air on Specimens Coated with Lanoline Grease.
△-·-·- Tests *in Vacuo*.

The comparative results of the " air " and " lanoline " tests lead to the same conclusion as derived from the beam tests, *i.e.* that the lanoline coating has had no appreciable consistent effect on the fatigue strength of the materials. A general consideration of the S/N curves and of the values of the ratio given in the last column of Table III led the authors to the definite opinion that, in general, the substitution of a partial vacuum for air, as the environment, had effected a definite improvement in the fatigue strengths, although the quantitative effect of the improvement was obscured by the somewhat irregular results obtained. It is clear, however, that the effect of the atmosphere on the fatigue strength of *steels* and the *magnesium alloy* cannot be great; it *may* be larger for Duralumin.

Obviously, to obtain definite quantitative information, further tests were required using materials in which the air endurance limits were much more closely defined. Metals of the type required were available in the materials issued by the Aeronautical Research Committee to investigators on fatigue researches: these materials were 0·13 per cent. carbon steel, annealed copper, annealed 70 : 30 brass, and 80 : 20 cupro-nickel, and determinations of the fatigue limits of these materials—under reversed direct stresses—were accordingly put in hand. The conditions of the tests were exactly similar to those used in the previous experiments.

RESULTS OF FATIGUE TESTS ON MILD STEEL, COPPER, BRASS, CUPRO-NICKEL, AND NICKEL-CHROMIUM STEEL.

Particulars of the composition, heat-treatment, and static properties of these materials are given in Tables I and II. The results of the fatigue tests are plotted in Figs. 6 and 7, and are summarized in Table IV.

In the tests on the mild steel and annealed copper, all the specimens could not be cut from the same bar; the fatigue range (in air) was therefore carefully determined for each bar, the differences, however, being found to be extremely small. In order to determine whether the presence of the vacuum chamber, as such, had any effect on the loads imposed on the specimens during the tests made *in vacuo*, an extra series of tests was made on the mild steel in which the vacuum chamber was placed in position, but the pipe normally connected to the vacuum pump was left open at the end, the air within the chamber being thus maintained at the atmospheric pressure. The fatigue limit obtained in this way differed from that obtained in the air test by a negligible amount. This series of tests is sufficient to show that any differences between the results obtained in air and *in vacuo* can be ascribed solely to the change in ambient conditions.

Each material, under each set of test conditions, exhibited great uniformity and enabled very close values of the fatigue limits to be determined.

TABLE IV.—*Summary of Results of Reversed Direct Stress Fatigue Tests made on Mild Steel, Brass, Copper, Cupro-Nickel and Nickel-Chromium Steel.*

Material.		*Column A.* Ultimate Tensile Strength. Tons/in.^{2}.	Fatigue Limit: Semi-range of Stress (Tons/in.^{2}).			
Description.	Test Mark of Bar.		*Column B.* In Air.	Ratio $\frac{B}{A}$.	In Lanoline.	*In Vacuo.*
0·13% Carbon steel (hot-rolled)	FQL	28·0	13·0 (1·00)	0·46	...	13·7 (1·05)
	GDL		$12{\cdot}8_5$ (1·00)	0·46	12·9 (1·00)	...
Annealed 70 : 30 brass	B1F1	19·8	$7{\cdot}2_5$ (1·00)	0·37	$7{\cdot}0_5$ (0·97)	$9{\cdot}1_5$ (1·26)
Annealed copper (99·96% pure)	B1F3	11·4	$4{\cdot}3_5$ (1·00)	0·30	...	4·9 (1·13)
	B1F4		$4{\cdot}4_5$ (1·00)	0·31	$4{\cdot}3_5$ (0·98)	...
Cupro-nickel 80 : 20	B1X2	22·5	8·1 (1·00)	0·36	7·9 (0·98)	8·1 (1·00)
Nickel-chromium steel	S7B	90 °	35·5 (1·00)	0·39	...	36·5 (1·03)

° Estimated from Brinell Hardness Number.

The outstanding feature of the results is the increased fatigue resistance conferred on the brass and copper by the substitution of a partial vacuum, as the ambient condition, for the atmosphere. Somewhat surprisingly, no similar effect is observed in cupro-nickel. The effect on the steels is small (not exceeding 5 per cent.), although it is particularly well defined in the mild steel. Some general increase was certainly expected, but the actual improvements obtained for brass (26 per cent.) and copper (13 per cent.) are unexpectedly great. Accordingly, every possibility has been examined to ensure that no other factor was entering into the problem. All the tests have been confined to one machine, and tests on different materials under different ambient conditions have been purposely mixed up in sequence; the majority of the results, however, fall on extremely smooth curves, and "machine" effects can be dismissed. The possible effect of the presence of the vacuum chamber has been shown to be negligible by the special series of tests undertaken for this purpose. It may appear possible that the effect of the cleaning of the specimens by acetone, thus exposing a fresh surface to the atmosphere, might have produced an unduly low value of the fatigue limit in air, but this supposition is definitely disproved by the following observations. Some years previously (1926) the fatigue limits of the copper and brass were determined on specimens cut from the same bar and tested in the same machine as used in the present tests: no precautions were taken for protecting the surface of the specimens, which were tested several months after the specimens were prepared. The fatigue limits obtained in these previous tests for the copper and brass (on a reversals basis of 30 to 40 millions) were ± 4·4 and ± 7·2 tons/in.^{2}, respectively: these values are identical with those obtained during the present tests. After careful consideration, therefore, the authors are satisfied that the beneficial effect of the vacuum is genuine. A superficial examination of the specimens tested in air and *in vacuo* reveals no differences in appearance. The faces of the fractures are all spoilt by the "hammering" action set up after fracture and before the machine comes to rest; the surfaces of the specimens show no obvious differences in brightness. In the absence of definite information, it will be assumed, for the present, that the tests indicate that, during a fatigue test made in air, conjoint stress and corrosion effects are in operation. Any "temperature" effect can, presumably, receive no serious consideration, as the capacity for conduction, through the specimens themselves, is practically the same under both conditions of test. To put this matter to the test, however, some experiments were put in hand in which the actual temperatures of specimens tested in air and *in vacuo* were observed throughout the lives of the specimens; the results of these tests are given in the appendix to the paper. Two possible responsible factors are the enormously reduced amount of oxygen, and the complete absence of water vapour, in the vacuum tests. To investigate one of these possibilities, it is proposed to carry out a series of tests in which the specimen is surrounded by dry oxygen of high purity. Polished specimens are also being prepared to discover if any clue is offered by changes in microstructure.

The effect of the lanoline grease coating is seen to be extremely small, the fatigue limit of the coated specimens being equal, for mild steel, brass, copper, and cupro–nickel, respectively, to 100, 97, 98, and 98 per cent. of the fatigue limit when tested in air. The simplest explanation of these results is that the coating either is not impervious to the atmosphere, or is discontinuous locally. If it is correct to assume that tests made under ordinary atmospheric conditions are, in effect, a form of corrosion-fatigue, then a surface coating of grease that is not impervious nor continuous would be expected to produce aggravated corrosion locally (vide the experiments of Speller, McCorkle, and Mumma), and the coated specimens would develop a fatigue resistance inferior to that of the uncoated specimens; this might account for the slightly inferior resistance of the lanolined specimens of brass and copper, but the reduction in fatigue limit in the present tests is so small as to be inconclusive, and it is wiser to interpret the results as showing that a coating of lanoline grease produced no appreciable effect on the resistance of the materials investigated.

The present results render consistent and intelligible many corrosion-fatigue experimental results which have hitherto been somewhat puzzling. It is now proved definitely and directly, for the first time, that the atmosphere plays a part in the fatigue resistance of metals when tested under normal laboratory conditions; this effect is shown to be negligible with some materials, such as the cupro-nickel used in the present research, is probably very small with steels (a maximum improvement of 5 per cent. has been obtained to date), and is considerable in the case of copper and brass, particularly the latter (where an improvement of 26 per cent. was obtained in a partial vacuum). It may be even greater in other metals and alloys. No longer can the air endurance limit be regarded as the "standard" limiting range of stress; the real standard is probably that value obtained when the tests are conducted in a perfect vacuum or in some other form of test in which corrosion or direct chemical attack is totally absent. In the future it should not be a matter of any surprise to find that the fatigue resistance of an alloy, when tested in an environment other than air, exceeds the air endurance limit. All previous corrosion-fatigue data are now consistent. To assist in obtaining an understanding of the fundamentals of fatigue, research workers might very usefully pay some attention to discovering if it is possible to obtain under any conditions a fatigue strength which exceeds the value obtained in a high degree of vacuum; should such a result be obtained, present ideas of the mechanism of corrosion-fatigue would require serious revision.

APPENDIX

TEMPERATURES OF SPECIMENS TESTED IN AIR AND *IN VACUO*.

In the tests carried out *in vacuo*, the conditions that affect the dissipation from the specimen of the heat generated by hysteretic action differ from those in the normal test in air in that convection is practically absent. It was felt that the major portion of the heat generated was in either case dissipated by conduction, the conditions for which did not differ in the two types of test. In order to settle this point definitely, however, some tests were carried out during which the temperature of the specimen was recorded; thermo-couples and a potentiometer were used for the purpose, a continuous automatic record from a Cambridge recorder being also taken as a check.

Three tests were carried out on 70 : 30 brass specimens—this material having shown the greatest increase in fatigue limit *in vacuo*. One of these (BIF2T) was tested in air at a stress range slightly below the air fatigue limit, *viz.* ± 7·1 tons/in.^{2}, and two at slightly below the vacuum fatigue limit, *viz.* ± 9 tons/in.^{2}, one in air (BIF2N) and one *in vacuo* (BIF2P). The temperatures of the test portions of these specimens are plotted in Fig. 8 as a function of the time from the commencement of each test. The curves of Fig. 8(a) show the temperatures during the first few hours of each test and those of Fig. 8(b) during the whole course of the tests. Specimens BIF2T (± 7·1 tons/in.^{2} in air) and BIF2P (±9·0 tons/in.^{2} *in vacuo*) were unbroken after 26·7 and 35·2 millions of cycles respectively, whilst specimen BIF2N (±9·0 tons/in.^{2} in air) broke after 0·36 million cycles; the results thus afforded a very good check on the previous results (see Table IV), *viz.* fatigue limit in air ±7·25 tons/in.^{2}, *in vacuo* ±9·15 tons/in.^{2}. The curves are of the usual form,

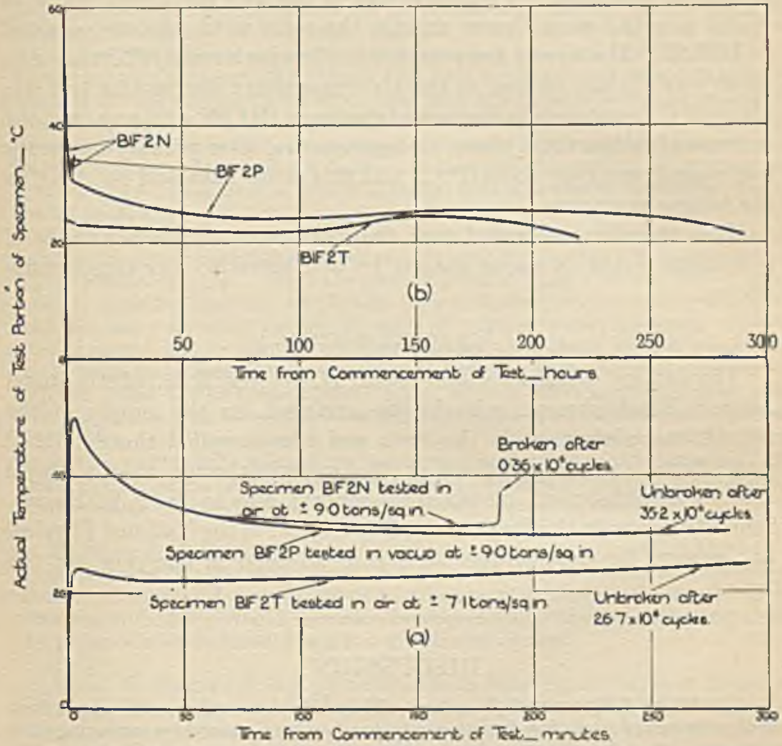

Fig. 8.—Curves Showing Actual Temperature of Test Portions of Specimens During Test.

showing an initial rise of temperature due to primary hysteresis, followed by a decrease to a fairly constant temperature, with, in the case of the broken specimen BIF2N, a final increase just before fracture. (*Note.*—The recorded temperatures for specimen BIF2T show a rise followed by a fall over the test time, 120–220 hrs. These variations are due to a general increase in room temperature and have no other significance.) It will be seen that the temperatures of the two specimens tested at $\pm$ 9·0 tons/in.^{2} were almost exactly the same until fracture occurred in BIF2N. The rise of temperature in the specimen BIF2P tested *in vacuo* was slightly higher, as the air temperature during this test was about 3° C. lower than in the case of specimen BIF2N. In any case, the increase of temperature above air temperature, after primary hysteresis had ceased, was only about 7° C., and this could have had no effect on the fatigue resistance.

It is therefore concluded that the increase in fatigue resistance of specimens tested *in vacuo* cannot be attributed to any temperature effects.

Acknowledgments.

The authors' thanks are due to Mr. H. Sutton, M.Sc., of the Royal Aircraft Establishment, who kindly arranged for the supply of the aircraft materials used in the tests and who supplied the details of static tests and examinations of the materials made at the Royal Aircraft Establishment quoted in the report; also to Mr. P. L. Thorpe, Senior Observer in the Engineering Department of the National Physical Laboratory, for considerable assistance afforded in carrying out the tests.

DISCUSSION.

Dr. W. H. J. Vernon * (Member) : The authors mention in the paper that in the history of corrosion-fatigue confusion has been caused by assuming that various coatings, such as vaseline, rubber, &c., act as oxygen excluders, when in fact there is no evidence to that effect. Similarly, in corrosion research, products have been assumed to act as oxygen screens, whereas when submitted to quantitative examination they have failed to show any such screening effect. The lesson clearly is that it is not safe to assume anything, but that it is only by careful if laborious quantitative examination at every step that a sure foundation can be established. So far as the relation between fatigue phenomena and atmospheric corrosion is concerned, there are just one or two points that I would like briefly to raise. First, what is the external stimulus in atmospheric corrosion-fatigue ? The authors appear to regard oxygen as the sole responsible agent, but is this necessarily so ? Furthermore, what is the relation between atmospheric corrosion-fatigue as understood in the paper,

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and the phenomenon of "season-cracking"? Mechanical distinctions may perhaps be drawn from the type of failure to be observed in each case, but I feel that on the chemical side the connection may be closer than appears to be suspected.

It has long been known that season-cracking is brought about by traces of atmospheric impurities, and that these impurities are very specific, the most potent being ammonia and sulphur dioxide. We know that traces of sulphur dioxide are usually present in the atmosphere, and the same may be said of ammonia, for although it is true that sulphur dioxide usually predominates, ammonia *may* predominate, and the combination of the two in the form of ammonium sulphate is invariably present. This was shown in a paper * which I recently presented to the Institute and it was confirmed by Dr. J. S. Owens in the discussion. In view of this, is it not cogent to inquire whether some of the effects attributed to oxygen may not in fact be due to traces of such compounds? In the authors' tests a definite difference in behaviour was found in most cases between the metal tested in air and the same metal tested *in vacuo*. It is perhaps significant that the only exception was found in the copper–nickel alloy, a type of material that is known to be immune from season-cracking.

With these considerations in mind, I am glad to have the authors' statement in the paper that they propose to carry out fatigue tests on specimens in highly purified oxygen. From the present point of view, however, they might possibly consider carrying out parallel tests with ordinary laboratory air, and with the same air after passing through an efficient purifying train. Moreover, I would like to ask the authors whether they think that it would be worth while to include tests in an inert gas, both dry and saturated with water vapour. This would show whether water vapour plays any vital part. It seems probable that here we are dealing with metal–gas reactions, and that at any rate a film of moisture is not necessary. I am tempted to make this suggestion particularly because we have found in the case of the "fogging" of nickel that, whereas primary adsorbed films of moisture have a negligible effect, primary films of adsorbed gas have a relatively enormous effect.

Professor G. I. TAYLOR,† F.R.S.: To an engineer a millionth of an atmosphere seems extraordinarily small, but to a physicist it means an enormous number of atoms. I am wondering whether there is likely to be anything in that last millionth: would corrosion be appreciably different supposing that the pressure were reduced down to a hundredth of that?

Dr. C. H. DESCH,‡ F.R.S. (Vice-President) (*referring to Professor Taylor's remarks*): It is rather curious that the same idea has been passing through my mind. I have been making a rough calculation, and I find that even with the vacuum used the number of oxygen molecules would still be of the order of 10^{16}. The fatigue values that are now being obtained must be tending towards a limit. The actual fatigue range may be considerably above that which has been found at present.

There is also the factor to which Dr. Vernon alluded: the presence of the absorbed film of oxygen which is certainly not removed by mere exposure to such a vacuum as that. The important thing is, as Dr. Gough told us, that when the oxygen is removed there is a distinct improvement in the fatigue limit. I want to make the suggestion that in the Haigh test, when a certain

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* *J. Inst. Metals*, 1932, 48, 121.

† Yarrow Research Professor of the Royal Society.

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formation of slip-bands occurs at the surface, possibly ultra-microscopic cracks appear which have no appreciable effect on the strength in the ordinary way, but the oxygen or other chemically-active agents admitted during the tensile pulse become enclosed during the compression pulse so that they are actually present under an increased pressure, and possibly increase the chemical activity.

Dr. N. P. INGLIS *: I should like to ask the authors whether they consider it worth while that an investigation should be made of the size effect—that is, the size of the specimen. All the specimens which the authors and other investigators have dealt with are very small specimens indeed, and I wonder what would be the effect on specimens 2 in. or 3 in. in diameter. I ask the question because of some work with which I was concerned a few years ago in connection with the detection of cracks in railway car axles, where we found a specimen which was about 1·5 in. in diameter to exist for a very large number of reversals after a crack had formed, whereas in a small specimen once a crack had formed the specimen fractured after very few reversals. I do not suggest that the size effect may influence the actual corrosion-fatigue limit, but it might have the effect of altering the position of the S–N curve, which would be quite an important effect as far as practical problems are concerned.

Mr. J. C. CHASTON,† B.Sc., A.R.S.M. (Member): It has been suggested that intense local concentration of stress brought about by pitting may be a general cause of failure by corrosion-fatigue. I think that it may be significant, however, that, in the tests which have been described, the metals which are most affected by oxygen during a fatigue test are the very ones in which pits would be thought least likely to cause stress concentration. In both lead and copper, it is to be expected that the local stresses caused by small cracks would readily be relieved by the yielding of the soft metal, and it is difficult to understand how, in these metals, intense local stress concentrations could exist.

Dr. H. W. BROWNSDON,‡ M.Sc. (Member of Council): This paper interests me especially on account of the improved behaviour of copper and brass when submitted to fatigue tests in a vacuum. Copper is largely used in aeronautical work for petrol and oil pipes which should have a high fatigue limit, and seeing that the fatigue limit is lower in air than in a vacuum, it would be of considerable interest to know to what extent the fatigue limit is influenced by the impurities and gaseous constituents commonly present in copper. Commercial copper is one of the most complex materials of which I know. It contains, in addition to numerous small amounts of metallic impurities, cuprous and other metallic oxides, condensed water vapour, carbon monoxide, carbon dioxide, hydrogen, and perhaps other gases. Whilst the oxygen in the atmosphere undoubtedly plays a part in lowering the fatigue limit, its effect may become evident only in the presence of some one or other of these impurities or gases. From this point of view, it would be extremely interesting, and would perhaps throw some further light of a valuable metallurgical nature on the phenomena observed by the authors, if fatigue tests both in air and *in vacuo* were carried out on a series of coppers specially prepared so as to eliminate one or more of the constituent impurities, both solid and gaseous.

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In addition to oxygen, moisture is one of the chief accelerators in corrosion phenomena, and one might anticipate that in the complete absence of moisture even in the presence of oxygen, some raising of the fatigue limit might be observed.

Dr. H. Moore,* C.B.E. (Vice-President): I have little to say on this paper except to ask for more! We want a great deal more information about the action of the atmosphere in producing corrosion-fatigue. I think that Dr. Gough is contemplating a considerable programme, and we shall look forward to the results with the greatest interest. It is fairly obvious what sort of information is required, *e.g.*, what materials are affected by corrosion-fatigue due to the atmosphere, the extent to which they are affected, the constituents of the atmosphere which are responsible for the effect, and the actual mechanism of the corrosion-fatigue action.

It may or may not be significant (I think that probably it is not) that the material in which Dr. Gough has found the maximum effects—70 : 30 brass—is in certain circumstances singularly susceptible to intercrystalline attack; but I think that Dr. Gough made it clear in his Autumn Lecture † that corrosion-fatigue is probably rarely due to intercrystalline failure. Dr. Gough has, I think, for the first time fully proved what has been suspected for a number of years—namely, that the atmosphere is capable of producing corrosion fatigue. In our work on lead, at Woolwich, we showed some years ago that the exclusion of the atmosphere from the specimen increased the endurance limit of lead considerably. Professor B. P. Haigh, as Dr. Gough mentioned in his Autumn Lecture, introduced an ingenious theory to account for the action of the atmosphere on lead subjected to fatigue—a theory which did not greatly appeal to me. That theory now appears to be untenable; the action is most probably on the surface and not below the surface, as Professor Haigh suggested.

I should like to direct attention to the great value of Dr. Gough's Autumn Lecture in its printed form. It is a lecture of unusual length, which has cost the Institute a good deal to publish, and I recommend everybody who is interested in the subject of corrosion-fatigue to study it closely.

Dr. Gough (*in reply*): I will reply very briefly to the major points raised, and will later reply more fully in writing, if necessary. Dr. Vernon's suggestion that sulphur dioxide and ammonia may be the principal operative factors is a new and extremely valuable suggestion. In this subject, in which fatigue and corrosion both enter so largely, we engineers look to corrosion experts for valuable suggestions of this type, based on their specialized knowledge. I thank Dr. Vernon for his remarks, and hope to investigate the influence of the suggested factors.

Professor Taylor suggested further experiments employing a higher degree of vacuum. It is hoped to carry out some work on these lines. As a first step, however, we are studying the changes occurring in microstructure during fatigue tests made in air and *in vacuo*, of the 70 : 30 brass which gave the big reduction of 26 per cent., hoping to find the *reason* for the reduction: in these further tests a pressure of 10^{-3} mm. is again being employed. Professor Desch also referred to the desirability of investigating the effect of a more perfect vacuum. He also raised the interesting possibility of the enhanced corrosivity of the metal within ultramicroscopic cracks due to the compression of entrapped air during the strain cycle. I have no experience of the possibilities of this action, and should like to consider the matter before replying.

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[*] Research Department, Woolwich.

[†] See this volume, p. 17.

Dr. Inglis inquired about the size or scale effect. McAdam has done a little work on this aspect, using specimens of 0·5 in. and 2·5 in. diameter, and found little difference in behaviour under corrosion-fatigue. I have discussed this aspect more fully in the Autumn Lecture. Although "size effect" appears to be small, I would point out that the percentage wastage by general corrosion is naturally greater in thin sheets than in large bars, thus tending to produce different performances: this is not a scale effect, however, in the strict sense in which the term is used in elastic and fatigue problems.

Mr. Chaston suggested that the metals found to give the largest differences in fatigue values are essentially "soft" and would not be expected to be susceptible to "notch" effects. This would appear to be true, yet I would recall to his memory Haigh's paper on some fatigue experiments on soft lead, in which he published a photograph showing that, even with this metal, the path of the fatigue fracture was definitely influenced by the presence of a small surface scratch.

Dr. Brownsdon made a valuable suggestion regarding the possible effect of dissolved gases. This has been carefully considered, but it is difficult, at first sight, to believe that an appreciable amount of gas would be liberated at air temperature. The matter should, however, be investigated, and I should greatly value Dr. Brownsdon's co-operation.

We thank Dr. Moore for his very kind remarks concerning the paper and for outlining many suggestions for further research. It is hoped to attempt some of the suggested work if time permits. Arising from the very valuable work that has been carried out in the Research Department at Woolwich on the subject of atmospheric corrosion of lead, it appears desirable to make tests on lead *in vacuo*. I look forward to being able to do this, and also to secure Dr. Moore's kind co-operation regarding the supply of material.

CORRESPONDENCE.

Dr. U. R. Evans,* M.A. (Member): The present research, especially when studied in connection with Dr. Gough's masterly Autumn Lecture, is most welcome; the combination of clear thinking with the well-planned, accurate research now in progress at the National Physical Laboratory will surely elucidate this difficult subject. I feel in general agreement with Dr. Gough on nearly all essential points. It is unfortunate that some of those present at Dr. Gough's lecture came away with the impression that our views are irreconcilable. There are so many real disagreements on the question of corrosion that it is a pity to confuse the subject further by imagining disagreements which do not in truth exist. Perhaps, therefore, I may be allowed to define my point of view, emphasizing the points on which I share Dr. Gough's views. My opinion on the influences of stress and strain on corrosion is largely derived from experimental work on abrasion and the after-effects of bending; in recent years, however, work has been conducted, in the Cambridge laboratory, on the effect of alternating and intermittent stresses on corrosion by Dr. A. J. Gould, who, I hope, will shortly publish his results.

I agree with Dr. Gough that the apparent increase of corrosion-damage by stress is, in the main, not the direct effect of stressing the metal itself, but is due to the damage done to the protective quality of surface films. In 1929 I carried out work to distinguish between the direct and indirect effects of the internal stresses left after bending.† Strips of copper were abraded, bent locally, and immersed in silver nitrate; immediate blackening resulted, without special intensity at the bend. Similar strips were abraded, exposed

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* Cambridge.

† *J. Chem. Soc.*, 1929, p. 101.

to dry air for 9 days (to produce an oxide film*), bent locally (to damage the film) and immersed in silver nitrate; the reaction now occurred preferentially at the bend, the rest being almost unchanged. Other strips, bent immediately after abrasion, and afterwards exposed 9 days to dry air (so as to allow the damage at the bend to heal up), and then immersed in silver nitrate, showed scarcely more attack at the bend than elsewhere. Damage to the film here was evidently the important influence at work. I am, however, well aware that a disordered space-lattice is a less stable system than a perfect lattice, and that, under suitable conditions, disorganization of the crystal structure might be expected to cause preferential attack, quite apart from any damage to a film; indeed, the tendency for corrosion to occur preferentially on the site of previously formed slip-bands, discovered in another research by Dr. Gough and Mr. Sopwith,† may perhaps provide an example.

That local mechanical damage to the film covering the metal may make the damaged part anodic towards the rest was indicated by some measurements of "abrasion currents" using 36 combinations of metals and liquids,‡ the results of which I published in 1925. Two electrodes of the same metal were surrounded by the same liquid, one only being abraded, and the current passing between the two was measured. When the liquid was one which produced a protective film on the metal, the abraded electrode was the anode. In cases where there was a slimy secondary corrosion-product, its removal renewed the supply of oxygen locally, and thus the abrasion-current was masked by a differential aeration current in the opposite direction; I believe that, if it were possible in all cases to damage the primary skin without increasing the oxygen-concentration, local damage would always produce an anodic area at the point of damage. If that point is small compared with the undamaged area, the corrosion (the amount of which is determined mainly by the rate of oxygen-supply to the *large* cathodic area, but which is all concentrated on the *small* anodic area) may be very intense.

Now these conditions are actually realized at the bottom of a pit running into a specimen which is subjected to alternating stresses in a direction parallel to the general surface (see Fig. A). It is not necessary to postulate that the oxygen-concentration at the pit-bottom (E) shall be lower than that elsewhere (although in practice this will probably be the case, and may contribute to the electrochemical effect). Even assuming uniform oxygen-concentration, the probability that the film will become damaged or porous will be a maximum at E and minimal along the surfaces ABC and FGH, where the stresses clearly cannot assist any "natural" tendency to breakdown. Of course it is not certain that the breakdown will occur exactly at E; it may occur, say, at D, causing corrosion to advance to a new front shown by the dotted circle JKL; but now the probability of fresh damage will be maximal at or near the lowest point J, and therefore the fissure will continue to advance, *on the whole*, in a direction perpendicular to the stress-direction, although there may be temporary deviations to right and left; thus we are led naturally to a course for the crack such as is shown in Figs. 37 and 38 (Plate XV) of Dr. Gough's Autumn Lecture. A very little destruction of metal will cause an appreciable decrease in the effective cross-section (a matter which may be of importance in corrosion-fatigue of *wires*); furthermore (and this is of far more importance in the corrosion-fatigue of *rods*), the action tends to keep the shape of the fissure extremely *acute*, a fact which will ensure rapid loss of fatigue-strength by stress-concentration, as Dr. Gough points out.

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* See W. H. J. Vernon, *J. Chem. Soc.*, 1926, p. 2273.

† *Proc. Roy. Soc.*, 1932, [A], 135, 392.

‡ *J. Inst. Metals*, 1925, 33, 31–35.

The shape of the fissure developed under stresses which keep damaging the bottom will thus be far more prone to reduce fatigue-strength than that developed *under stressless conditions* through ordinary differential aeration, which is likely to produce *broader and blunter pits.* Our knowledge is still incomplete, but it appears that whilst the *probability* of corrosion is diminished by increase of oxygen-concentration (being therefore minimal at *A* and maximal at *E*), the *conditional velocity* of attack (*i.e.* the corrosion-rate which will develop, *provided that* corrosion has once fairly started) is favoured by high oxygen-concentration, and is thus maximal at *A* and minimal at *E*. The *expected velocity*, which is the product of the probability and the conditional velocity, will be a maximum at some intermediate point, say at *B* or *C*. The short, rounded type of pits resulting in this way (Fig. B) is not likely to reduce fatigue strength seriously by stress-concentration, whilst the long, sharp-ended pits produced under alternating stress conditions (Fig. C) will certainly do so.

Fig. A.

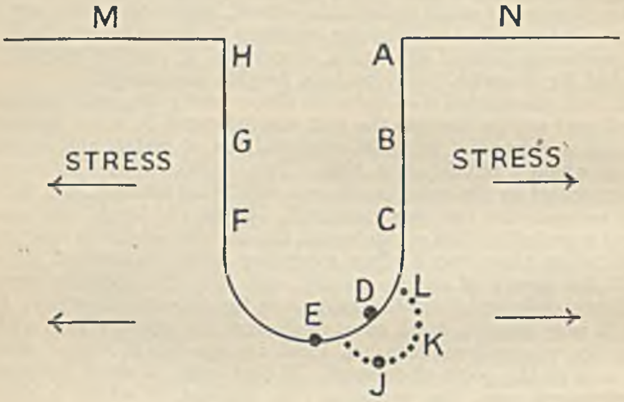

Fig. B.

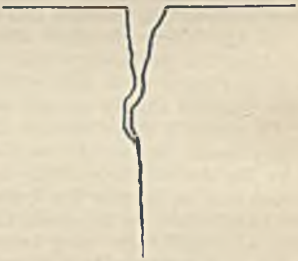

Fig. C.

Thus differential aeration, whilst doubtless at work in many of the pits on a corrosion-fatigue specimen, is probably not of direct importance in producing the mechanical weakening. Of course, the principle cannot be altogether neglected; the effect of the rubber rings in the experiments of Speller, McCorkle, and Mumma * is probably due to the restriction of diffusion of oxygen and/or chromate in the early stages of the attack, but in an experiment as normally conducted it seems at least possible that, in the case of those pits which develop downwards into fatigue cracks, some oxygen may be present in the upper part of the pit, and that it is this oxygen which prevents the corrosion spreading sideways instead of downwards. This admission of oxygen may perhaps be assisted by the "breathing action" of the alternating stress; oxygen or oxygen-saturated liquid is to some extent drawn into the cracks during the tension, and obstructive secondary corrosion-product pushed out during the compression; this would explain why alternating stresses are more destructive than static stresses. It may be objected that the maintenance of the conditions favourable to this breathing action would seem to be an exceptional occurrence, but it appears that actually only a *small proportion* of the pits *do* develop into fatigue fractures. If, provisionally, we assume in the upper part of the pits the presence of some oxygen (which is needed for cathodic depolarization), then the cathodic product, which is generally sodium or calcium hydroxide, can be formed *within* the pit itself, and any metallic salts which ooze through the films covering the side walls (*ABC* or *FGH*) will be precipitated *in physical contact* with the walls, thus healing any porosity which the film may here show, and *putting a stop to the attack*. Such a healing of temporary weak points has become very familiar to the Cambridge workers in studying the upper parts of vertical corrosion-specimens standing in potassium or sodium chloride; the film of hydrated oxide, in optical contact with the surface, frequently becomes thick enough in the late stages to give interference tints.† Similar tints are often seen on corrosion-fatigue fractures of lead, and are well illustrated on some specimens kindly sent me by Professor B. P. Haigh some years ago. Alternative explanation is, however, possible—namely, that the alkali is formed outside the pit, say at *M* or *N* (where there is without doubt oxygen), and "creeps" into the pit; the astonishing power of caustic alkali to creep through imperceptible crevices is well known to chemical engineers; I have also encountered surprising examples of it in work on paint-films.‡

If it is considered that oxygen can enter those pits which are developing into fatigue fissures, then it is clear that the insoluble metallic hydroxide (usually procured by interaction between the anodic product, a soluble metallic salt, and the cathodic product, an alkali) must be precipitated deep down in the pit. Now the precipitation of a bulky corrosion-product below the surface must have one of three results: (1) it may disrupt the metal, (2) it may block the crevice and stop further corrosion, (3) it may be squeezed out. In a previous paper § I have given examples of these three effects. Blockage and cessation of attack often occur under static conditions; alternating stresses may assist the expulsion, and thus allow attack to continue where otherwise it would cease. Dr. Gough apparently thinks that, under corrosion-fatigue conditions, the idea of the corrosion-product assisting materially in the disruption of the metal is not to be entertained.‖ I will not press this point, but I would mention that I know of cases where plates have been forced apart, rivets broken, metal swollen to double its original thickness simply

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* *Proc. Amer. Soc. Test. Mat.*, 1928, **28**, (II), 159; 1929, **29**, (II), 238.

† *J. Chem. Soc.*, 1929, p. 111.

‡ *Trans. Amer. Electrochem. Soc.*, 1929, **55**, 251.

§ *J. Chem. Soc. Ind.*, 1928, **47**, 61T.

‖ Gough, Autumn Lecture, this volume, p. 17.

by the expansive force of rust; also that Rosa, McCollum, and Peters * have measured the expansive force, and have obtained values as high as 1 ton/in.^{2}.

I accept Dr. Gough's suggestion † that the "frequency" effect on corrosion-fatigue is not so much due to relative rates of film rupture and repair, as to the increasing effect of velocity on the permeability of the film, an increased rate of agitation producing greater porosity. This seems to explain the results of Speller, McCorkle, and Mumma‡ better than the explanation which I put forward in the discussion of papers by McAdam.§ Nevertheless, it must not be forgotten that the *sudden* breakdown of a film, followed by its gradual repair, is a well-established occurrence. I have obtained direct ocular evidence of sudden cracking in the case of thick oxide films on copper; Pilling and Bedworth ‖ have published evidence for the same phenomenon based on conductivity measurements on heated copper; Vernon ¶ has obtained additional proof in his beautiful micro-gravimetric work on aluminium, whilst further confirmation is provided by the time-current and time-potential curves traced by my collaborators, Britton ** and Hoar.††

If, for the sake of argument, we assume that, either through the breathing action already suggested or in some other way, oxygen is effectually introduced into the upper parts of the pits, and that the excess of bulky corrosion-product is effectually expelled, then the hotly debated point as to whether various corrosion-products do or do not act as oxygen-screens becomes of little importance in corrosion-fatigue, although it remains of importance in other branches of corrosion-science. Nevertheless, since Dr. Gough, and also Dr. Vernon, have referred to this matter, I desire to state the position. Bengough, Lee, and Wormwell ‡‡ have produced very accurate corrosion-time curves, to which they apply an interpretation which assumes that the corrosion product has no screening action. Other interpretations, however, appear to be possible. Furthermore, those authors themselves state §§ that the corrosion-product formed *under certain conditions* (namely, in very dilute solutions) *does* act as an oxygen screen. It must not be overlooked that Bengough's experimental conditions are less favourable to screening than those of other workers. In the study of vertical iron specimens, my collaborator, T. P. Hoar,‖‖ has found that the ferroso-ferric rust is a voluminous body which absorbs oxygen when shaken with air; Bengough's ferroso-ferric product is a compact magnetite which is remarkably stable towards oxygen. Thus, even if Bengough's interpretation of his own work be accepted, it affords no valid criticism of the conclusions from work on differential aeration. This communication itself, I hope, bears witness that I do not desire the Differential Aeration Principle to be dragged in in cases where it is clearly inapplicable.

Dr. G. D. Bengough,¶¶ M.A. (Member), and Mr. F. Wormwell ¶¶ : Dr. Evans has kindly sent to us a copy of his contribution to the discussion on

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* *U.S. Bur. Stand., Tech. Paper* No. 18, 1913.

† Gough, Autumn Lecture, this volume, p. 17.

‡ *Proc. Amer. Soc. Test. Mat.*, 1928, 28, (II), 159; 1929, 29, (II), 238.

§ *Proc. Amer. Soc. Test. Mat.*, 1929, 29, (II), 307; 1930, 30, (II), 445.

‖ *J. Inst. Metals*, 1923, 29, 551.

¶ *Trans. Faraday Soc.*, 1927, 23, 154.

** *J. Chem. Soc.*, 1930, p. 1778.

†† *J. Iron Steel Inst.*, 1932, 126.

‡‡ *Proc. Roy. Soc.*, 1931, [A], 134, 327.

§§ *Proc. Roy. Soc.*, 1931, [A], 134, 337.

‖‖ *Proc. Roy. Soc.*, 1932, [A], 137, 354; also unpublished work.

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

Dr. Gough and Mr. Sopwith's paper. It contains references to our work which seem to call for reply, particularly as regards our statements that zinc hydroxide, magnetic iron oxide, and ferric oxide do not behave as oxygen screens in stagnant solutions of sodium chloride and potassium chloride. The question has not been hotly debated, as Dr. Evans states, because no one has yet put forward either: (1) rebutting quantitative experimental evidence, or, (2) any reasonable explanation of our results other than our own which has obtained wide acceptance by those who are acquainted with it.*

Dr. Evans remarks that we "state that the corrosion product formed *under certain conditions* (namely, in very dilute solutions) *does* act as an oxygen screen"; he omits to state (1) that they never so acted in presence of air in which corrosion-fatigue experiments are usually performed, and (2) that in the exceptional conditions when they did so act, corrosion was greatly reduced and eventually stopped.

Dr. Evans' further remarks that our experimental conditions are less favourable to screening than those of other workers (presumably his own associates) seem to be definitely wrong. In the partly immersed conditions used by Hoar and himself, practically the whole of the oxygen used has free access to the cathodes without passing through thick masses of ferric and magnetic oxides; consequently their screening action cannot be tested. Hoar's experiment, to which Dr. Evans refers, has no bearing on the matter; it merely confirms that in his experimental conditions little oxygen is getting down into the liquid; consequently there is much ferrous material in the corrosion product, but this is not due to any screening effect of ferric or magnetic oxide, but to the fact that the oxygen is removed near the surface by reaction with hydrogen. In many of our experiments, on the other hand, both attacked and unattacked areas have become *completely covered* with ferric and magnetic oxides so that all the oxygen used was forced to pass through them. Yet the corrosion rate did not alter as the masses accumulated.

The final point made by Dr. Evans is that our corrosion products differ from his, which may, therefore, serve as oxygen screens, though ours do not. We may point out that Dr. Evans' corrosion products are no more likely to be typical of common industrial conditions than ours; in fact, a mixture of ferric and black magnetic oxides constitutes quite a large proportion of ordinary rust in many conditions.

The AUTHORS (*in further reply to the oral discussion*): There is little to add, in further reply to the discussion, but to express our appreciation of the kind reception accorded to the paper and our thanks for the generous offers of advice and co-operation made concerning future work. Much more experimental work requires to be carried out, and we hope to be able to communicate the results of further research at some future date.

Dr. GOUGH: I welcome very greatly the contributions made to the discussion by Dr. Evans, Dr. Bengough, and Mr. Wormwell; as these relate more to the Autumn Lecture than to the present paper by Mr. Sopwith and myself, it is, perhaps, more fitting that I should reply personally. At the same time, I would remark that both papers deal with essentially the same subject, and that the present is an appropriate occasion for discussion on the wider issues of corrosion-fatigue.

The remarks by Dr. Evans, Dr. Bengough, and Mr. Wormwell will be read with great interest by all those interested in corrosion-fatigue. There are certain fundamental characteristics of the subject which can be explained

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* For our complete statements see *Proc. Roy. Soc.*, 1931, [A], 131, 506, and 1931, [A], 134, 337.

adequately only by those who are making an intimate study of the intricate and fascinating problems relating to corrosion. We have now before us the considered views of two groups of such experts. At the moment, it appears that the fundamental researches of these writers are such that somewhat opposing views are expressed. The divergence thus brought out will, I trust, inspire the investigators to make some critical tests to investigate some of the aspects of corrosion which are, perhaps, peculiar to corrosion-fatigue conditions; valuable additions to our knowledge are certain to accrue. As an engineer worker on corrosion-fatigue I welcome the attention of the chemists being thus attracted to an aspect of the subject of fatigue, and if my Autumn Lecture has been instrumental in exciting this interest, I feel well repaid for any trouble to which I may have been put. I would again welcome the contributions, and express my thanks to Dr. Evans, Dr. Bengough, and Mr. Wormwell, and shall look forward to their further writings on the subject.

A MODIFIED IMPINGEMENT CORROSION APPARATUS.*

By H. W. BROWNSDON,† M.Sc., Ph.D., Member of Council,
and L. C. BANNISTER,‡ M.Sc., Ph.D., Member.

Synopsis.

Owing to difficulties experienced with apparatus hitherto used for carrying out impingement corrosion experiments, a modified apparatus has been devised which is simple in design and permits of the many factors influencing this type of corrosion being readily controlled; details are given regarding its construction and use. Some preliminary results obtained are given as illustrating the use of the apparatus in the study of corrosion phenomena.

It is frequently necessary to be able to predict, within fairly wide limits, the probable corrosion-resistance of any material to service conditions in order to gauge approximately its life, the safety margin in constructional dimensions, and any precautions to be taken during use. Clearly, any progress in the manufacture and application of new alloys is bound to be very slow if development is dictated solely by practical experience or by the results of prolonged tests under working conditions. In many instances the desired information concerning a material has been sought by reproducing the conditions of practice as closely as possible and making very careful observations and measurements during the early stages of corrosion. In some cases this procedure has yielded very trustworthy indications. Nevertheless, it is in general exceedingly difficult to imitate, on a laboratory scale, actual working conditions, and even if this can be done, the later stages of corrosive attack frequently take on a form quite different from that shown during the early stages.

Many attempts have been made from time to time to devise tests for reflecting the probable service behaviour of a given metal by accelerating the corrosion above its natural rate so that visible or easily measurable changes occur within a comparatively short period. Even if such tests do not accurately reproduce working conditions, they help

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

very considerably in elucidating some of the phenomena associated with corrosion.

Some two years ago it was decided to study the behaviour of a large number of alloys when subjected to impingement corrosion. This special type of attack, which may be caused when a liquid carrying entangled air passes rapidly over the surface of a metal, has been studied by G. D. Bengough, R. May, and R. Pirret.* Whilst the method of testing they worked out has been applied mainly to the study of condenser-tube corrosion, the present authors considered that the test might be helpful in throwing light on other types of corrosion problems and in advancing a knowledge of the part played by protective surface films.

Apparatus of the type developed by R. May † was installed, but after considerable experience the conclusion was reached that it was not suitable for the wider applications involved, mainly owing to the difficulties encountered with the running of such comparatively complicated apparatus, the lack of agreement between duplicates, the use of a common corroding solution for metals of different composition, and the relatively small number of specimens that could be dealt with on one apparatus. The results were obtained very slowly and not infrequently were contradictory. It was realized that some radical modifications were desirable in order to be able to use the jet impingement test with the degree of control necessary for obtaining consistent results in a limited time. It is understood that workers in other laboratories ‡ have also found this form of apparatus not entirely satisfactory, and in the United States modifications have already been adopted.§

A much simpler form of jet impingement test was therefore devised of which a full description is given at the end of the paper. The underlying idea consists in immersing a metal specimen in a corroding liquid and blowing air on to it by means of a jet made of drawn-out glass tubing. The main virtue of the method lies in the accurate control obtainable over the various factors which influence the special type of corrosion produced. The principle involved is not new and had previously been employed in experiments on the corrosion of resistant alloys by acids,|| but the value of the method for studying the phenomena associated with more general types of corrosion seems to have been overlooked. A few preliminary experiments with the apparatus showed that with several different alloys the types of attack produced were

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* "The Causes of Rapid Corrosion of Condenser Tubes," *Trans. N.E. Coast Inst. Eng. and Ship.*, 1923, **40**, 20.

† *J. Inst. Metals*, 1928, **40**, 141.

‡ Private communications.

§ A. Morris, *Amer. Inst. Min. Met. Eng., Tech. Publ.*, No. 431, 1931.

|| J. F. Thompson and R. J. McKay, *Indust. and Eng. Chem.*, 1923, **15**, 1115.

similar to those given with the May apparatus, and that a 500-hr. period of impingement sufficed for obtaining the necessary evidence regarding relative resistance to corrosion.

The apparatus lends itself to the study of the various factors influencing corrosion, such as the composition of the metal, the solution, or the gaseous phase, any one of which may be varied while the other two are maintained constant. Most of the experimental work done up to the present has been with sea water as the liquid medium and air as the gas, the composition of the metal having been the variable factor studied. Other experiments have been carried out, however, on the same metal in varying solutions containing air as the gas, and experiments are in hand in which the air is being replaced by other gases. The temperature of the solution is another factor which can easily be controlled in this apparatus.

The form of corrosion produced by this test in some typically different alloys is illustrated in Figs. 1–8 (Plates XXII and XXIII). In these alloys the corrosion was most severe at the position of air impingement, and quite distinct types of attack, both as regards area, depth, and form, were produced with the different alloys. Cupro-nickel and Admiralty mixture, for example, develop concave areas, much smoother in the case of cupro-nickel than in the case of Admiralty mixture, whereas with 70 : 30 brass and aluminium–brass the attack is more in the nature of a pit, angular and jagged. The appearance of cupro-nickel during the early stages of testing is characterized by small bright circular cavities which are not dissimilar to Brinell ball impressions. When viewed under the microscope the characteristic difference between the pits formed on different alloys is clearly defined, and micro-examination is therefore a most valuable method for studying the different types of corrosion which are produced.

Another interesting point to be noticed is the area of the alloy which is attacked during the test. It will be seen that in the case of aluminium–brass this is very restricted, less restricted in the case of 70 : 30 brass, and still less restricted in Admiralty mixture or cupro-nickel. In the case of the latter it is sometimes difficult to say where the attacked portions begins, whereas this is more readily seen with Admiralty mixture, and quite sharply defined in the cases of 70 : 30 brass and aluminium–brass. From these observations it will be appreciated that weight loss determinations alone might give unreliable information as to the serviceability of a material, as a knowledge of the degree to which the attack is localized is of greater importance than the actual weight loss. Further information may be obtained by measuring the depth of the pit formed. Roughly speaking, this is found to be a linear function of the duration of the test and some of the figures obtained are plotted in Fig. 9.

The reasons for these characteristic differences of pit form, area, and depth, are probably associated with the breakdown of protective films. The results illustrated were all obtained with an air pressure equivalent to 20 inches of mercury, which should be kept in mind when attempting to translate into practice the results obtained by this test. The evidence given indicates that of these four typical alloys, the aluminium brass produced the most protective film, and that this alloy resisted corrosion except in the limited area just under the jet, where the intensity of impingement was greatest. Whilst the breakdown of the protective film on aluminium-brass occurred at 20 in. of mercury pressure, it was found that at the pressure of 4 in. of mercury or less no such film breakdown was apparent.

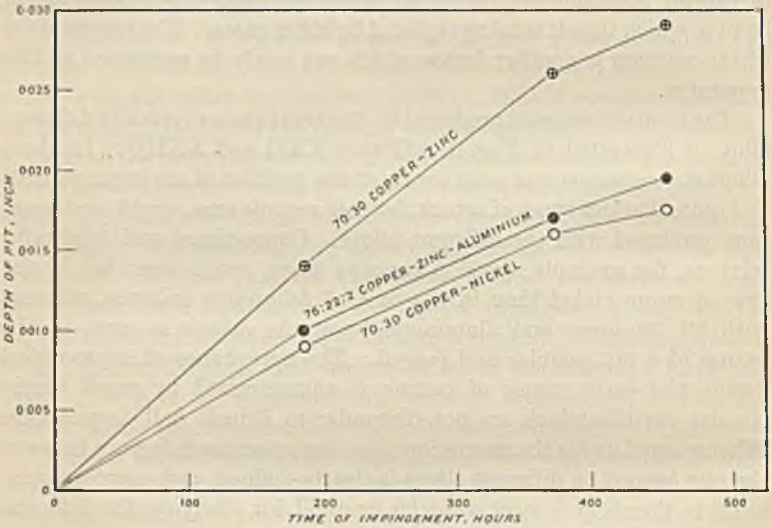

FIG. 9.—Some Alloys in Brighton Sea-Water.

Reviewed in this manner, this test can be used for determining the velocity of impingement necessary to break down any protective films that may have formed.

The influence of the nature of the solution on the depth of pitting produced is shown in Fig. 10 for aluminium-brass in Brighton sea-water, in the same diluted to 24 per cent. of its natural strength, and in a synthetic sea-water. The depths of pits produced in the two latter solutions are given for three different experiments in each case, and serve to illustrate the degree of reproducibility obtained with the apparatus. The open circles and triangles show the depths of pits produced on two specimens immersed together in one beaker, whilst the filled-in circles and triangles represent the figures obtained on another specimen in another beaker. By taking mean figures from such closely agreeing experiments a single smoothed curve, such as is shown for Brighton sea-water, may be accepted with some degree of assurance.

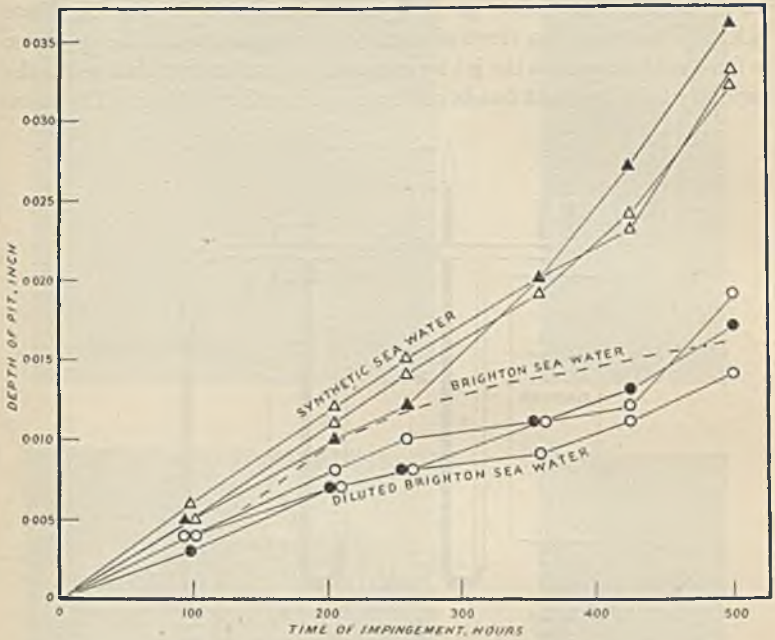

Fig. 10.—Aluminium–Brass in Some Solutions.

Other effects of the composition of the solution can naturally be experimented with in a similar manner. For example, by carrying out a series of comparative tests it was found that bichromates present to the extent of 1 per cent. inhibit the corrosive effect of sea-water on 70 : 30 brass, the metal surface remaining quite bright.

Therefore, quite apart from its value for comparing the resistance to corrosion of different alloys in various solutions, the impingement apparatus described in this paper is a useful laboratory instrument for studying the behaviour of surface films and the factors, such as composition of alloy, heat-treatment, &c., which influence their resistance to this special type of corrosion.

DESCRIPTION OF APPARATUS.

Compressed air, filtered through wood straw and cotton wool packing, then bubbled through water to clean it further and partly saturate it with moisture, is forced at a pressure of 20 in. of mercury through a capillary tube, 7 mm. in external diameter and of 1 mm. bore, drawn out to a final internal diameter of approximately 0·35 mm., so that a stream of air bubbles impinges vertically downwards through the solution on to the surface of the specimen under test. Fig. 11 (Plate XXIV) illustrates two views of a unit of the apparatus. The specimen is fixed with respect to the jet by means of a glass bracket clamped to the capillary tube by stout bands cut from indiarubber tubing. The metal being tested is fixed to the lower portion of the glass bracket also by rubber bands, as seen in the photograph.

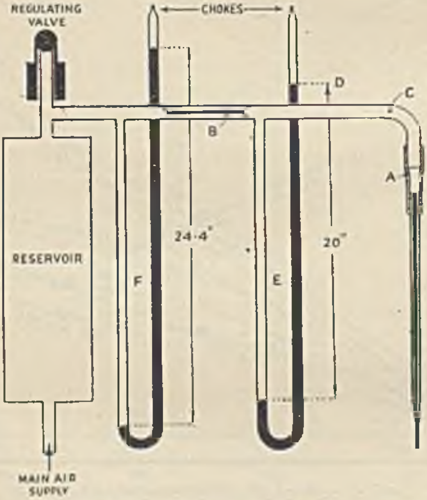

FIG. 13.—The Jet Calibration Apparatus.

Experience showed that it is most important to have jets of identical shape and size. The jets used in this work are such as to allow 2,220 c.c. of air to escape per minute under a constant pressure difference of 20 in. of mercury. Variations in the internal diameter of the drawn-out portion of the jet—even if much too small to be detected by the naked eye—give rise to very large variations in the amount of air passing through and so greatly influence the rate of corrosion. It is therefore necessary to adopt some special precautions in order to produce standard jets and a short account of how they are made follows.

PLATE XXII.

70 : 30 Copper–Zinc.

Fig. 1.—Plan. × 20.

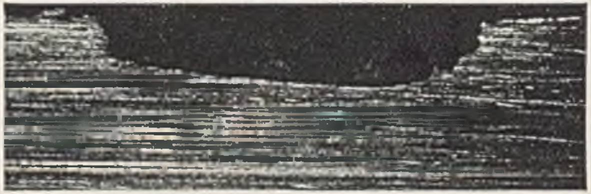

Fig. 2.—Section. × 20.

70 : 29 : 1. Copper–Zinc–Tin.

Fig. 3.—Plan. × 20.

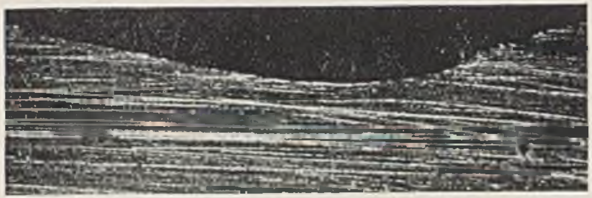

Fig. 4.—Section. × 20.

[*To face p.* 128.

PLATE XXIII.

76 : 22 : 2 Copper–Zinc–Aluminium.

FIG. 5.—Plan. × 20.

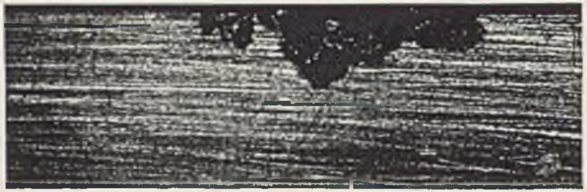

FIG. 6.—Section. × 20.

70 : 30 Copper–Nickel.

FIG. 7.—Plan. × 20.

FIG. 8.—Section. × 20.

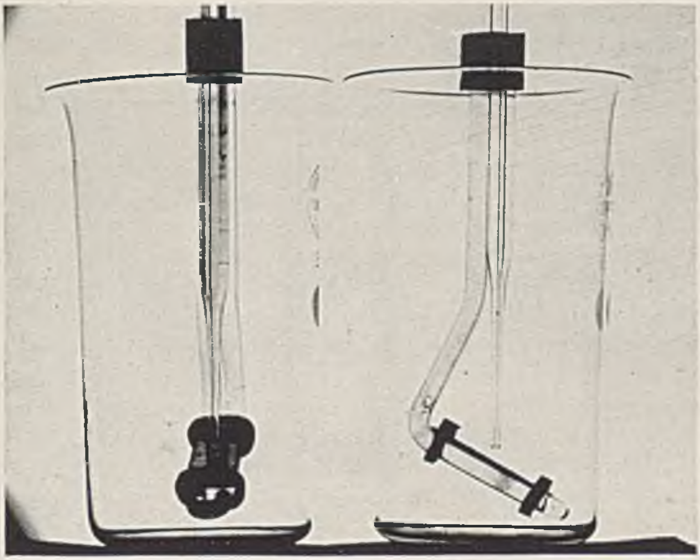

Fig. 11.—Two Views of a Unit of the Apparatus, Showing Specimen in Position.

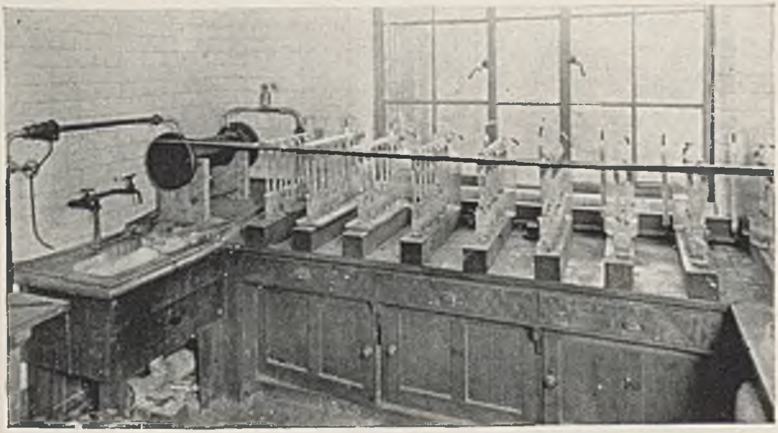

Fig. 12.—General View of the Impingement Corrosion Apparatus.

A 50 cm. length of the capillary tubing is heated at its mid point in a large Bunsen flame and drawn out until its new length becomes 61 cm. When cold the tube is severed in the middle of its constricted portion and the two halves are stored away for some weeks prior to conversion into standard jets. The time interval between drawing-out and standardization is essential, since glass shrinkage is often high during this period and may lead to variability of results if the jets are finished and used immediately after hot-working. The final operation for converting the capillary tube to a finished jet is made with the aid of the apparatus sketched in Fig. 13, which consists essentially of a reservoir under air pressure, the pressure being regulated by means of a weighted regulating valve and measured by a gauge *F*. This gauge is followed by a capillary tube *B* of such dimensions as to pass 3,930 c.c. of air per minute at 20 in. of mercury pressure. Standardization of a jet is effected by connecting it to the indiarubber tube *A*, and observing the height of the mercury in the manometer *E*. If the bore at the tip of the jet is too small, the rate of flow of air through it will be slow compared with the rate of flow through the fixed comparison tube *B*, and the pressure in *C* will rise until the mercury reaches somewhere above the mark *D*, which represents 20 in. of mercury. To correct this, the "resistance" of the jet to the passage of air is progressively reduced by cutting off very short lengths until the pressure falls to the 20 in. mark. If the bore is already too large, the pressure in *C* will not rise to 20 in. and the tube must be rejected. Only jets showing a divergence of less than ±0·1 in. of mercury are used.

The type of attack occurring during impingement was found to depend to a certain extent on the distance of the specimen from the jet. When the tip of the jet made contact with the specimen, a brown mark alone was produced with a piece of 70 : 30 brass in sea-water after continuous bubbling for 150 hrs., but with a clearance of 1·7 mm. between the end of the jet and the specimen a definite corrosion pit was produced. At the same time it was noticed that at clearances of 1·7 mm. and above, a certain rather characteristic type of bubbling was produced, which was much finer and more broken up than when the jet was touching the metal. The effect of increasing the clearance much beyond 1·7 mm. produced merely a spreading out of this stream of fine bubbles, with the result that the attack was no longer concentrated, but dissipated over a larger area.

The reason for having the air stream impinging at an angle of 60° to the surface plane of the specimen is to induce all the bubbles to rise up on one side of the glass jet. It has been found that more consistent results are obtained by this arrangement than when the bubbles rise up intermittently at different positions round the jet, such as occurs when impingement is normal to the specimen.

The standard procedure was therefore to subject a flat or slightly concave surface of area 1·3 × 3·3 cm. to impingement attack for 500 hrs. at an angle of 60° and with a clearance of 1·8 mm. between the sample and the glass jet. During this period the solution, contained in a 250-c.c. beaker, was completely changed every 24 hrs. and the air impingement was stopped every week-end for a period of 42 hrs. By arranging the various units of the apparatus in some such form as that shown in Fig. 12 (Plate XXIV), it is easily possible to test more than one hundred specimens at the same time all in duplicate and under the same conditions of temperature, pressure, &c.

The surface of the metal being tested was either mechanically abraded with emery paper (Hubert 0), polished, or left in the cold-rolled or drawn condition and merely degreased with carbon tetrachloride.

Several methods were investigated for measuring quantitatively the extent of attack. In some experiments the specimen was weighed before the test and again at the end after removing the adherent corrosion products, the nett loss giving the amount of metal removed or dissolved. This, however, was considered an unfair procedure with samples that are not freely suspended during the attack, and further, the specimens which suffered the greatest losses of weight were not infrequently those which showed least signs of pitting. The most satisfactory way of expressing quantitatively the severity of attack seems to lie in a combination of the weight loss of a freely suspended specimen, and the depth of pit produced on a similar specimen when normally fixed under the jet. The depth of pit at any time during the 500 hr. run can be measured by means of a micrometer or a microscope with calibrated fine adjustment.

ACKNOWLEDGMENTS.

The authors wish to express their thanks to the Management Board of I.C.I. Metals, Limited, for permission to publish this paper.

DISCUSSION.

MR. KENNETH GRAY * (Member): I cannot hope to throw light on this interesting paper, but I wish to speak on the question of propeller corrosion. Much expense is incurred on trawlers owing to propeller corrosion, and although it is almost negligible in the smaller vessels having propellers say of 8 ft. to 8 ft. 6 in. in diameter, with an indicated horse power of about 300–350, in the larger boats with a propeller of, say, 9 ft. 6 in. to 10 ft. in diameter, and 600 indicated horse power, the corrosion is severe enough to eat through locally, and to condemn a propeller within two years, whilst several cases have been found where this has happened in 15 months.

The time at which this defect is first apparent varies, but it is, in most

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* Director, Mellowes and Company, Ltd., Sheffield.

cases, noticeable at the end of 6 months, and again, in most cases it is necessary at the end of 9 to 12 months to fill up with Portland cement the cavities made by the corrosion.

All these propellers are of cast iron, cast solid with four blades, and are of normal proportions, having a disc area ratio of about 0·48, and a pitch ratio varying from 1 to 1·1. The quality of the mixture used does not appear to have any great effect on the problem of corrosion, although close-grained metal lasts slightly longer.

The corrosion is on the back of each blade, and in the same position. Cases have been noted in which a template could be made of corrosion on one blade, and this fitted almost perfectly on the other three blades.

The position of the corrosion is shown in Fig. A, and although this can be altered by varying the shape of the blade, it cannot be eliminated.

With the exception of this particular part, the remainder of the propeller is entirely clear of corrosion, and at the end of two years the original painting can, in many cases, be found. The same propeller fitted on a coaster and run at about 85 r.p.m. instead of, say, 115 r.p.m., as in the case of the trawler, has lasted for from 7 to 8 years, and has been found in fair condition. The peripheral speed of the blade tips appears to be the governing factor, assisted by increased blade pressure causing partial cavitation.

I have been interested in the description given in the paper of the corrosion that takes place in the 70 : 30 brass. The cavity is described as a pit, jagged and angular. I have an example of a very deep pit (Mr. Gray here exhibited the specimen, the plan of which is shown hatched in Fig. A) which might almost be called "bottomless."

I should like to know whether the apparatus described could be used practically in works where these propellers are prepared, with the idea of testing various precautions which could be applied to the ordinary cast-iron propeller prior to its use, and so devising some better defence against the rapid corrosion which takes place. The trouble appears to be due to the breakdown of the protective film with increased pressure of impingement, and the question is how this is to be avoided.

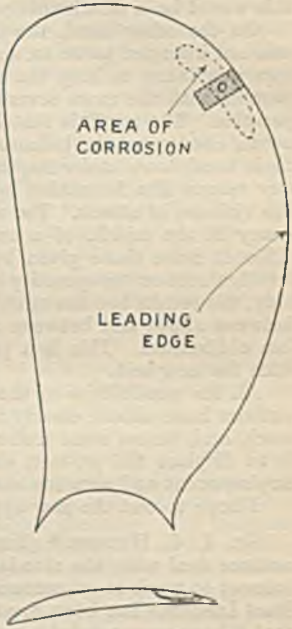

Fig. A. *Note.*—The small hatched portion indicates the position from which the specimen was taken.

Mr. R. May,* A.R.S.M. (Member): I am very much interested in this new type of impingement corrosion apparatus, and I think that the authors are to be complimented on having evolved a good practical test, particularly suitable for routine purposes.

I am not altogether satisfied that the corrosion which they have obtained could be described as true "impingement attack" or "corrosion-erosion." The photographs show what appears to be an area of intense oxide pitting surrounded by a zone of mild impingement attack, particularly in the case of the 70 : 30 brass and the 70 : 29 : 1 alloy. Similar attack is often produced in the Corrosion Research Committee type of jet-test when more than the

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* Investigator, Institute of Metals Corrosion Research, British Non-Ferrous Metals Research Association, London.

normal amount of air is admitted. With less air the attack is usually much smoother, and oxide attack is often entirely absent. It would be interesting to know if the smooth type of attack can be obtained by means of air-jet impingement, or whether oxide attack is always present.

The attack shown by the aluminium-brass appears to be of a type which has been obtained under certain exceptional conditions in the jet test, and which is at times extremely rapid; on one occasion a tube was penetrated in 6 days. Fortunately this type of attack has not yet been observed in actual practice. It must be remembered that the new arrangement is definitely an acceleration test, in which the acceleration of attack is produced by a great increase in the amount of air introduced into the water (about 150 times the amount used in the original jet-test apparatus). The proportions of air and water actually reaching the specimen are not known, nor is the actual velocity of impingement capable of direct measurement. Obviously this would be a disadvantage for some types of work.

On the other hand, the Corrosion Research Committee type of jet-test was not intended to be an acceleration test in the same sense; in its design care was taken to keep the velocity of impingement and the aeration comparable with the more severe conditions likely to be met with in condenser practice. The result is that in the jet-test, just as in tests carried out in an actual condenser, the balance between the formation of protective films and their breakdown under impingement action is rather a delicate one. If for any reason film formation is encouraged, this at once causes a decrease in the violence of attack. For example, if the pump is stopped for a few hours —say in the middle of a one-month test—the final results are often very different from those given by a test run continuously. If the velocity of impingement or the quantity of entangled air, or both, are increased considerably, the results become more certain, but some of the more subtle differences between alloys and between different samples of sea-water may be more or less obliterated. This is a point which might be considered in connection with the new test.

All the possibilities of the new test have not yet been explored, but the authors have shown clearly its superiority to the older jet-test for routine work, and, unless some unforeseen difficulty should arise, one would expect it to displace the jet-test, except in special cases where the conditions of impingement and aeration must be under independent control.

I hope to test the new apparatus at the earliest opportunity.

Dr. J. C. Hudson [*] (Member): That part of the paper in which the authors deal with the standardization of jets will I think prove of general interest to workers on corrosion, The Corrosion Committee of the Iron and Steel Institute has been investigating laboratory tests, and one of the tests that it has recommended is an intermittent spray test. One of the difficulties encountered with regard to this test is that of obtaining reproducible sprays. Although the spray recommended by the Committee is not of exactly the same type as that used by the present authors, I feel that it is quite possible that the simple and ingenious method they have described for obtaining reproducible sprays will be of assistance to us in that connection.

I have no direct experience of the type of corrosion test discussed by the authors in this paper and therefore will not comment on the experimental results obtained, especially as they are of a preliminary nature. I should, however, like to see made—if the authors have not already carried them out —a series of tests by this method on the same material, but under different conditions of hardness and different conditions of grain size. It is quite clear,

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[*] Investigator, Corrosion Committee, Iron and Steel Institute and National Federation of Iron and Steel Manufacturers, Birmingham.

as I think everyone will agree, that the results obtained are a composite effect of corrosion and erosion; therefore the hardness factor may come into play, and the authors would make a valuable contribution to our general knowledge of corrosion if they would elucidate its effect with their apparatus, which seems admirably suited for the purpose.

Dr. L. B. Pfeil,* A.R.S.M. (Member): I have undertaken during the last year or so a series of corrosion tests with a view to arrange a number of alloys in an order of merit with respect to resistance to sea-water corrosion, and have therefore read this paper with special interest. I have found that when impingement corrosion tests are made on cupro-nickel and brass immersed together in the same bath of sea-water, the results of the tests differ from those obtained when copper–nickel alloys alone are under test.

The apparatus described by the authors permits the simultaneous testing of a large number of different alloys each in a supply of uncontaminated reagent. This change from the corrosion Research Committee's apparatus described by Mr. May should prove a great improvement, but the other alterations may result in the test not being one primarily of impingement resistance, since, as Mr. May has just indicated, it is possible that oxide pitting as well as impingement attack caused the corrosion shown in the authors' photographs. Impingement attack is of special interest in connection with condenser tube materials, but the very high air velocities used by the authors make their test very different from the service conditions of a condenser tube. For this reason it would be desirable to have further information regarding the particular type of corrosion occurring in their test. No doubt the authors have considered the measurement of film potential of alloys while under test in their apparatus, and it seems likely that interesting results would be obtained from measurements of the film potential changes produced by increasing air velocities.

Dr. Bannister (*in reply*): The discussion on this paper has been most stimulating, but as the numerous points raised cannot be dealt with in the few minutes at my disposal, our reply must be made in writing.

I should like, however, to reply briefly to the question raised regarding the excessive volume of air used in most of our experiments and the effect of this on the type of corrosion produced. By means of the apparatus described it has been possible to carry out experiments with different quantities of air, and to study the effect of varying the air pressure. For instance, with aluminium–brass, which is known to have an oxide film on its surface, a "depth of pit/pressure" curve was obtained of a character which shows that at low air pressures the film does remain intact, whereas beyond a certain air pressure the film breaks down and corrosion proceeds in the form of pitting described in the paper.

CORRESPONDENCE

The Authors (*in further reply to the discussion*): The conditions mentioned by Mr. Gray under which certain propellers deteriorate and others do not are quite outside the range of our experience, and it is very difficult to say whether our apparatus would help him in solving his problems. It may be that the greater velocity of the larger diameter propeller blades causes a breakdown of some type of film which is not broken down in the case of the smaller propeller at the slower speed, in which case the apparatus

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* Research Laboratory, Mond Nickel Co., Ltd., Birmingham.

may be useful in experimenting with air impingement on cast-iron at different air pressures, and he may find that there is some critical pressure above which deep pitting sets in.

Mr. May raises several interesting points, and with his wide experience of jet impingement we are very glad to have his criticisms. We do admit that the method adopted for producing pitting is different from that used by Mr. May in the Corrosion Research Committee type of jet-test, for whilst we impinge air which carries water with it, he impinges water which carries air. Nevertheless, when Mr. May has had an opportunity of using the apparatus, we believe that he will find, as we have found, that the results obtained by the two methods are very similar. There is some acceleration when using our apparatus, as we obtain a depth of pitting in 200 hrs. about the same as that obtained by the other apparatus in 670 hrs., but since the latter apparatus itself accelerates impingement attack, by having the water stream at right angles to the surface of the metal such as would be very rare in practice, this question of acceleration is only a matter of degree. So long as the final results are similar, we consider acceleration an advantage and not a defect, and we are satisfied that in our experiments the pits result from the continual removal of corrosion products or surface oxide films, no matter whether this phenomenon be termed impingement attack or oxide pitting.

Mr. May further suggests that some loss of sensitivity is likely to result from the greater volume of air used. On this point we can scarcely agree, as we have been able to trace by means of our apparatus very small differences both in alloy composition and in water composition, and not only do we believe that he will find this apparatus sensitive in this way, but, what is perhaps more important, reproducible as far as results are concerned. We feel confident that many of the doubts that Mr. May naturally has in mind will be removed when he has had an opportunity of testing this apparatus.

In reply to Dr. J. C. Hudson regarding the effects of grain-size, hardness, and the like, on resistance to impingement corrosion, we believe that these can be very satisfactorily dealt with by this apparatus, and the conclusions that we have come to as a result of comparatively few experiments indicate that hardness and grain-size are not important factors. We have emphasized the importance of standardizing jets in this apparatus, and sympathize with Dr. Hudson in the difficulties he has experienced in this respect. Since writing the paper, we have considered other perhaps more simple means of standardizing jets, and a method for comparing the shapes as well as the velocities of the air streams delivered by different jets is to pass an inflammable gas through them and allow it to burn on issuing. A comparison of the heights and shapes of flames produced at different gas pressures of the order of those used in the apparatus provides an alternative method of ensuring identity of size and shape of a number of jets.

We agree with Dr. Pfeil as to the desirability of having each metal in its own liquid in corrosion tests, and we feel that our apparatus supplies this requirement in a very simple manner. He raises similar criticisms to Mr. May as to the type of corrosion obtained and the large volumes of air used, and our reply to Mr. May covers these.

Potential measurements during impingement attack would naturally be very interesting, but these have not been carried out up to the present, our results having been based only on visual examination, depth of pitting, and weight loss.

We would wish to make it quite clear that in this paper we have primarily described an apparatus which has given interesting results, and although these are similar to those already obtained, further detailed observations may reveal some slight differences in the types of attack produced.

TWO YEARS' CORROSION TESTS WITH DURALPLAT IN THE NORTH SEA *

By K. L. MEISSNER,† Dr.-Ing., Member.

Synopsis.

Corrosion tests were carried out with Duralplat from January 7, 1930, to January 8, 1932, in the North Sea at the Isle of Norderney. The specimens consisted of strips of 4 different thicknesses, drawn profiles of 2 thicknesses, and riveted strips. With the exception of the last-mentioned, all samples were exposed in two series, *i.e.* at ebb and flow of the tide and always under water. Samples were taken every three months.

The appearance of the surface, loss in weight, reduction in yield-point, tensile strength, and elongation were noted and the type of attack was examined microscopically. The last-named was especially useful in the case of riveted strips.

Introduction.

The registered trade-mark "Duralplat" ‡ comprises Duralumin alloys which are coated with Duralumin. This definition seems at first sight to be nonsense and has been misunderstood by those who erroneously supposed Duralumin to be only one alloy containing copper, magnesium, and manganese or a group of alloys containing these elements within certain limits.§ This error was caused and maintained for a long time by the fact that the group mentioned—in Germany called "group 681"—has always been the most important one from the point of view of application as constructional material. Originally, it comprised alloys containing 0·5 per cent. magnesium and rising amounts of copper and manganese in the proportion of 7 : 1, beginning with "681 A" which contains 3·5 per cent. copper and 0·5 per cent. manganese and ending with "681 E" with 7·0 per cent. copper and 1·0 per cent. manganese. The alloys "681 C to E" were never important, and for some years the alloys "681 A" and "681 B" were the only ones of this group. The alloy "681 B" may be regarded as the standard Duralumin alloy which is understood if no closer designation is given.

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† Chief Metallurgist, Dürener Metallwerke A.G., Düren, Germany.

‡ British Patent Specification No. 318999, August 16, 1929.

§ A definition of Duralumin is given by the author in one of his earlier papers; see *J. Inst. Metals*, 1930, **44**, 207, footnote.

Later the alloy "681 B 1/3" was developed by reducing the manganese content to one third of the normal amount of 681 B, *i.e.* from 0·6 to 0·2 per cent. Although the manganese content was in the meantime again raised to 0·25–0·3 per cent., the term B 1/3 was maintained.

In addition to the group 681, there have been in existence for a long time some other alloys, containing less copper or even entirely free from copper, which are related to the Duralumin groups. These alloys were defined as group K and comprise Duralumin alloys with 0·25–2·0 per cent. magnesium, with or without additions of manganese, but without copper. This group of alloys has been a little neglected and has never been manufactured in the quantities of the 681 alloys, the mechanical properties of which were, of course, superior.

Returning now to the definition of Duralplat, given above, this includes alloys of "681," especially "681 B," as the base metal with a coating of the K alloys, so that the base metal is a Duralumin alloy containing copper, with high tensile properties, whilst the coating metal is a Duralumin alloy, containing magnesium and manganese, but no copper, with lower tensile properties, but with high resistance to corrosion. In the compound alloy Duralplat the coating layer is electronegative towards the base alloy, so that the latter is protected against corrosion also by an electro-chemical effect. Compared with the aluminium-coated material which is known under the name Alclad,* developed by the Aluminum Company of America, Duralplat has the advantage of possessing a layer which is not only harder and stronger than pure aluminium alone, but which is also capable of age-hardening under the same conditions of heat-treatment and ageing as the base alloy. On the other hand, the aluminium layer of Alclad is only annealed by the heat-treatment which is to be applied for the age-hardening of the base alloy, generally the alloy "17 S," which is similar to the alloy "681 B." In this way, the same tensile properties can be guaranteed for Duralplat as for the unplated alloy "681 B," whilst in an alloy coated with pure aluminium, only about 90 per cent. of the tensile properties of the base alloy, according to the thickness of the layers, may be reckoned on.

EXPERIMENTAL DATA.

In order to test the corrosion-resistance properties of Duralplat, specimens of 3 different kinds were prepared:

(1) Strips of dimensions 250 × 30 mm. and 0·5, 1·0, 1·5, and 2·0 mm. thick.

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* British Patent No. 271798, March 28, 1927.

(2) Profiles of ⊔ shape, drawn from strips of 1·0 and 1·4 mm. thickness and cut into specimens 250 mm. in length.
(3) Riveted strips of dimensions 250 × 30 × 2 mm. with 2 rivets of the normal alloy "681 A."

Samples of (1) and (2) were exposed in two different series, one at ebb and flow of the tide so that they were in the water for about 7–8 hrs. and in the air for about 4–5 hrs. The other series was first exposed so that it was always covered by water, but during the test it was necessary to move them a little further back because it became too dangerous to take specimens. After this change in the conditions of exposure these specimens also emerged from the water for a short time according to wind conditions. Nevertheless, the two series may be called:

ebb and flow series (series I),
always under water series (series II).

The riveted strips were exposed only at ebb and flow. All specimens were exposed in wooden frames which were fixed to beams of a crane bridge stretching into the sea. After about 6 months most of the specimens were covered with marine growth and shells. Typical examples are given in Fig. 1 (Plate XXV), showing a profile and a riveted strip after 6 months' exposure.

It was originally intended that the whole investigation should extend over one year, samples being taken every 2 months, with 3 parallel specimens of each series. Occasionally, however, the first test-pieces were removed only after 3 months and the result was such an excellent one that this period was continued. During the test the original plan was further altered with regard to the number of specimens. In order to prolong the corrosion test it was necessary to confine the number of samples to two or even to one. By this means the period of test could be prolonged to 2 years with the materials of 0·5 and 1·0 mm. thickness, whilst some of the thicker specimens are still under test. Unfortunately the last riveted strips were lost in the stormy days of the autumn of 1931 so that this part of the test could be continued only for 18 months.

RESULTS.

The results of the corrosion test are given in the diagrams Figs. 2 to 7 for the strips and the profiles. Figs. 2 and 3 show the loss in weight of the strips and of the profiles, respectively. As was to be expected, the corrosion attack was greater with the thinner material and, in general, was greater in series II than in series I, and only the profiles of

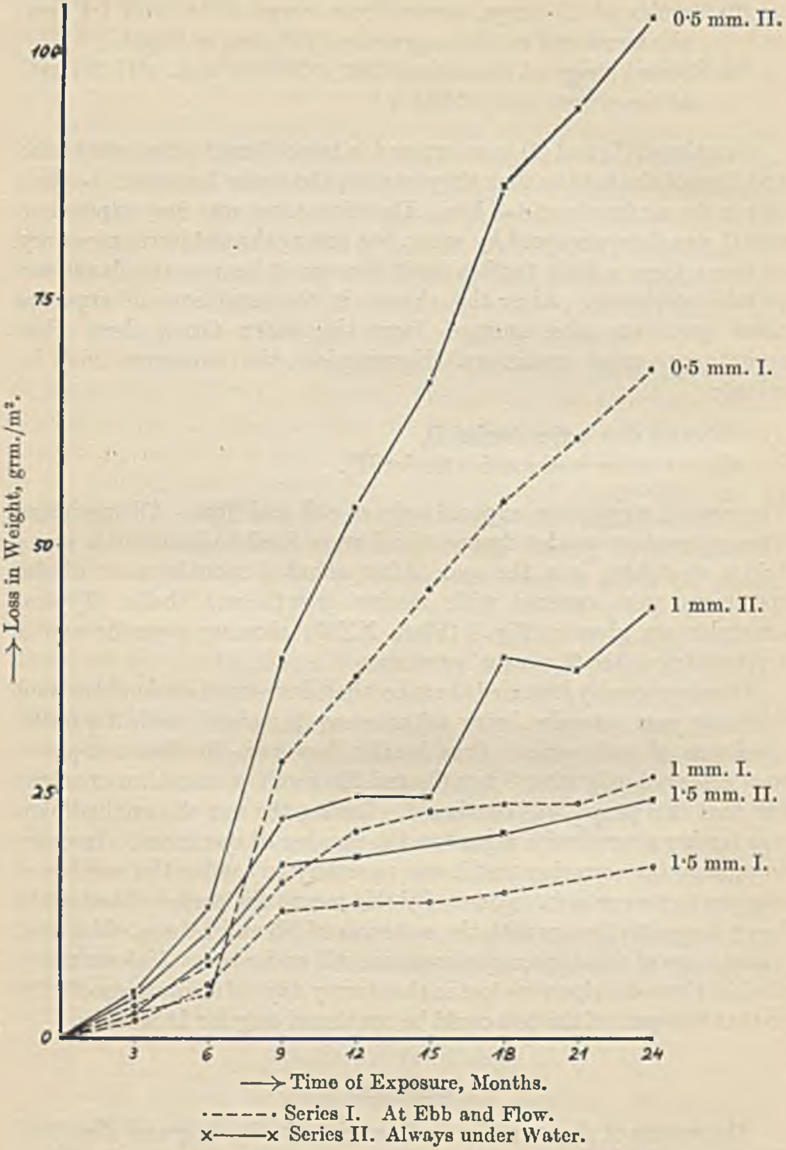

FIG. 2.—Duralplat Strips, North Sea. Loss in Weight.

1·4 mm. thickness show some irregularities in this respect. Further, it is interesting to note that the loss in weight rises rather steadily for the thinner material of 0·5 mm. thickness and partly for that of 1·0 mm., at least for series II of the latter. For the thicker material, however, loss-in-weight curves run nearly parallel to the abscissa after about 9 months. Since there was almost no difference between 1·5 and 2·0 mm., the curves of the latter strips are not included in Fig. 2.

In contrast to unplated light alloys,* the loss in weight of the coated material Duralplat gives a good idea of the corrosion attack of the alloy because, owing to the electro-negative character of the coating layer, corrosion takes place at first only in the layer alloy. In no case was there any trace of the corrosion attack having penetrated into the base alloy of Duralplat before the whole coating layer was quantitatively eaten away. As a matter of fact, the specimens of 0·5 mm. thickness of series II which were always most severely attacked still possessed surprising tensile properties for many months after microscopic

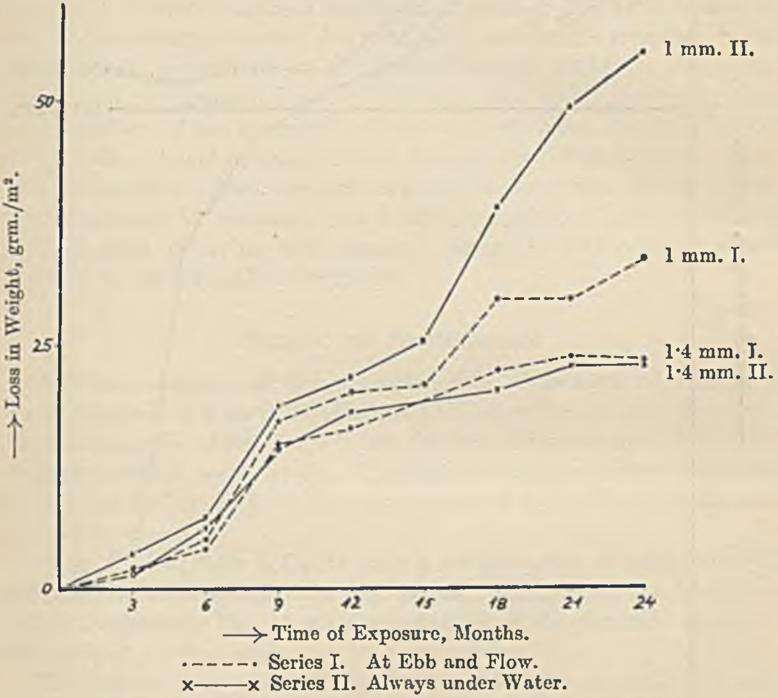

Fig. 3.—Duralplat Profiles, North Sea. Loss in Weight.

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* See K. L. Meissner, *J. Inst. Metals*, 1931, 45, 187–201.

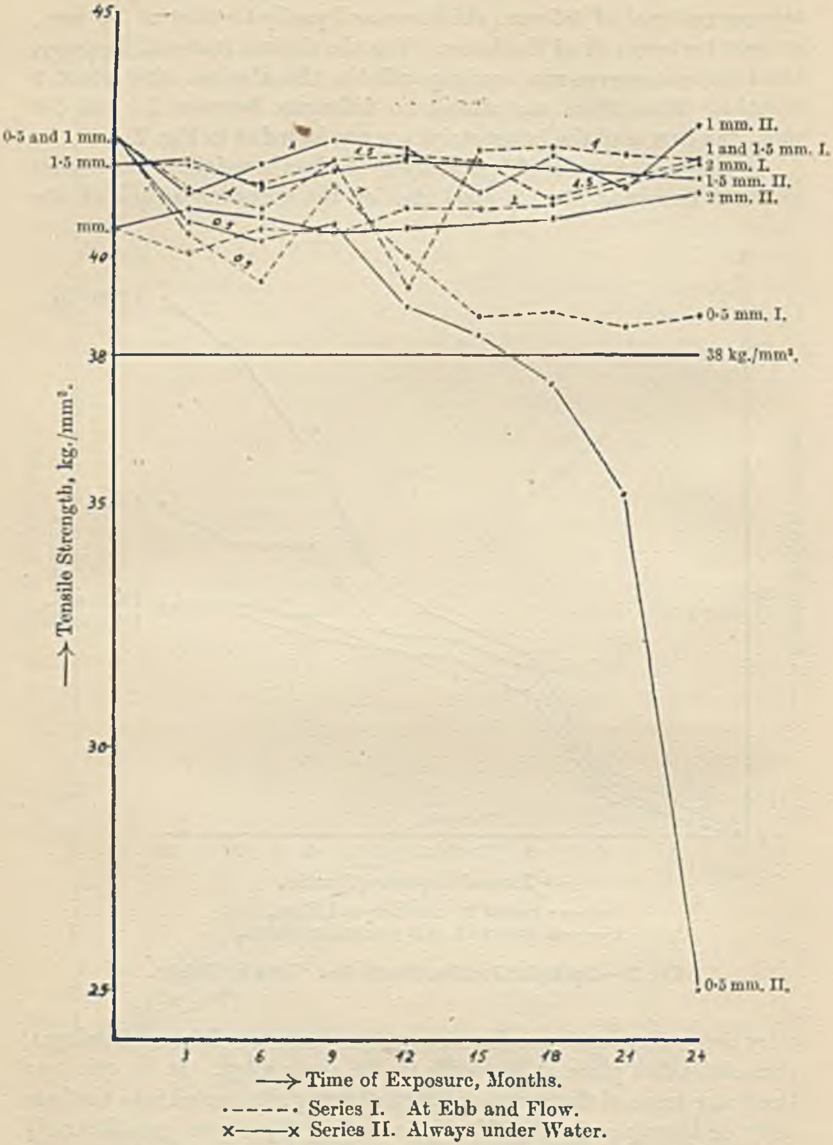

FIG. 4.—Duralplat Strips, North Sea. Tensile Strength.

examination showed that nearly the whole plating layer seemed to be removed.

Figs. 4 and 5, which respectively give the results of tensile strength and elongation of the strips, show that only series II of 0·5 mm. thickness failed after 24 months, showing only after this period the first corrosion attack of the base metal. All the other materials, including the strips of 0·5 mm. thickness of series I, still have tensile properties above the limits of guarantee. As may be seen from Figs. 6 * and 7, the tensile properties of the profiles are also practically unaffected after 24 months.

Owing to the electro-chemical protection of the base alloy by the coating, it is important from the practical point of view that, as long as any of the coating remains, the yield-point and tensile strength should be at least 90 per cent. of the uncorroded material whilst the elongation should not be diminished at all. It was thus rather surprising that the elongation of the corroded material was very often distinctly higher than of the original material, as can be seen from Figs. 5 and 7. It is well known from experience with unplated material that the elongation is first affected by corrosion and is often remarkably reduced without striking signs of having been attacked, especially with material which is prone to intercrystalline corrosion.

Microscopic Examination.

Typical examples of the microstructure of sections of Duralplat strips are given in Figs. 8–11 (Plate XXVI), showing the base alloy with the coating layer of 0·5, 1·0, 1·5, and 2·0 mm. thickness after 3 months' corrosion attack, respectively. The microsections are etched according to Dix and Keller, with an aqueous solution of hydrochloric, nitric, and hydrofluoric acids.

Figs. 12–15 (Plate XXVII) show a further series of strips after 18 months' corrosion attack. In Fig. 12, the coating layer can be seen in only a few areas. Fig. 15 gives an example of the corrosion attack of the layer of a 2 mm. strip.

Whilst the base metal of the 0·5 mm. samples of series I is still unattacked (see Fig. 16, Plate XXVIII) after 2 years' exposure, the strips of series II were the only ones in which serious corrosion attack of the base alloy could be seen under the microscope. This is quite in accordance with the slight reduction in tensile properties in series I and the reduction of 41·1 per cent. in tensile strength and of 93·3 per cent. in elongation in series II, as may be seen from Figs. 4 and 5. Fig. 17 (Plate XXVIII) shows the deterioration of the base alloy of such a strip after 24 months' corrosion.

Since there were no important differences in the microstructure of

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* The yield-point is the stress at which 0·2 per cent. permanent elongation occurs.

the strips and that of the profiles, it does not seem necessary to give examples of the latter. According to the tensile properties of the profiles which remained practically constant for 2 years, the base alloy was not attacked in any case.

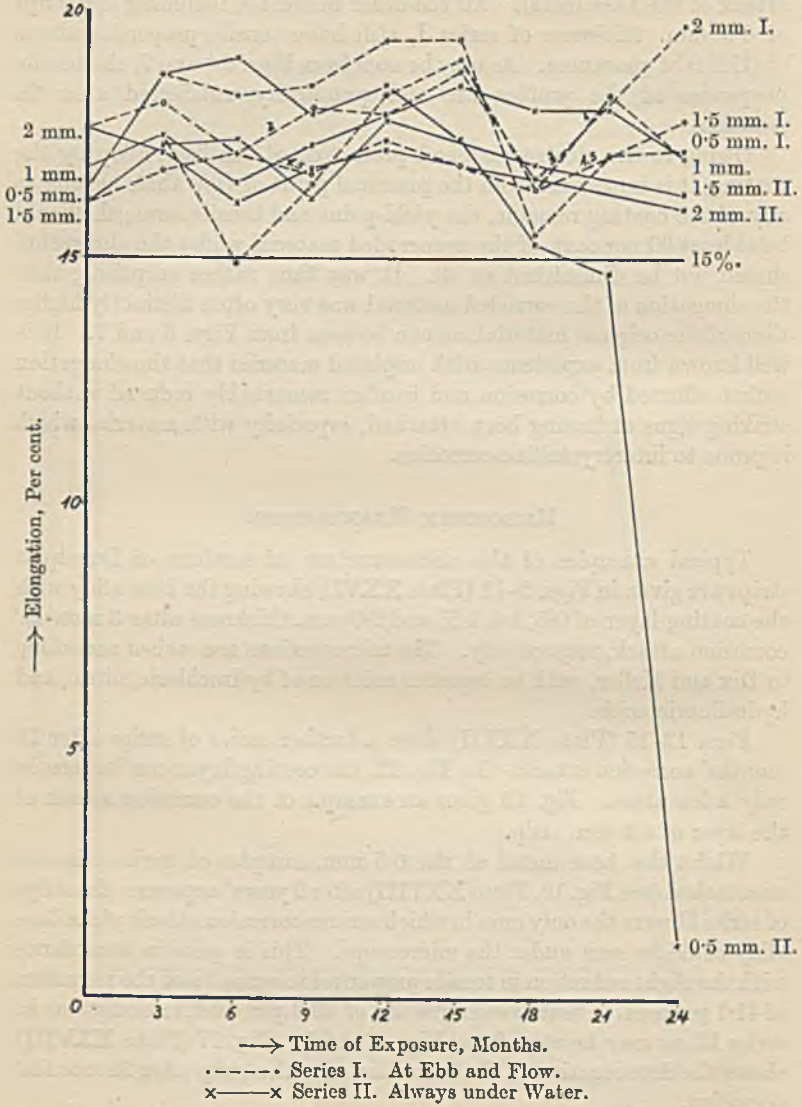

FIG. 5.—Duralplat Strips, North Sea. Elongation.

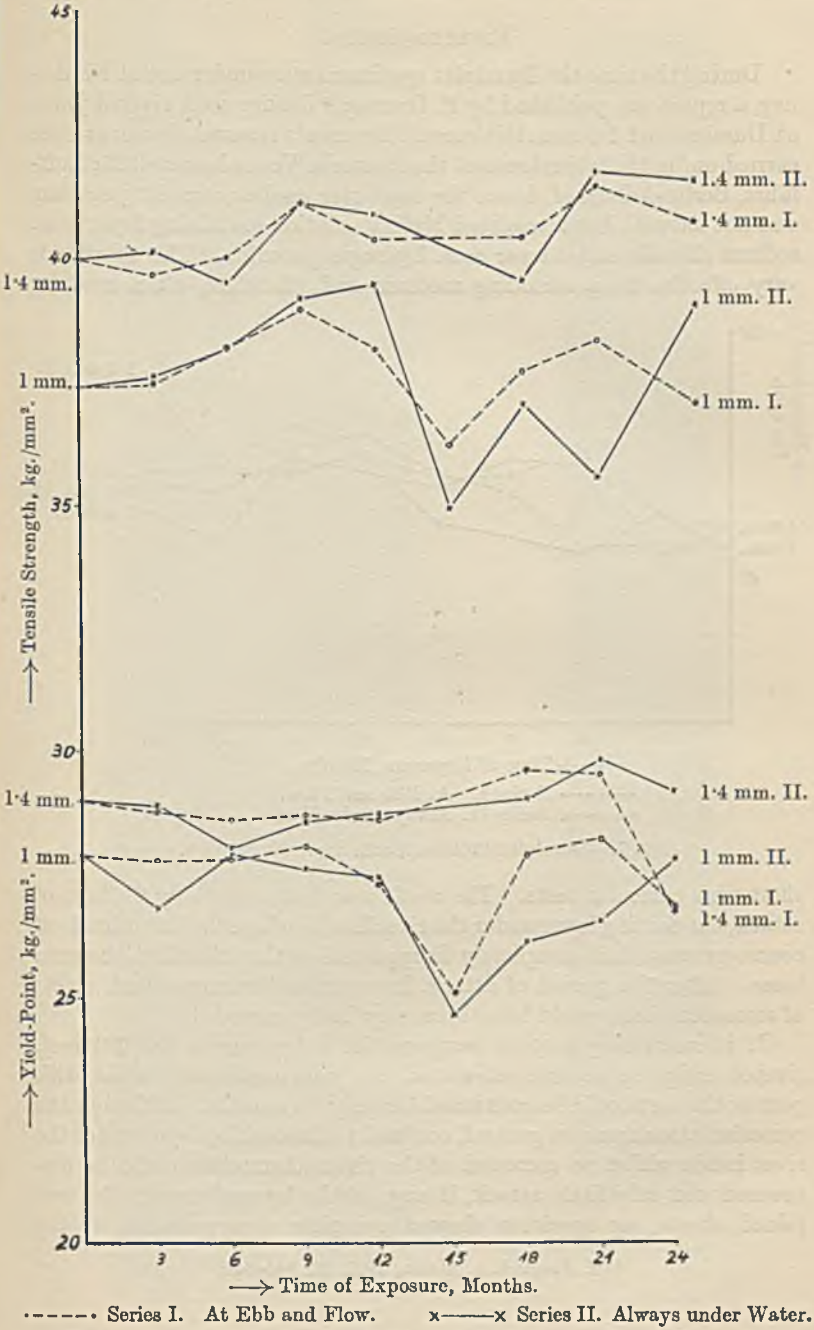

FIG. 6.—Duralplat Profiles, North Sea. Yield-Point and Tensile Strength.

RIVETED STRIPS.

During the time the Duralplat specimens were under test at Norderney, a report was published by P. Brenner,* dealing with riveted joints of Duralplat of 1·5 mm. thickness. Brenner's research, however, was carried out in the laboratories of the Deutsche Versuchsanstalt für Luftfahrt, Berlin-Adlershof, hence the sea-water used as corroding medium was not natural, but a modified Mylius' solution containing 3 per cent. sodium chloride and 0·1 per cent. hydrogen peroxide. This solution is very effective as a corroding medium and, therefore, often used for short-time corrosion tests. The result was that, after only 21 days of attack, the coating layer under the rivet heads, where the corrosion is of course greatest, had completely disappeared so that the rivets became loose. After this period of attack, however, as Brenner stated, rivets of uncoated sheet would have been very badly corroded.

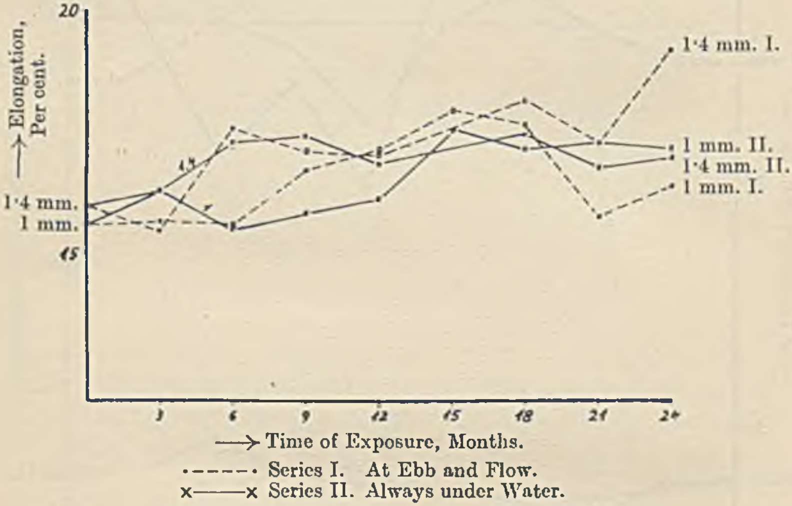

FIG. 7.—Duralplat Profiles, North Sea. Elongation.

It is interesting now to compare the behaviour of the 2·0 mm. riveted strips in natural sea-water. As was mentioned earlier, this part of the test could be continued for only 18 months. Although the corrosion attack was, in general, confined to the coating layer under the rivet heads whilst no corrosion of the rivets themselves could be discovered and only little attack, if any, of the layers between the two joined sheets, no specimen showed complete disappearance of the

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* *Z. Flugtech. u. Motor.*, 1931, 22, 344–346.

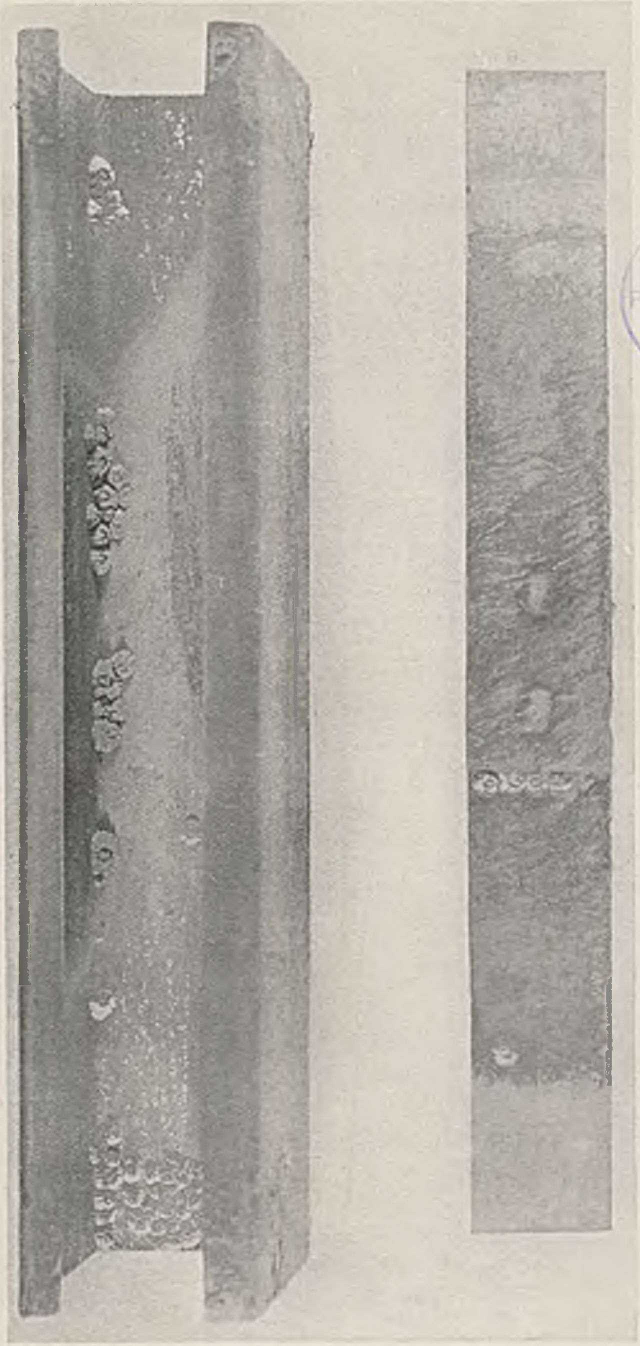

FIG. 1.—Profile and Riveted Strip after 6 months' Exposure. × 0·8. Reduced by ⅓ in reproduction.

[*To face p.* 144.

PLATE XXVI.

FIG. 8.—0·5 mm. Strip after 3 months' Exposure. × 100.

FIG. 9.—1·0 mm. Strip after 3 months' Exposure. × 100.

FIG. 10.—1·5 mm. Strip after 3 months' Exposure. × 100.

FIG. 11.—2·0 mm. Strip after 3 months' Exposure. × 100.

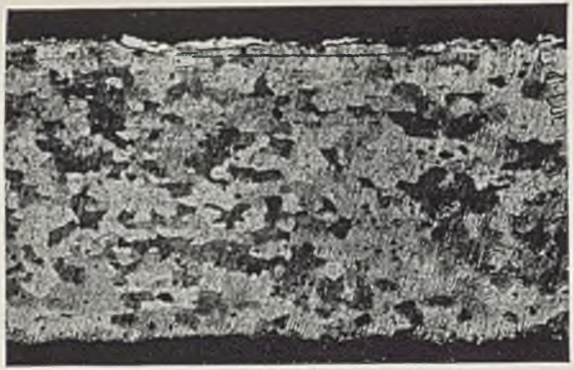

FIG. 12.—0·5 mm. Strip after 18 months' Exposure. × 100.

FIG. 13.—1·0 mm. Strip after 18 months' Exposure. × 100.

FIG. 14.—1·5 mm. Strip after 18 months' Exposure. × 100.

FIG. 15.—2·0 mm. Strip after 18 months' Exposure. × 100.

FIG. 16.—0·5 mm. Strip after 24 months' Exposure.
Series I. × 100.

FIG. 17.—0·5 mm. Strip after 24 months' Exposure.
Series II. × 100.

PLATE XXIX.

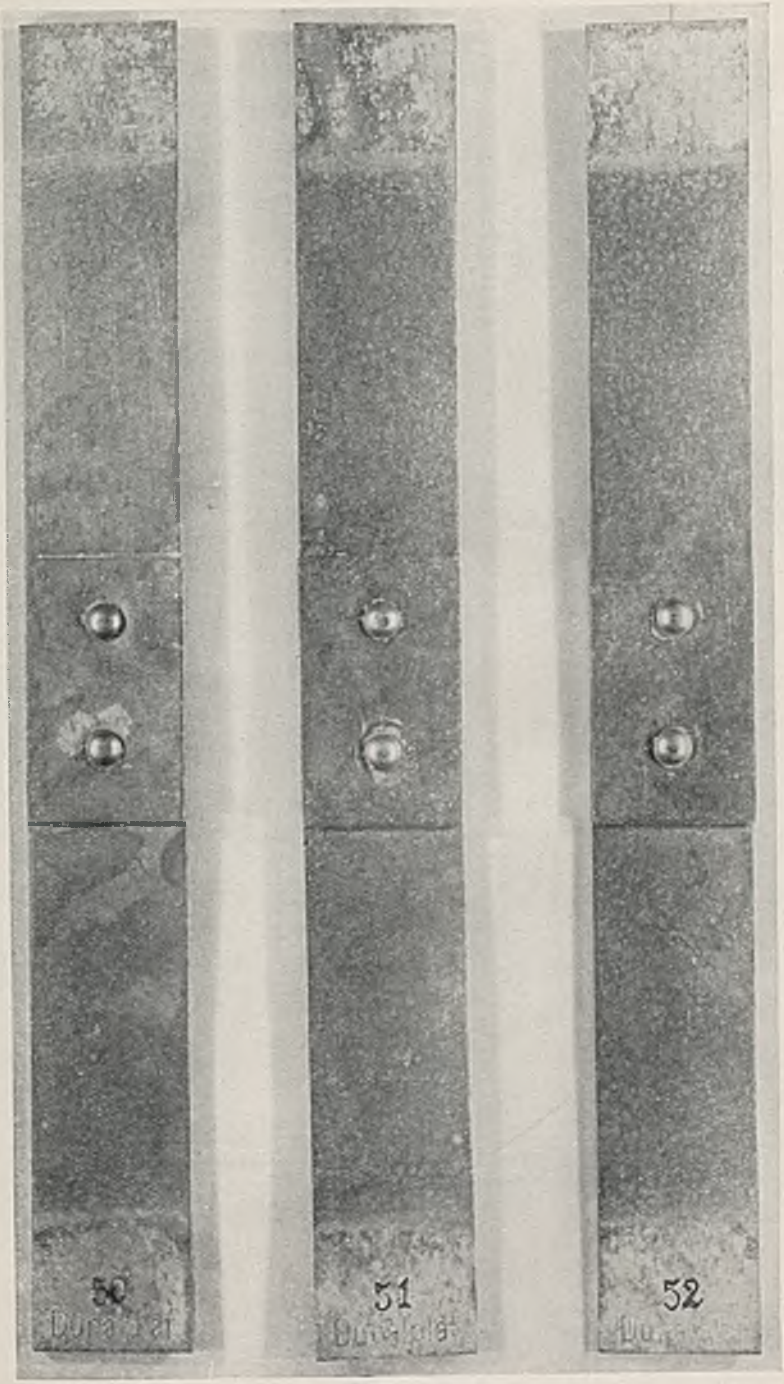

FIG. 18.—Riveted Strips after 12 months' Exposure. × 0·8. Reduced by $\frac{1}{5}$ in reproduction.

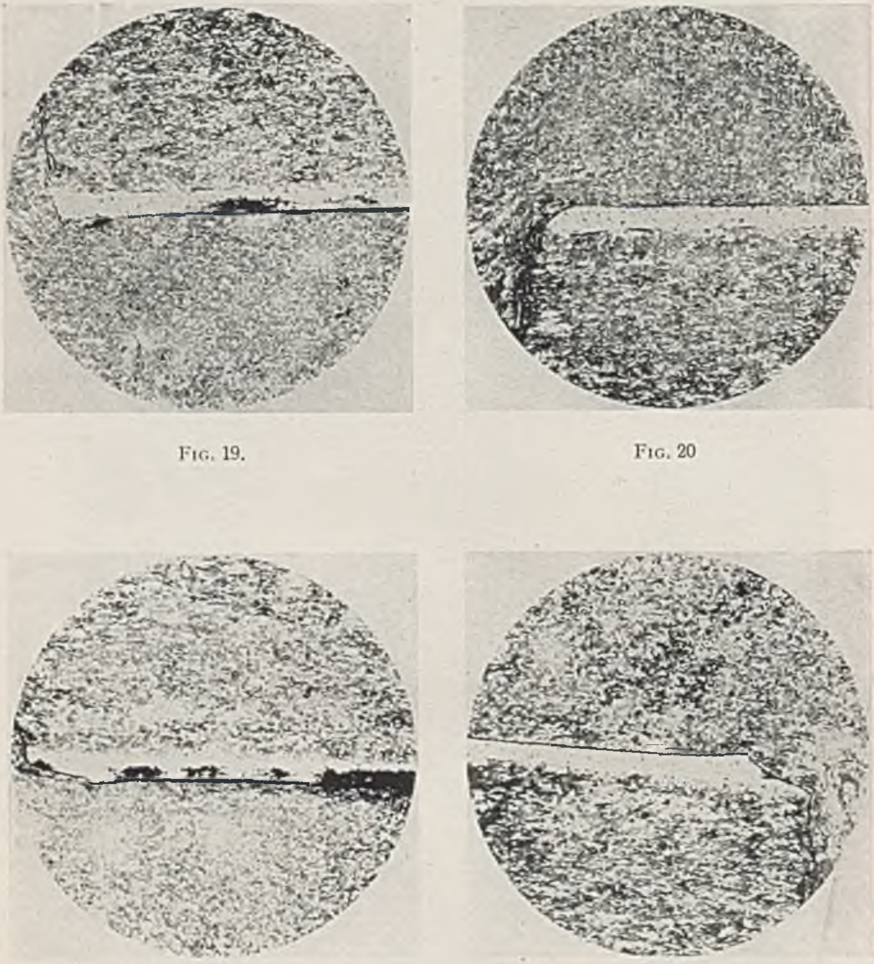

FIG. 19.

FIG. 20

FIG. 21.

FIG. 22.

FIGS. 19–22.—Micro-sections of Riveted Strips after 12 months' Exposure. × 50.
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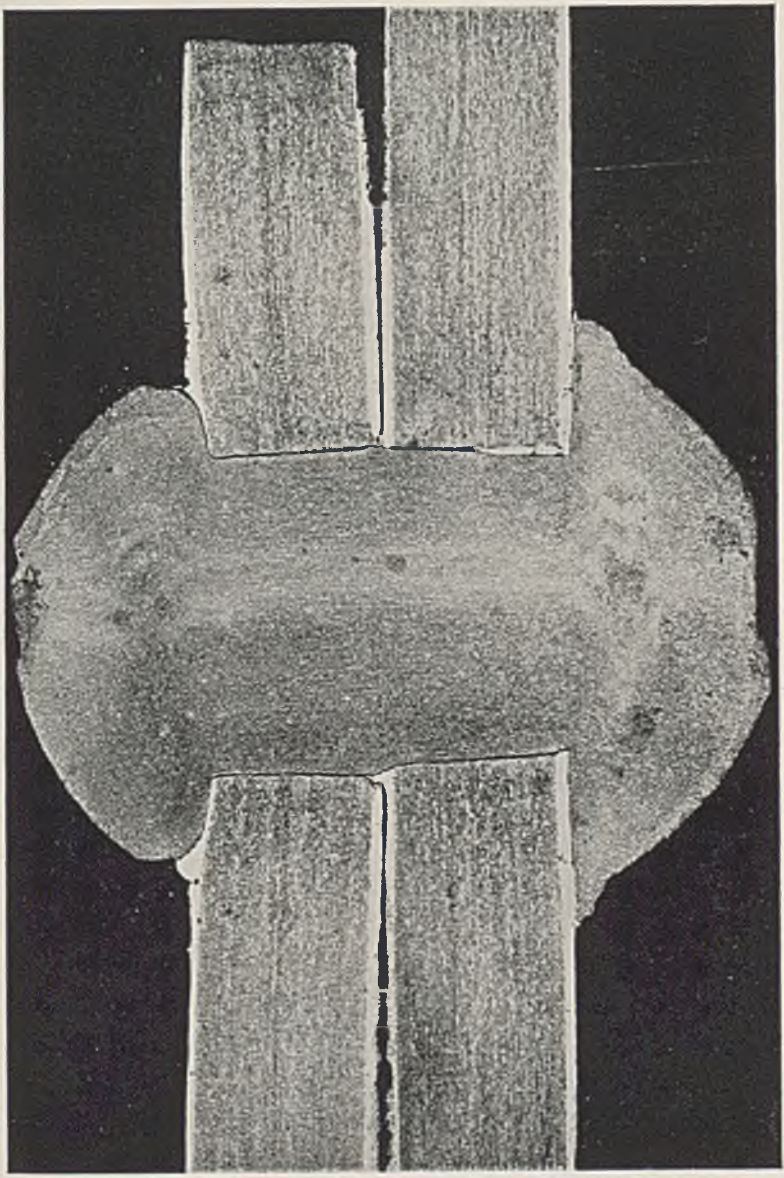

FIG. A.—Photomicrograph of cross-section of riveted joint of Alclad "17ST," which had been exposed for 18 months to the spray of a 20% salt solution. Note the electrolytic protection of the rivet and exposed upper edge of left sheet, and the flow of the soft aluminium under the rivet, causing it to act as a gasket. × 15. Etched: HF–HCl–HNO_3.

(Reduced by $\frac{1}{5}$th in reproduction.)

layers with consequent loosening of the rivets, as observed by Brenner with the Mylius' solution. As it is not possible to reproduce in the paper all the photographs of the micro-sections of the rivets, only some typical examples are given in Figs. 18–22 (Plates XXIX and XXX). In Fig. 18 the appearance of the three riveted strips may be seen, taken after 12 months. The rivets themselves are entirely unattacked. Figs. 19–22 show that the coating layer under the rivet heads is still partially unaffected or only attacked to some extent, but not entirely removed as in the case of Brenner's short-time tests. Even after 18 months' exposure, the plating layer was only locally affected.

Conclusion.

Two years' corrosion tests with Duralplat in the North Sea showed the excellent corrosion resistance of this material. Only one group of the thinnest specimens of 0·5 mm. thickness which were almost entirely under water for the whole time was found to be attacked in the interior so that the tensile properties were reduced to a serious degree. On the other hand, the base metal of strips of the same thickness which were exposed only at ebb and flow of the tide was not yet corroded; in these the coating layer only was affected, hence they still maintained excellent tensile strength and elongation so that this material could be used unhesitatingly even after this period for constructional purposes, though no further protection was applied, as for example by a lacquer or varnish. The life of thicker materials, especially of more than 1 mm., is undoubtedly very long.

The electro-chemical protection of the base alloy by the coating is so pronounced that no corrosion takes place in the base metal before the layer has entirely disappeared. Normal rivets are protected in the same way. The corrosion is practically confined to the parts of the coating under the heads of the rivets. In 18 months, however, no case was observed in which the rivets became loose owing to its complete disappearance.

CORRESPONDENCE.

Mr. E. H. Dix, Jr. * (Member): Dr. Meissner's paper presents results of great practical importance to the designer and to the user of strong aluminium alloys, for he has shown how effectively a corrodible strong aluminium alloy is protected by a metallic coating, which is electronegative to the core metal, under conditions of actual exposure in the sea.

Dr. Meissner has unfortunately given the wrong impression concerning Alclad materials, probably because complete information concerning these materials is not available in Germany. The Alclad trade mark designates

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* Chief Metallurgist, Aluminium Research Laboratories, Aluminum Company of America.

broadly a group of products in which a corrodible strong aluminium alloy is protected from corrosion by surface layers of a corrosion-resistant aluminous metal. In fact, the British patent referred to in Dr. Meissner's paper * describes and claims "corrosion-resistant articles of corrodible aluminium alloys having a wrought non-porous coating of corrosion-resistant aluminium *or aluminium alloy* cohesively united with the main body and obtained by casting the corrodible alloy in a mould in contact with a plate or plates of corrosion-resistant metal *or alloy* and subjecting the casting thus formed to pressure and heat." In the original experiments leading to the development of the Alclad products, one combination tested consisted of a strong aluminium alloy core covered with surface layers of "51S" alloy. "51S" alloy contains substantially 0·7 per cent. magnesium and 0·9 per cent. silicon, and after a heat-treatment similar to that normally given "17S," a solution heat-treatment without artificial ageing, is designated as "51SW." Dr. Meissner has not mentioned the silicon content of the alloys defined as group "K," but it is well known that the susceptibility to heat-treatment ascribed to these alloys by Dr. Meissner depends on the content of the compound Mg_2Si and not on the magnesium or manganese alone.

The particular grade of Alclad material to which Dr. Meissner refers—namely, a "17S" core coated with surface layers of high-purity aluminium—has become especially prominent because of the excellent corrosion-resistance of the high-purity aluminium. The results of a very extensive corrosion-testing programme on aluminium alloys conducted over a period of the past 8 years gives a preponderance of evidence indicating that high-purity aluminium possesses a higher corrosion-resistance than any aluminium alloy. There are, however, certain elements such as manganese, and to a lesser extent magnesium, which can be added to high-purity aluminium without appreciably decreasing its corrosion-resistance, and it is also possible that certain elements may influence the film-forming characteristics, and so tend to improve the resistance of the alloy to mild corrosive influences.

In considering, then, the practical application of the various grades of Alclad materials, we find that the grade composed of the strong alloy core with high-purity aluminium coating is used under conditions requiring maximum corrosion-resistance. The user is usually willing to sacrifice something in tensile strength in order to obtain this maximum corrosion protection. Often the weight added by the high-purity aluminium coating is not much more than the weight of a satisfactory paint covering which would be required to protect a less corrosion-resistant material. The softness of the pure aluminium coating may be a disadvantage, in that the metal is more easily scratched and the surface marred, but it is also a very definite advantage in other respects. For instance, the experience in the United States shows that corrosion of Alclad sheet having a pure aluminium surface does not occur under the heads of rivets, as shown by Dr. Meissner in his Figs. 19 and 21, but is confined to an unimportant attack immediately adjacent to the rivets. This is illustrated in Fig. A (Plate XXXI). Apparently the pure aluminium surface is soft enough to act as a gasket, and so prevent the corrosive medium from penetrating between the rivet head and the sheet. The soft, pure aluminium coating also acts as a very satisfactory vibration damper which is highly important in aircraft work and particularly noticeable in the lack of vibration in the hull of the "ZMC2" metalclad airship.†

For applications where a hard surface is more important than maximum corrosion-resistance, a grade of Alclad material having the same core but a heat-treatable *alloy* coating of good corrosion resistance, is employed.

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* British Patent No. 271,798. See also U.S. Patents 1,805,448 and 1,865,089.

† Carl B. Fritsche, "The Metalclad Airship," *Roy. Aeronaut. Soc. Preprint* No. 61, 1931.

Although the tensile strength of this coating is approximately three times that of the pure aluminium coating, the actual gain in tensile strength and yield strength is only of the order of 2000 or 3000 lb./in.^{2}. In order to meet the requirements of maximum corrosion-resistance, together with maximum tensile strength and yield strength, a grade of Alclad material has recently been put on the market under the designation of "Alclad 24ST," in which the strength of the core has been increased sufficiently to make up for the loss caused by the high-purity aluminium coating. Owing to the high-purity aluminium coating, this alloy has a corrosion-resistance equivalent to that of Alclad "17ST," and yet it meets slightly higher guaranteed minimum tensile strength and yield strength. The tensile strength and yield strength may be further increased by a small amount of cold-work after heat-treatment. This product, designated Alclad "24SRT," also has a corrosion-resistance equal to that of Alclad "17ST" and exhibits the following average properties in sheet form: tensile strength, 62,000 lb./in.^{2}; yield-strength, 49,000 lb./in.^{2}; elongation, 12 per cent. on 2 in.

Accelerated corrosion tests on Alclad products previously described by me * † are quite in accord with those obtained by Dr. Meissner in the North Sea. The following results are typical of these accelerated tests, and represent the effect of exposure for 3 years to continuous spray from a 20 per cent. salt solution using American Society for Testing Materials standard tensile specimens of 14 gauge (0·064 in.) sheet:

Coating.	Core.	Original Properties.		Change by Corrosion, %.	
		Tensile Strength, lb./in.^{2}.	Elongation on 2 in. %.	Tensile Strength.	Elongation.
High-purity aluminium	17ST	56,220	21·2	0	− 6
"51SW" . . .	17ST	59,260	21·6	− 4	− 12

The results of tests on Alclad material of three different gauges exposed for 1 year to salt air and fog on the Atlantic sea-coast may be of interest. These samples were exposed on a projection of the coast of Rhode Island known as Point Judith. The test location is bordered on two sides by the ocean and on the third side by a salt marsh, thus making an extremely severe exposure.

It is quite evident from these figures that in the two heavier gauges the

Thickness.	Coating.	Core.	Original Properties.		Change, %.	
			Tensile Strength, lb./in.^{2}.	Elongation on 2 in. %.	Tensile Strength.	Elongation.
0·064	High-purity aluminium	"17ST"	53,480	20·0	− 1	− 7
0·064	"51SW"	"17ST"	55,480	20·5	+ 2	− 4
0·032	High-purity aluminium	"17ST"	54,200	18·1	− 2	− 8
0·032	"51SW"	"17ST"	56,290	19·0	− 2	− 5
0·010	High-purity aluminium	"17ST"	54,570	16·2	− 16	− 60
0·010	"51SW"	"17ST"	57,290	18·6	− 28	− 81

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* "'Alclad': A New Corrosion Resistant Aluminium Product," *U.S. Nat. Advis. Cttee. Aeronautics*, No. 259, 1927.

† "Application of 'Alclad' Aluminium Alloy Sheet to the Aircraft Industry," *Aviation*, 25, (26).

alloy coating has successfully protected the core, so that there is no appreciable loss in tensile properties. However, in the very thin sheet, the high-purity aluminium has resisted corrosion to an appreciably greater extent than the "51SW," and hence has offered a better protection to the "17ST" core, where most of the strength resides.

Dr. J. C. Hudson * (Member): I have read this paper by Dr. Meissner with very great interest, since he has made a combined use of loss-in-weight and tensile strength determinations in measuring the corrosion of his specimens—a method that I have also found of considerable value. There is no doubt that Dr. Meissner has clearly demonstrated the excellent resistance to corrosion by sea-water of the coated Duralumin alloys in which he is interested and he is to be congratulated on this achievement; from the point of view of the general principles of corrosion-testing there are, however, one or two observations that I should like to make, which I hope Dr. Meissner will regard as constructive suggestions for future work rather than as criticism of the present results.

In tests on compound materials, such as these coated Duralumin strips, it is desirable that the thickness of the protective coat should be stated. In general, when the protective coat affords electrochemical protection—as in the present instance or in that of galvanized-iron wire—the breaking load of the test-piece will not be appreciably affected until the protective layer has failed completely. In the case of Dr. Meissner's tests on 0·5 mm. strip (Series II—always under water), this occurred after about 18 months' exposure. From the photomicrographs (Plate XXVI) the approximate thickness of the protective layers on the strips appears to be 0·04 mm. for the 0·5 mm. strip, 0·06 mm. for the 1 and 1·5 mm. strips, and 0·07 for the 2 mm. strip. By simple proportion, therefore, one might expect failure on the thicker strips to begin after some 27 to 32 months' exposure, which was unfortunately slightly longer than the duration of Dr. Meissner's tests.

In atmospheric corrosion, there is a definite seasonal variation of the corrosivity of the atmosphere; it is possible that a similar variation may occur in the case of marine corrosion (*e.g.* as a result of variation in the sea-water temperature). Some of the curves in Fig. 3 seem to support this view, and a statement of Dr. Meissner's experience on the subject would be very welcome.

As Dr. Meissner is no doubt aware, tensile tests on isolated specimens are of limited accuracy when applied to corrosion measurements, since the effect of corrosion is represented by the difference between uncorroded and corroded specimens. In my work on the corrosion of non-ferrous wires,† each test was made on twelve specimens, whilst for some work now in progress on ferrous materials, six specimens are being used. An isolated erratic result can thus be eliminated, as in the following series:

		Breaking Load.						Mean.
H.C. copper wire. 100 lb./mile.	Unexposed.	330	330	326	330	330	(325)	...
		(320)	330	332	(312)	331	330	329·9
	Exposed for 2 years.	324	324	323	323	326	323	...
		320	324	324	324	325	325	323·75
Mild steel wire. 0·128 in.	Unexposed.	1492	1506	1510	1496	1490	1493	1497·8
	Sprayed intermittently with $N/100$ sulphuric acid for 1 year.	1460	1470	1485	1470	(1525)	1470	1471·0

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

† *J. Inst. Metals*, 1930, 44, 409.

It is quite clear from these examples of actual experimental results that tests on isolated samples may be misleading although it must be remembered that, in the present instance, Dr. Meissner was probably more concerned with demonstrating the absence of gross deterioration than in measuring accurately the initial stages of corrosion.

It is further desirable to conduct control determinations on similar uncorroded specimens stored in the laboratory during the tests, since the tensile properties of the materials change on ageing quite apart from corrosion. Thus, after 12 months the breaking load of a mild steel wire had fallen from 1600 to 1498 lb./in.^{2}, whilst after 2 years that of a 70 : 30 brass wire had risen from 295·6 to 303·2 lb./in.^{2}.* It is probable that alloys of the Duralumin class are particularly liable to variation of this type and, as this is a matter on which Dr. Meissner can speak with great authority, it would be interesting if he would state whether he observed any evidence of this in the course of his experiments.

It is rather difficult to reconcile the data in Figs. 2, 4, 8, and 12 (Plates XXVI and XXVII) referring to 0·5 mm. strip. Judging from Figs. 8 and 12, after 18 months' exposure the whole coating layer had been removed and the thickness of the strip reduced from 0·48 to 0·39 mm., say by 0·09 mm. or 18 per cent. The loss in weight of the specimen should, therefore, be of the order of $0{\cdot}009 \times 3$ † $= 0{\cdot}027$ grm./cm.^{2} or 270 grm./m.^{2}, whereas the corresponding value read from the curve given in Fig. 2 is 54·5 grm./m.^{2} for Series I and 87 grm./m.^{2} for Series II, equivalent to, say, 3·6 and 5·8 per cent. of the original weight. Moreover, from Fig. 4 it appears that the tensile strength of this 0·5 mm. strip had fallen from 42·3 kg./mm.^{2} to 38·9 kg./mm.^{2} (I) and 37·4 kg./mm.^{2} (II)—that is, by 8·0 and 11·6 per cent., respectively.‡ It will be seen that the data for the reduction in tensile strength are in much better agreement with the photomicrographs shown in Figs. 8 and 12 than the values for the loss in weight, and the discrepancy points to the fact that some pitting or localized attack, possibly penetrating to the core metal itself, had occurred even after 18 months' exposure. No doubt Dr. Meissner will be able to elucidate this point in his reply, and it would also be advantageous if, at the same time, he would kindly give the results embodied in Fig. 4 in tabular form.

In conclusion, I would say that I was very glad to note that Dr. Meissner had fully recognized the importance of determining the corrosion-time curves for the materials under test. Isolated determinations after one or two periods are of limited value and for elucidating the behaviour of materials under service conditions, curves of the type shown in Figs. 2 and 4 are required. In addition, the testing of the materials in different thicknesses is a valuable feature of Dr. Meissner's work, and I hope that he will be able to undertake further tests on the thicker materials extending over longer periods to test the correctness of the views that I have advanced.

The AUTHOR (*in reply*): I was very interested to read the contributions to the discussion by Mr. Dix and Dr. Hudson. As Mr. Dix states, the Alclad trade mark designates not only corrosion-resistant aluminium alloys coated with high-purity aluminium, but also coated with aluminium alloys. He mentions as an example the well-known alloy "51S" as a plating layer.

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* *J. Inst. Metals*, 1930, 44, 409.

† An approximate density of 3 has been assumed in this and the following calculations.

‡ Incidentally, it is not stated in the paper whether the values for tensile strength plotted in Fig. 4 represent the actual breaking load as determined on each specimen or whether a correction has been applied for the reduction in area due to corrosion. It is probably preferable, when applying the tensile strength method to corrosion measurements, to give the actual breaking load for each specimen as determined.

At the time that I was writing my paper, I was only aware of the aluminium-coated Alclad according to the British Patent No. 271,798. In this specification, however, and in the corresponding U.S. Patent No. 1,865,089, which has been published in the meantime, no claim is made to use an alloy of the "51S" type. The only alloys mentioned are aluminium alloys having adequate resistance to corrosion, such as, for example, aluminium–manganese and aluminium–beryllium alloys. As I had heard nothing about Alclad material coated with aluminium alloys of that kind, and Mr. Dix himself does not mention such alloys as having been actually made up hitherto, I thought that Alclad consisted only of aluminium alloys coated with pure aluminium.

The use of the alloy "51S," however, is claimed in a special patent specification * which was applied for in the United States about fourteen months later than Duralplat in Germany.† Duralplat has not been developed from the point of view of the improvement of corrosion-resistance properties, which should be about the same as those of Alclad, but from the point of view of making a compound alloy the surface of which is stronger and harder than pure aluminium and which is primarily age-hardenable under the same conditions of heat-treatment as the core. According to these considerations, an alloy of the K group of Duralumin has been selected. Since these alloys are made up from technical aluminium, their silicon content, in general about 0·3 per cent., is high enough to form the compound Mg_2Si, at least in the case of the most generally used alloy containing 0·5 per cent. magnesium.

I have read with great interest the results of corrosion tests with different Alclad materials which are referred to by Mr. Dix. There is a striking change in elongation; in my own experiments, this did not change—or at least it was not diminished, as is shown in the paper. In other words: yield-point and tensile strength at first decreased proportionally to the extent of corrosion of the plating layer, whilst the elongation did not diminish until the core itself was seriously attacked. In contradistinction to this observation, the percentage loss in elongation in the tables, referred to by Mr. Dix, is always higher than that of the tensile strength. This behaviour seems normal only in the case of the two 0·010 mm. sheets where the cores are undoubtedly attacked, so that the normally higher loss in elongation takes place as in the case of corrosion of an unplated alloy.

I do not agree with Dr. Hudson's opinion that, for the thicker sheets, failure may be expected to be simply proportional to the thickness of the coating layer which is, in general, 5 per cent. of the whole on each side. There is no doubt that the thinner material is much more corroded, and much more quickly, than the thicker, as is already known from unplated alloys. It may be seen from Figs. 2 and 3 of the paper that the loss in weight is always higher for the thinner strips and profiles. If Dr. Hudson's opinion were correct these curves must be nearly coincident. Since it has been possible, in the meantime, to continue the research for the strips of 1·5 and 2·0 mm. and also for the profiles, it may be of interest to note that after 30 months' exposure none of these specimens has failed. As a matter of fact, it must be stated that the loss in weight rises only very little for the thicker strips after the first 9 months of exposure, as referred to on p. 139 of the paper. Since the loss in weight gives a good idea of the corrosion attack of coated alloys—in contrast to unplated ones—it may undoubtedly be expected that the life-time of the thicker material may extend over many years. What Dr. Hudson says about the limited accuracy of isolated specimens in corrosion tests is certainly quite right, but, as was mentioned on p. 137

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* U.S. Patent No. 1,805,448, Nov. 30, 1929. British Patent No. 370,947, Oct. 7, 1930.

† Sept. 14, 1928.

of the paper, it was originally intended that the investigation should extend only over one year, so that 3 specimens of each series and thickness should be taken each time. It was only owing to the very good agreement of the parallel specimens that I had no hesitation in limiting the number of samples to two or even to one, in order to make it possible to extend the research over 2 years, or even longer for the thicker material which is still under test after 33 months. The next samples will be taken after 3 years. I think that one more difference in the corrosion behaviour of unplated and plated material is that the plated alloys show such a good agreement of parallel samples as regards loss in weight and change in tensile properties. It is well known that in the corrosion of unplated alloys the difference is often so great that no average value can be given, especially if pitting or intercrystalline attack takes place. In these cases, the loss in weight, for example, is quite unreliable, and must be regarded as useless or even misleading.

It does not seem probable to me that alloys of the Duralumin type are liable to variations of the tensile properties when merely stored under conditions where no corrosion takes place, as Dr. Hudson states is the case with mild steel and brass wires. After complete age-hardening, *i.e.* about 5 to 10 days after quenching from the annealing treatment, Duralumin does not undergo further variations to such an extent that a corrosion test may be affected in any way. On the other hand, it is certainly necessary that the material be made up carefully, so that no greater differences may be found in determining the original values of the uncorroded samples.

Unfortunately, there is a discrepancy in the thickness of the strips, shown in Figs. 8 and 12 of the paper, as Dr. Hudson has remarked. This discrepancy seems to be caused by an error in determining the magnification in Fig. 12, which is obviously smaller than 100 (about 87). I must confess I noticed this error too late to correct it. The actual thickness of the sample was measured as 0·46 mm. Taking this into consideration, the values of the tensile strength are in rather good agreement with those of the loss in weight, so far as the percentage reduction is concerned.

The loss in weight of series I and II of 0·5 mm. after 18 months was, on an average, 8·0 and 12·7 per cent., corresponding with 54·5 and 86·5 grm./m.^{2}, respectively, whilst the loss in tensile strength was 8·5 and 12·0 per cent. The original strength of the 0·5 mm. strips was 42·5 kg./mm.^{2}, not 42·3 kg./mm.^{2}, as Dr. Hudson suggests from Fig. 4. It may be emphasized that in no case, with the only exception of series II of 0·5 mm. after 24 months, had any deterioration of the core itself occurred, especially not by intergranular attack. This would inevitably be combined with a serious reduction in elongation which was still 15·3 per cent. after 18 months for series II of 0·5 mm. (see Fig. 5 of the paper).

Finally, it may be mentioned that the tensile strength of the corroded specimens has always been determined according to the original thickness of each sample in the uncorroded condition. The strength is, therefore, higher if the reduction in area due to corrosion be considered.

THE OPEN-AIR CORROSION OF COPPER. PART III.—ARTIFICIAL PRODUCTION OF GREEN PATINA.*

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

Synopsis.

Following on the observation that the "natural" green patina on copper consists normally of basic copper sulphate, methods have been worked out for the rapid production of an artificial patina of this substance. Treatment with ammonuim sulphate solution followed by a solution in which basic copper sulphate is suspended gives a green patina, which, however, breaks down under severe weather conditions. A patina stable under the latter conditions is produced by anodic treatment for 15 minutes in a suitable electrolyte; it has a good green colour and is quite insoluble in water. The deposit on leaving the bath has a composition represented by the formula $CuSO_4.Cu(OH)_2$; on exposure to the open air a progressive increase in basicity takes place, leading ultimately, it is believed, to the formula $CuSO_4.3Cu(OH)_2$.

Certain synthetic coatings other than basic copper sulphate, although initially green, readily blacken on free exposure to town air. The application of linseed oil and more especially of lanoline to the primary coating gives marked protection to the underlying metal but does not prevent discoloration; water glass and silicon ester, on the other hand, appreciably increase the corrosion.

Previous papers in this series ‡ dealt with the composition of the "natural" green patina on copper. Except at the seaboard, where basic copper chloride entered (predominantly if remote from the town), the essential constituent was found to be basic copper sulphate having the limiting composition $CuSO_4.3Cu(OH)_2$. Arising out of this work the behaviour of copper in synthetic atmospheres containing various concentrations of sulphur dioxide and of water vapour has recently been investigated, with particular regard to the mechanism whereby sulphate or basic sulphate is produced at the metal surface.§

When once established, the natural patina is highly protective; it has also a definite æsthetic value, which, however, is offset, from the

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

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

§ Vernon, *Trans. Faraday Soc.*, 1931, **27**, 255, 582; *Korrosion u. Metallschutz*, 1932, **8**, 141.

point of view of the architect and the builder, by the long period normally required for its development. In inland districts this ranges from 10 to 20 years, during the greater part of which time the metal presents an unsightly black appearance. In the early stages, moreover, there may be considerable loss of metal as normal copper sulphate,* a familiar consequence of which is the disfigurement of stonework by the washings from adjacent copper structures. Various methods have been proposed for producing within a relatively short space of time a patina resembling the ultimate natural product; these have depended, however, on the production of either basic carbonate, basic chloride, or basic acetate, none of which appears to be stable under ordinary open-air conditions.

Following on the observation that the natural patina consists essentially of basic copper sulphate, tests have been carried out with the view to produce at the outset a coating of this substance; and the main object of the present communication is to describe the more important results that have been obtained. Reference is made to tests in which it was sought to preserve patina of other compositions by subsequent treatment and the opportunity is taken to report further observations bearing on the conclusions of the earlier papers.

BEHAVIOUR OF COPPER IN ATMOSPHERES REMOTE FROM TOWN.

In recording the virtual absence of basic carbonate from the "rural" samples, the following statement was made: † "The authors have not succeeded in tracing any example of the green patina on copper exposed to conditions still further remote from both sea and town. It is possible, indeed, that the normal concentration of carbon dioxide in the atmosphere is not sufficient, of itself, to build up a patina consisting essentially of basic carbonate, even in the complete absence of chlorides and sulphates." In other words, in districts sufficiently remote from sea and town the formation of green patina should be inhibited. This state of affairs appears to been have realized in an example, recently communicated by Mr. J. H. Coste,‡ of copper spires in a remote part of Switzerland which are still bright, except for yellow to rosy-red interference colours, after at least 30 years' exposure.

For another cognate example the author is indebted to the cooperation of Dr. C. A. MacConkey, and of Mr. F. E. Lathe, Director of Research Information, National Research Council of Canada. A

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* Vernon, "Second Report to Atmospheric Corrosion Research Committee," *Trans. Faraday Soc.*, 1927, 23, 167.

† *J. Inst. Metals*, 1929, 42, 185.

‡ In a paper by Vernon and Jordan, *J. Soc. Chem. Ind.*, 1931, 50, 1058.

length of copper transmission wire was submitted, after 20 years' service at a point approximately half-way between Ottawa and Montreal on the north shore of the Ottawa river; the wire was covered with a continuous black film, the extreme thinness of which precluded analysis by ordinary chemical methods. Through the kindness of Dr. G. Shearer, the film was examined at the National Physical Laboratory by X-ray diffraction methods and was shown to consist definitely of cupric oxide (CuO); an approximate estimate of its thickness gave a value of between 0·0005 and 0·00005 cm., "probably nearer the 0·0005 limit." In this case the position is complicated owing to the higher temperature that would be reached in service by the transmission wire as compared with the metal through which no current is passing; * nevertheless, the example is interesting as showing the complete absence of basic salts.

The absence of any trace of green patina on a copper lightning conductor situated in the Balearic Isles, 10 miles from the sea, after 10 years' exposure, has been reported to the author by Mr. A. N. Cathcart. The available evidence thus supports the conclusion that basic carbonate is a characteristic of urban conditions of exposure, when it is necessarily accompanied by much larger amounts of basic sulphate, and that at comparatively long distances from the town, and much shorter distances from the sea, the formation of green patina ceases.

FIRST SERIES OF PATINA EXPERIMENTS. PROTECTION BY OIL AND LANOLINE.

In 1927 a series of artificial patina was obtained by treating specimens respectively with aqueous solutions of the following: ammonium chloride, sodium carbonate, ammoniacal copper sulphate, sodium arsenite. On subsequent exposure to the open air (the tests were conducted on the roof of the Royal School of Mines, South Kensington) the deposits proved to be unstable, discoloration occurring with the first approach of fog. In order, primarily, to ascertain whether the patina might be preserved, or possibly augmented, by subsequent treatment, a further series of specimens (each measuring 10 cm. × 5 cm.) was prepared. Following the initial treatments, representatives of each group were treated respectively with the following (a single coating being applied to the dry specimen): boiled linseed oil, lanoline (solution in an organic reagent), water glass (aqueous solution, sp. gr. 1·32), silicon ester. From the æsthetic viewpoint no useful purpose was served, for within a few months all specimens had blackened. Nevertheless, there remained the further question to what extent the under-

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* See von Zeerleder and Bourgeois, *J. Inst. Metals*, 1929, **42**, 321.

lying metal was protected by the treatment, and to settle this the tests were continued. Half the specimens were taken down at 2¼ years' exposure and the remainder after 4½ years, losses in weight being determined after removal of all loosely adhering material by scrubbing with a hard brush under benzene and under water successively. The results presented several interesting features. In every case corrosion had been increased by the application of water glass or silicon ester, and considerably reduced by oil or lanoline. In general both these effects were more marked on specimens that had been chemically treated; and both were more marked at the earlier period of exposure.

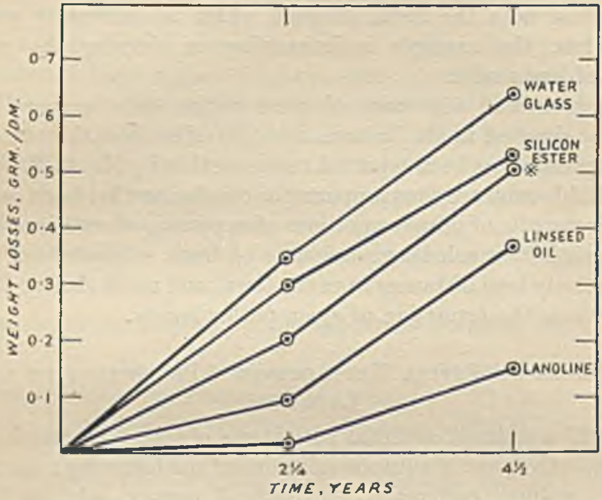

FIG. 1.—Effect of Various Coatings on Specimens Treated Initially with Ammonium Chloride Solution.

* Initial Treatment with Ammonium Chloride, but no Subsequent Coating.

In Fig. 1 time–corrosion graphs are plotted for specimens treated initially with ammonium chloride solution (a similar disposition was shown by groups representing other initial treatments). Rate of attack is falling off in the case of the "stimulative" coatings, whilst it is increasing in the case of the "protective" coatings; clearly, both effects are to be attributed to the gradual removal of the coating during exposure. The final corrosion values for the water-glass and lanoline-treated specimens are respectively the highest and lowest of the series; the efficiency of lanoline when applied to the previously treated surface is especially noteworthy.

Final values for the whole series are given in Table I.

TABLE I.—*Weight Losses.* (*Grm./dm.*^{2}.) 4½ *years' Exposure.*

Initial Treatment.	Subsequent Treatment.				No Subsequent Treatment.
	Water Glass.	Silicon Ester.	Linseed Oil.	Lanoline.	
Ammonium chloride	0·657 0·617	0·516 0·552	0·351 0·398	0·173 0·123	0·518 0·491
Sodium carbonate	0·626 0·589	0·538 0·452	0·211 0·206	0·206 0·232	0·289 0·388
Sodium arsenite	0·608 0·603	0·546 0·497	0·262 0·246	0·234 0·245	0·500 0·419
Ammoniacal copper sulphate	0·647 0·624	0·597 0·530	0·236 0·224	0·177 0·213	0·475 0·333
No initial treatment	0·545 0·602	0·439 0·491	0·288 0·263	0·223 0·225	0·440 0·536

SECOND SERIES OF PATINA EXPERIMENTS. DEVELOPMENT OF SYNTHETIC PATINA OF BASIC COPPER SULPHATE.

Chemical Methods.

An entirely new turn was given to the search for an artificial green patina suitable for withstanding prolonged weathering when it was found * that basic copper sulphate, so far from being a mere "impurity" in the town products, is actually the essential constituent of the green patina on copper structures after many years' exposure in various localities. The problem then resolved itself into the more specific one of producing a synthetic patina of basic copper sulphate. Such a patina clearly should require no further protective coating; moreover, there should be a tendency for any removal of the patina during service to be made good by the normal action of the weather. Accordingly various methods of chemical treatment were tried out, the criterion being, not merely the initial appearance of the coating, but the extent to which it would resist subsequent exposure to the open air. It became evident at an early stage that much depends on the physical condition of the deposit in addition to its chemical composition. The reagents tried included ammonium sulphate, copper sulphate (with various additions), and various sulphites and bisulphites.

The most promising results were obtained from treatment with an aqueous solution of ammonium sulphate of about 10 per cent. concentration; the commercial material was found to be more effective

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* Vernon and Whitby, 1929, *loc. cit.*

than the pure salt; and arsenical copper gave better results than copper of high purity. In this method the solution is applied at intervals (*e.g.*, twice daily), the specimen meanwhile being freely exposed to the air but sheltered from excessive rain and from direct sun. After about 6 days, one or two applications are made of a mixture consisting of a 10 per cent. solution of copper sulphate to which have been added 1 per cent. sodium hydroxide and 5 per cent. ammonium nitrate. The precipitate of basic copper sulphate adheres to the surface and fills the interstices left by the initial treatment with ammonium sulphate. After a short period of normal exposure the deposit closely resembles the natural patina.

Field tests on specimens treated in this way were carried out at Teddington. Several months' exposure, which included considerable fog, were withstood satisfactorily; breakdown occurred, however, during the first period of frost, when the deposit commenced to peel away in small flakes from the underlying metal.* Further deterioration slowly proceeded, but the position was definitely worse in the case of specimens that had received only the simple treatment with ammonium sulphate, without subsequent application of the mixture containing precipitated basic sulphate. It is evident that coatings produced by the chemical method are not suited for withstanding drastic open-air conditions, although it is possible that they would hold up satisfactorily under milder conditions of indoor exposure.

Electrolytic Method.

As an alternative to the chemical method it was sought to produce a synthetic green patina of basic sulphate by making the specimen the anode in a suitable electrolyte. A series of experiments was accordingly carried out, employing small test specimens and a carbon cathode. Out of many electrolytes that were tried, under various conditions of current and temperature, the best results were obtained from a solution containing:

10 per cent. magnesium sulphate,
2 per cent. magnesium hydroxide,
2 per cent. potassium bromate.

The presence of an oxidizing agent is essential to the success of the process, and potassium bromate has yielded results much superior to

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* According to J. Michel (*Coloration des Métaux*, Paris: 1931) the natural patina is similarly affected when temperature changes are sufficiently marked; thus, "severe or very frosty climates are unfavourable to the formation of patina, which tends to scale off during the winter, leaving the metal to be attacked anew at the points thus left unprotected."

those obtained from other oxidizing agents. The bath is used preferably nearly boiling (temperature approximately 95° C.). The optimum current density is approximately 4 amp./dm.^{2}; with the electrodes 1·5 in. apart (as in the experiments) this corresponds to a potential difference of approximately 5 v. The treatment is continued for 15 minutes, when the specimen is removed and rinsed; it is then ready for exposure, no further treatment being necessary. A current density of 2 amp./dm.^{2} for 30 minutes has also been used satisfactorily. The bath is capable of treating a total surface area of 10 dm.^{2} for every litre of electrolyte before becoming exhausted.

As with the chemical method, the electrolytic method yields definitely better results on arsenical copper than on copper of high purity. In the main series of experiments, therefore, arsenical copper containing 0·45 per cent. arsenic has been used. Specimens of copper containing 0·8 per cent. tin and 2·5 per cent. nickel respectively have yielded definitely inferior results.

The deposit, immediately on leaving the bath, has a good green colour and is practically insoluble in water, even when finely powdered. Analyses have shown that its composition is given by the formula $CuSO_4.Cu(OH)_2$. Approximately, therefore, it corresponds in composition to the "natural patina" on emerging from the prolonged "black stage," except that it is contaminated neither by other compounds (*e.g.*, carbonate and sulphide in town samples) nor by extraneous (wind-borne) matter which is always present in the natural patina.

A series of prepared specimens (10 cm. × 5 cm.) has been exposed with the object of ascertaining any changes in composition of the deposit in the course of time. Results obtained so far are as follows:

At start	$CuSO_4.Cu(OH)_2$.
After 14 weeks	$CuSO_4.1{\cdot}34Cu(OH)_2$.
After 28 weeks	$CuSO_4.1{\cdot}51Cu(OH)_2$.
After 42 weeks	$CuSO_4.1{\cdot}63Cu(OH)_2$.

It is evident that a gradual increase in basicity is already in progress and there seems little doubt that the composition of the deposit will ultimately coincide with that of the natural patina after long exposure ($CuSO_4.3Cu(OH)_2$), the net result being the elimination of the prolonged interim period during which the deposit presents its unsightly black appearance.

Other treated specimens (10 cm. × 5 cm.) have been exposed for the purpose of long-period tests, some at Teddington in a field adjoining the Laboratory, and others, through the courtesy of the authorities concerned, on the roof of His Majesty's Office of Works building at

Storey's Gate, Westminster. At Teddington a maximum of exposure of 8 months has now been reached without any visible deterioration of patina; this period has included the winter months, and has included also the spell of frosty weather which was responsible for the breakdown of the deposits on chemically treated specimens. A specimen that was sprayed twice daily for 3½ months with seawater spray in order to simulate marine conditions took on a darker shade of green.

Partly in view of the trouble that arises in practice through washings from bronze statuary disfiguring the supporting stonework, specimens of statuary bronze were included in the tests. Two alloys were employed—a simple copper–tin alloy (10 per cent. tin) and one containing zinc 15, tin 3, lead 1·5 per cent. The concentration of zinc in the latter was the highest for which precedent could be obtained in a statuary bronze. Fortunately (considering the greater extent to which this type of alloy is used in practice) the complex bronze yielded the better patina.

Deposits produced by the electrolytic process on brass and on bronze have a bluish-green colour in contrast with the true green of the copper patina. This may be explained by the analyses which have yielded basicity values in the neighbourhood of 0·8 (experimental values for 60 : 40 brass, 90 : 10 bronze, 70 : 30 brass were 0·74, 0·76, and 0·85 respectively) in place of the unit basicity which characterizes the newly-formed deposit on copper. In view of the increase in basicity that takes place in the copper product, there seems little doubt that a similar increase, with consequent improvement in appearance, would also take place in the brass and bronze deposits in the course of subsequent exposure.

A provisional patent (No. 6757/32) has been filed in respect to the electrolytic method.

Summary and Conclusions.

Previous work showed that the "natural" green patina on copper consists essentially of basic copper sulphate, except at the seaboard, when it is accompanied by more or less basic copper chloride; confirmation has now been obtained that at relatively long distances from the town, and at much shorter distances from the sea, the formation of green patina ceases. Methods have been worked out for the rapid production of an artificial patina, with consequent elimination of the long interim period normally required for the development of the natural product. Certain synthetic coatings other than basic copper sulphate, although initially green, readily blacken on exposure to town air. The application of linseed oil and more especially of lanoline to the primary coating gives marked protection to the underlying metal but does not prevent discoloration; the application of water glass and of silicon ester, on the other hand, appreciably increases corrosion.

A green patina of basic copper sulphate may be obtained by treating the metal with a solution of ammonium sulphate, preferably followed by application of a mixture in which basic copper sulphate is suspended. The coating breaks down under severe weather conditions, probably through physical causes. A patina that is stable under similar conditions is produced by an anodic treatment of 15 minutes' duration in a suitable electrolyte; it has a good green colour and is quite insoluble in water. On leaving the bath the deposit has the formula $CuSO_4.Cu(OH)_2$, but on exposure to the open-air a progressive increase in basicity takes place. It is believed that the composition of the coating will ultimately reach that of the natural patina after long exposure (previously shown to be $CuSO_4.3Cu(OH)_2$). On brass and bronze the electrolytically produced coating has initially a slightly bluish tinge and its basicity is lower than that of the corresponding deposit on copper; during subsequent exposure, however, it is likely to approach more nearly to the copper patina in appearance and in composition.

ACKNOWLEDGMENTS.

Acknowledgments are due to Mr. E. G. Stroud for the valuable part he has taken in the later experimental work, to Mr. L. Whitby for assistance in the early tests at South Kensington, and to Mr. W. H. Sullivan for assistance in recent field tests. The author is indebted also to Mr. G.W. Mullins, M.B.E., Chairman of the Copper and Brass Extended Uses Council, at whose suggestion the early patina experiments were commenced, under the auspices of the British Non-ferrous Metals Research Association. The main investigation has been carried out for the Corrosion of Metals Research Committee of the Department of Scientific and Industrial Research, and the thanks of the author are due to the Chairman, Professor Sir Harold Carpenter, Kt., F.R.S., and to Professor G. T. Morgan, O.B.E., F.R.S., Director of Chemical Research, for facilities afforded and for permission to publish.

DISCUSSION.

MR. A. N. CATHCART * (Member): Dr. Vernon's experiments are important not only from the scientific aspect, but also from the practical point of view to those of us who are using copper for roofing purposes.

For many years we have worked on the assumption that the green patina

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* Ewart and Son, Ltd., London.

is a basic carbonate, and that its appearance must necessarily be more rapid in a clean country atmosphere than in the neighbourhood of a town. The fact that in large towns it remains black for many years encouraged this theory, and it was not realized that the characteristic green colour was merely obscured by the deposition of soot.

In spite of the increasing use of gas and electricity, in the City and East End of London the conditions still seem to preclude the appearance of the green patina. Examples of copper that has remained black after many years may be seen on a number of City churches, notably St. Botolph's, Aldersgate Street, where the copper was laid as far back as 1790. The dome of the Stock Exchange (1884) may also be mentioned. On the other hand, copper roofs on the Russell Hotel and the Imperial Hotel, Bloomsbury, are changing after about thirty years, and the dome of the Gaiety Theatre, laid about 1905, is also changing. In cleaner air, or when the building is very high, the change is much more rapid; thus the dome of St. Joseph's Retreat, Highgate, which was laid in 1909, took only about ten years to turn colour.

An interesting example can be seen in the copper domes of the new Admiralty building, near St. James's Park; these are about 30 years old, and on the south and west sides facing the park they are now distinctly green, but on the northern side they are still in the black stage. Winds blowing over the park possibly deposit their soot before reaching the domes, whilst the northern winds have no opportunity of doing so.

The position seems to be summed up well by a Danish saying that "When a young architect covers his roof with copper it will turn green when his hair turns grey." This was told to me by the city architect at Copenhagen when I was visiting Denmark and Sweden recently, a visit during which I had many opportunities of obtaining information about copper work. What I gathered from this substantially confirms the conclusions that have been arrived at by Dr. Vernon. Several architects told me independently that copper takes longer to turn green in Denmark than in England, presumably because of the general use of wood fuel in place of coal. In Stockholm I was told that now that central heating and coal or coke fuel are being adopted for the generation of steam, the patina appears in about 10 years, whereas it used to take upwards of 50 years. Even so, the thickness of the green film appears to be much less than in this country, the green being fainter and less regular than in our best examples. In the larger city of Copenhagen, where wood is not so much used, there is a greater incidence of green copper than at Stockholm, and the green is more intense.

The architect of the famous Town Hall at Stockholm attached importance to the direction of the wind, because the green appeared more readily on the northern side. He also informed me that he had tried artificial colouring, and that it was much admired at first; after 2 or 3 years, however, it flaked off under the influence of frost and ice, leaving the usual black deposit. This question of frost—again confirming one of the conclusions in the present paper—appears to be the principal difficulty, the variations of temperature being much greater than in England. Both at Stockholm and Copenhagen I was informed that artificial colouring is more successful on bronze than on copper, one example in Stockholm having withstood the frost and ice for more than 4 years.

As illustrating the protective effect of the natural green patina, I may mention an example that I recently inspected at Londonderry Cathedral. In this case the main roof was covered with slates, and the water was collected at various points and delivered through long, vertical down-pipes on to the side roofs, which were covered with copper. In the places where the water impinged on the copper there was no patina, and the copper had corroded badly; in one case a bad leak had developed. The remainder of the roof, however, appeared to be perfectly sound, and was covered with the characteristic green.

With regard to the artificial colouring of copper, many architects are anxious to have a method for treating the metal; up to the present, however, I do not know of any treatment that will give satisfactory results, and, indeed, such methods as have been tried seem to retard the appearance of the "natural" colour.

It is a matter of regret that the chemical method described by Dr. Vernon for producing the basic sulphate has not proved successful under severe weather conditions, as this would be easy to apply *in situ* after the metal has been fixed, and would be of great use when a speedy colouring was required by the architect.

The electrical process appears to be very effective, as shown by Dr. Vernon's samples, but I think that this process is more applicable to bronzes and small articles that can be fixed in position without much handling; for if the prepared sheets were used on roofs or domes where it is necessary to fix the sheets into position by careful welting, entailing much hammering, the patina would be much defaced, and the results might be disappointing.

The results obtained by Dr. Vernon are certainly of great value to practical men, and should prevent the considerable disappointment experienced when buildings are treated and the colour disappears after a short period.

Dr. J. C. HUDSON * (Member): I had not intended to speak on this paper, because there is very little on which I can comment, beyond congratulating Dr. Vernon on having successfully carried his valuable work a stage farther. The only thing that did occur to me has already been dealt with by the previous speaker. It seemed to me that Sweden is a country where one would expect to find a long delay in the development of the patina because the atmosphere there is remarkably free from atmospheric pollution, and I was glad to learn from Mr. Cathcart that this is actually the case.

I may say that, so far as my own experiments go, I believe that the natural patina will develop more rapidly on a copper that is alloyed than on a pure copper. Dr. Vernon refers to the better results obtained with arsenical copper; I believe that this is also true for copper containing a small percentage of nickel, but my own experiments related to wires and not to sheets, and it is difficult to get a marked patina on a wire. I am certainly under the impression, however, that a wire containing, say, 2 per cent. of nickel shows the development of the patina rather more rapidly than a copper wire. A tin-bronze, with 6 per cent. of tin, certainly does so. In the case of the nickel alloys, I think that there is a selective leaching out of the nickel salts by rain water, which presumably leaves the residual copper corrosion product in a more porous condition and, therefore, more susceptible to the progressive weathering that is necessary to bring the film to the required basicity.

The AUTHOR (*in reply to the discussion at the meeting*): Mr. Cathcart has once again communicated data that are most welcome. The examples of copper roofs in the City that are still black after many years do not, of course, conflict with the conclusions of the previous papers. The potent atmospheric agent in the formation of green patina is sulphur dioxide; accompanying sooty matter serves only to hinder the development of patina and may, in extreme cases, prevent it. The influence of soot is felt most severely locally; the influence of gaseous pollution, on the other hand, extends to great distances. The most favourable conditions for patina formation would be

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expected to occur on the outskirts of the city, where locally-generated sulphur dioxide is augmented by that carried by wind, sooty matter having been largely deposited *en route*. All this is well brought out by the examples that Mr. Cathcart has cited. It may be significantly added that among the various examples of patina that have been examined in the course of the present work, the purest sample of basic copper sulphate was provided by the most rural specimen, that from the copper spire of North Mimms steeple (see Part II, *J. Inst. Metals*, 1930, **44**, Table IV, facing p. 392).

The information that Mr. Cathcart has gathered from his visit to Denmark and Sweden is of particular interest; and it is satisfactory that this should confirm conclusions reached during the present work. The influence of wind-direction was dealt with in the first paper of the series. With regard to the artificial colouring of copper as practised on the Town Hall at Stockholm, I understand from Mr. Cathcart that this probably aimed at the production of basic copper chloride. A coating of this substance would certainly have a better chance of surviving in the semi-marine atmosphere of Stockholm than it would in the atmosphere of an inland or industrial district, nevertheless, failure occurred; and frost appears to have been the deciding factor.

The corrosion of the copper roofing at Winchester Cathedral provides an interesting example of the "impingement type" of attack on a relatively incorrodible material. The local impingement of water from the large catchment area above evidently prevented the formation of the protective coating, which developed freely elsewhere; hence the localized corrosion at the unprotected places.

I very much appreciate Dr. Hudson's remarks. No doubt on the alloys that he mentions the natural patina forms more readily than on pure copper. So far as the production of artificial patina is concerned, however, we have found that the presence of nickel or of tin is of no advantage. On the other hand, the presence of arsenic is definitely advantageous, a fortunate circumstance in view of the superior resistance to atmospheric corrosion that is displayed by arsenical copper. Probably the explanation lies in a more intimate bond between the patina and the underlying metal.

CORRESPONDENCE.

MR. JOHN R. FREEMAN, Jr.,[*] B.S. (Member): The series of studies of "The Open-Air Corrosion of Copper" that has been reported by Dr. Vernon has been of great interest and value in clarifying the knowledge of the atmospheric corrosion of copper, and in particular his findings that the green coloration or patina that forms on copper is a basic sulphate rather than the traditional basic carbonate. It may be of interest to record quite independent and apparently contemporary confirmation of his results. In Table A analyses are given of several "patinas" taken from copper roofs in the north-eastern part of the United States. Although the roofs from which the samples were taken did not have the venerable antiquity of some of those reported by Dr. Vernon, it is evident that the industrial atmospheres of the United States are as effective as those of England in causing the development of the basic sulphate.

Dr. Vernon describes in the present paper the results of experiments to produce the patina artificially by the use of ammonium sulphate solution followed by treatment with a solution of copper sulphate, sodium hydroxide, and ammonium nitrate. I should like to direct attention to a recent article[†] describing a somewhat similar method of artificial production of patina, in

[*] Metallurgist, The American Brass Company, Waterbury, Conn., U.S.A.

[†] John R. Freeman, Jr., and P. H. Kirby, *Metals and Alloys*, 1932, 3, 190–194.

Source and Description of Sample.	Type of Atmosphere.	Composition of Patina.*						
		Copper %.	Sulphate SO_4 %.	Chloride Cl %.	Carbonate CO_3 %.	Sulphide %.	Other Elements.	Basic Copper Sulphate $CuSO_4.3Cu(OH)_2$.
Providence, R.I. Sample of flashing and gutter from freight shed showing fine light green patina. Roof laid in 1850. Sample taken in 1928. Period of exposure about 78 years.	Industrial seacoast							Very large amount ‡
Sample from railroad station. Period of exposure about 30 years.		49·70 (53·50)†	20·2	0·00	0·00	0·00	Iron oxide, silica, &c. 4·86	95·14
New Haven, Conn., Woolsey Hall, Yale University. Roof laid about 1901 or 1902. In place about 25 years.	Industrial seacoast	49·94 (50·50)	19·06	Very small amount	Very small amount	...	...	89·1
Waterbury, Conn., Waterbury Brass Goods Corpn. Sample of roof in place about 16 years.	Industrial. 25 miles from seacoast	51·33 (51·96)	19·61	Very small amount	Very small amount	...	...	91·6
Roofing from house at corner of Grand and State Streets. Light green uniform patina. Probably about 40 years old		50·17 (52·60)	19·85	0·00	0·00	Small amount	Iron 0·84	90·0
Prospect, Conn. (about 6 miles from Waterbury, Conn.). Copper telegraph wire. Light green patina. Length of exposure unknown.	Semi-rural		Very large amount	Very small amount	0·00	Very small amount	Cuprous oxide. Large amount	Very large amount ‡

* The marked similarity of the composition of the patinas to the copper ore brochantite was noted at the time of analysis by the chemist, Mr. J. A. Crane, who had had recent experience with these ores at the Chuiquiqamata mines in Chile, South America.

† Figures in parentheses are theoretical copper values required to satisfy the formula $CuSO_4.3Cu(OH)_2$.

‡ There was insufficient sample to make complete analysis. Qualitative tests showed corrosion products to be principally a basic sulphate of copper.

which ammonium sulphate only was used, but which is successful only after suitable " conditioning " of the solution. The patina formed by the method described has been found to be stable and adequately adherent even after exposure to the rather rigorous winter climate of New England.

Dr. Vernon quotes a statement by J. Michel that " severe or frosty climates are unfavourable to the formation of patina." As this might be interpreted as implying that patina does not readily form in climates having severe winter weather, I would point out that there are many copper roofs and domes with beautifully developed patinas in various parts of the United States where the winter climate is very severe and the temperature change on a roof very rapid.

The AUTHOR (*in reply*): I am greatly indebted to Mr. Freeman for his interesting and valuable contribution. Particularly noteworthy is the information that in the United States, as in England, the green patina consists of basic copper sulphate rather than of the traditional basic carbonate. Broadly, the position is evidently similar: there are, however, certain matters of detail that are rather difficult to understand. Thus, the analyses given in Mr. Freeman's table show a virtual absence of basic carbonate; whereas we have found that, especially in the atmosphere of the town, basic carbonate may reach appreciable dimensions (see Part II, Table IV). Equally unexpected is the " very small amount " of basic chloride in the industrial seacoast sample, and the absence and the smallness respectively of sulphide from the railroad station and the town. There is, moreover, a surprising freedom from wind-borne material throughout the analyses. The net result is that the samples examined by Mr. Freeman are very much richer in basic sulphate than any we have examined here. Owing to the very large and very variable amount of extraneous matter in our samples, the formula to be ascribed to the basic sulphate was far from obvious, and its determination formed the subject of the second paper in the series. The time factor was shown to be of great importance, and only after periods ranging from 70 to 100 years was complete identity with the brochantite (co-ordination) formula established.

I should like both to express my appreciation of the article in *Metals and Alloys* (the reference to which is very much to be welcomed) and also to congratulate Mr. Freeman on having achieved so much success with the ammonium sulphate process. Since the publication of our first paper in 1929, the chemical methods that we have tried in order to reproduce the basic sulphate patina have centred largely round the use of ammonium sulphate. Initially promising results have often proved disappointing when subjected to the test of subsequent exposure to the weather. Curiously enough, whereas Mr. Freeman has achieved greater success from a purely chemical method than from an electrolytic method, the reverse has obtained in our own experience. Neither process satisfies the objection raised by Mr. Cathcart, inasmuch as it cannot be applied to a roof *in situ*; nevertheless, I am not without hope that a way may be found of overcoming this difficulty. Incidentally, it does not seem unreasonable to expect some little modification of technique on the mechanical side, with the view to some of the more severe bending being effected before the plate is treated.

Mr. Freeman's statement that beautifully developed patinas may be found in various parts of the United States where the winter climate is very severe is significant as showing that when once a satisfactory patina is developed it is immune to quite drastic temperature changes. Nevertheless, our experience with certain of the artificial patinas, taken in conjunction with the Swedish experience quoted by Mr. Cathcart and also with the statement of Michel, goes to show that frost is an adverse factor in the development of patina; and the best results are therefore to be expected when the conditions have been relatively mild in the early stages of exposure.

In view of its bearing on several points raised in the discussion, I take the opportunity to refer to information lately gleaned from the examination of samples of green patina on copper and bronze at Guernsey in the Channel Islands; these were submitted to the Chemical Research Laboratory through the kindness of Miss I. M. Tunbridge, of the Ladies' College, Guernsey. The samples, the proximate analyses of which are given in the accompanying table, were scraped from the copper spire of the Church of St. Joseph, about ½ mile from the sea front, and from the bronze statue of Prince Albert, situated on the Quay.

	St. Joseph's Steeple.	Prince Albert Statue.
	%	%
Basic copper chloride . . .	48·4	73·0
Basic copper sulphate . . .	15·4	3·78
Basic copper carbonate . . .	24·9	0·49
Extraneous matter (not contributing to the green constituents of the deposit)	11·3	22·73
Ratio of copper in base to copper in normal salt	1·74	2·5
Age of structure : years . . .	33	69

Several interesting features emerge from the analyses. The Prince Albert Statue product has provided the highest proportion of basic chloride and the lowest proportion both of basic sulphate and of basic carbonate encountered in any of the samples yet examined. This is not surprising, bearing in mind the position of the statue and the fact that it would receive a certain amount of actual sea-spray. Another contrast is provided by the analysis of the steeple product, in which the basic carbonate figure is the highest experienced in the course of the investigation. Moreover, in only one other instance has basic carbonate exceeded basic sulphate and this also was a marine example (telegraph wire in Lowestoft district); as in the present example, the preponderating constituent was basic chloride. Finally (confirming the findings of the second paper) a correlation between basicity of product and age of structure may be noted, basicities of 1·74 and 2·5 corresponding with ages of structure of 33 and 69 years.

Another sample, from a bronze statue of Queen Victoria in Candie Gardens, gave an analysis which resembled the steeple product in respect to basic sulphate and the Albert Statue in respect to basic carbonate. The basicity of this product could not be satisfactorily obtained on account of a high proportion of zinc compounds; there was also present an abnormal amount of wind-borne material, including 29 per cent. of silica and alumina, representing, most probably, associated clayey matter. The amount of such extraneous matter which may be carried by a deposit without appreciably affecting the green appearance is certainly surprising.

SOME REACTIONS OCCURRING IN "HOT-DIPPING" PROCESSES.*

By EDWARD J. DANIELS,† M.Sc., Member.

Synopsis.

The part played by fluxes has been investigated and a general agreement found with diverse processes. The contamination of the liquid metal—"drossing"—is shown to be an inevitable factor in hot-dipping, soldering, &c., and methods for controlling it are indicated.

The coating of steel with cadmium and lead by hot-dipping is shown to be accompanied by the formation of the compounds $FeCd_2$ and $FePb_2$, which act as insulating layers preventing further attack. These compounds rise to the surface of the liquid bath, have high melting points and are magnetic.

The action of molten tin on 8 per cent. "aluminium–bronze" is shown to be anomalous.

Dross Formation in Hot-Galvanizing.

In a previous paper [1] evidence was adduced to show that at normal galvanizing temperatures, *i.e.* below 480° C., the zinc–iron alloy, approximately $FeZn_7$, which forms on the surface of articles being galvanized, is stable with respect to molten zinc, and remains firmly attached to the steel surface. It is highly improbable therefore that the reaction between molten zinc and iron is the source of the "dross" or "hard zinc" which accumulates at the bottom of the galvanizing kettle, as was formerly supposed.[2]

Several observers [3, 4, 5] have noted that molten zinc will decompose iron chloride with the formation of iron. As will be shown later, when mild steel articles are galvanized, contamination of the zinc will occur as a result of reduction of iron salts from the flux. It is of value, therefore, to study in some detail the factors affecting the entry of iron salts into the flux, and the experiments made to this end are described below.

The Washing of Pickled Sheets.

When a strip of mild steel is pickled in acid, even after washing in cold water, iron salts remain and can be removed by a jet of hot water.

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Tables I and II give data for sulphuric and hydrochloric acid pickles of various iron contents, using a constant volume of 180 c.c. of water for the removal of the attached salts after "normal" or no washing. It will be noted that "normal" washing removes the iron salt more completely after the hydrochloric acid pickle than after the sulphuric acid pickle, due doubtless to the greater solubility of the chloride.

TABLE I.—*Removal of Salts on Washing Pickled Steel.*

Pickle: 3 minutes in boiling 5% H_2SO_4 plus x% Iron as $FeSO_4$.

No.	Fe in Pickle. Per cent.	Washing Treatment.	Iron Washed Off as Salts by Jet of Boiling Water, grm./m.^{2}. Sheet Surface.
VI	0	Held for 1 minute in beaker into which water was running ("Normal")	0·03
III	1	,, ,, ,, ,,	0·04
V	2·5	,, ,, ,, ,,	0·06
IV	5	,, ,, ,, ,,	0·09
IX	10	,, ,, ,, ,,	0·13
X	15	,, ,, ,, ,,	0·15
VII	5	None (momentary dip in cold water)	0·90
VIII	5	Scrubbed under tap	0·03
XI	0	10 minutes in boiling water	0·02
XII	10	,, ,, ,, ,,	0·01

TABLE II.—*Removal of Salts on Washing Pickled Steel.*

Pickle: 15 minutes in 20% HCl plus x% Iron as $FeCl_2$ at 60°–70° C.

Washing Treatment.	Iron Washed Off as Salts by Jet of Boiling Water after Pickling in Hydrochloric Acid of the following Iron Contents, followed by the Washing Treatment Shown.		
	0% Iron.	5% Iron.	15% Iron.
None (momentary dip) .	0·07	0·13	0·43
Normal	0·02	0·01	0·02
10 minutes in boiling water .	0·01	0·02	0·02

Fluxing before Dipping.

In the so-called "dry" galvanizing process, the articles to be coated are immersed in a concentrated solution of flux, heated over a fire or in an oven to evaporate the water, and then plunged into the molten zinc.[6, 3] When the drying operation has been completed, the work itself is fluxed, but it must be covered with an excess of flux, since the surface of the zinc bath must be cleaned as the work passes through it, and in this process no flux is put on the bath. For this reason there is a maximum temperature at which any given flux can be "dried-off," consistent with a perfect coating. This temperature has been determined for a number of fluxes, the galvanizing being carried out in two baths, one of electrolytic zinc and the other of zinc containing 0·5 per cent. aluminium. No attempt has been made to determine the absolute values of time and temperature permissible for any given flux.

In all cases, the presence of aluminium in the zinc reduced the maximum permissible drying temperature, since a greater degree of fluxing is required when the molten zinc is covered with a film of alumina. For example, the presence of the aluminium reduced the maximum drying-off temperature from 410° C. to 280° C. with ammonium chloride as the flux, from 300° C. to less than 125° C. with aluminium–ammonium chloride, and from 405° C. to 295° C. with zinc–ammonium chloride.

A reaction occurs between the steel and the flux during drying, giving rise to iron halides, and to iron oxide if heated too long at high temperatures (see Tables III and IV, which refer to non-pickled sheet). Similar results were obtained with zinc bromide solution.

TABLE III.—*Formation of Soluble Iron Salts on Evaporation of $ZnCl_2.2NH_4Cl$ Solution on Emeried Strips.*

Salts Washed Off with Jet Hot Water and Reported as Iron per m.² of Sheet Surface.

Time. Minutes.	Temperature of Drying, ° C.			
	150.	200.	250.	300.
2				1·16
4				3·87
5	0·17	0·65	0·67	
10	0·25	0·44	2·15	4·39
20	0·40	0·97	1·31	
40	0·44	0·97	↓ 0·99	
			decrease due to increasing formation of oxide	

TABLE IV.—*Same as Table III, Flux being concentrated $ZnCl_2$ Solution.*

Time. Minutes.	Temperature of Drying, ° C.			
	150.	200.	250.	300.
2				0·41
4				0·67
5	0·34	0·86	0·62, 0·62, 0·62	
10	0·35	0·68	0·48, 0·58	1·39
20	0·81	0·99	0·57, 0·58	1·59
40	1·16	0·89	0·68, 0·65	

After pickling, washing, fluxing, drying, and galvanizing, the amount of iron picked up by the zinc was determined. The results are reported in Table V, where the effect of the various factors can be seen clearly. (It should be noted that in each experiment six sheets were dipped and the whole of the 180 grm. of zinc which formed the galvanizing bath were dissolved for analysis so that segregation of the dross did not interfere.)

TABLE V.—*Combined Effect of Pickling, Washing, Drying, and Galvanizing on the Iron Picked up by the Zinc.*

Flux : Saturated Zinc Chloride Solution.

No.	Pickle.	Washing.*	Drying.	Iron Picked Up by Zinc (grm./m.² Sheet Surface).†
D37	15 minutes 60°–70° C. 20% HCl, 15% Fe.	+	2 minutes 300° C.	0·69
36		−		2·81
38		+	15 ,, 200° C.	0·36
39		−		1·40
42		+	15 ,, 150° C.	1·27 ?
40		−		0·74
43		+	30 ,, 150° C.	1·95
41		−		2·18
46	3 minutes boiling 4% H_2SO_4, 5% Fe.	+	2 ,, 300° C.	1·07
44		−		3·12
47		+	4 ,, 300° C.	1·46
45		−		2·28 ?
48		+	15 ,, 150° C.	0·96
50		−		2·73
49		+	30 ,, 150° C.	2·03
51		−		2·80
52	15% Fe.	+	15 ,, 150° C.	1·33
54		−		3·62
53		+	30 ,, 150° C.	1·60
55		−		4·30

* + signifies "normal" washing ; — signifies no washing.
† grm./m.² × 0·0002 = lb./ft.².

Reactions Occurring in Molten Flux.

In the so-called "wet" galvanizing process the pickled and washed articles are passed into the molten zinc through a layer of molten flux usually having ammonium chloride as its basis. Actually the flux contains a considerable proportion of zinc chloride formed by reaction between ammonium chloride and the molten zinc.[7]

To examine the solvent action of various molten fluxes for iron oxide and mild steel, a small crucible furnace was employed in which the reactions were carried out in a small silica dish maintained at 475° C. in all cases. When the charge of molten flux had reached this temperature, a weighed quantity of ferric oxide powder (rouge), sufficient in amount to give a total iron content of 0·15 per cent. was added and stirred in, and the cover was replaced. When a definite time had elapsed, the contents of the dish were poured into 600 c.c. of distilled water containing about 10 c.c. of 50 : 50 acetic acid. After filtering the dissolved iron and the unattacked iron oxide on the filter paper were determined, so that the amount of iron halide formed and evaporated could be calculated. The results for the quantity of iron turned to halide are given in Table VI as percentages of the original iron addition. The addition of acetic acid is necessary in order to avoid the hydrolysis of the iron salts which otherwise occurs.

TABLE VI.—*Solution of Fe_2O_3 in Molten Flux at* 475° C.

Iron added to the Flux as Fe_2O_3 to give 0·15% Fe by Weight.

Time. Minutes.	Percentage of added Iron turned to Halide, the Flux being:		
	$ZnCl_2.2NH_4Cl$.	$ZnCl_2$.	$ZnBr_2$.
5	89·7		
15	88·7	2·3	
45	95·3		3·0
90	98·2	1·4	5·0
220		3·2	

The results obtained with $ZnCl_2.2NH_4Cl$ as a flux are of a very different order from those obtained with zinc chloride. Under the conditions of the experiment both these fluxes give rise to free hydrochloric acid, the first by decomposition of its ammonium chloride, and the second by reaction with water, the formation of hydrochloric acid being much greater in the case of the first-mentioned. This suggests that the active principle of the flux is hydrochloric acid, and that dry zinc chloride and iron oxide will have little tendency to react together. Table VII shows the results obtained on heating dry iron oxide and zinc chloride in sealed reaction tubes compared with similar tubes containing added water. It will be seen that the results are in the direction indicated, the slight amount of iron chloride formed in the dry tubes is probably due to the presence of a trace of water vapour introduced during the sealing of the tubes.

It may be assumed, therefore, that the active principle of chloride fluxes is hydrochloric acid. In confirmation of this it may be mentioned that stannous chloride is a less efficient flux for galvanizing than zinc chloride, and experiment shows that less hydrochloric acid is produced when steam is passed over molten stannous chloride than when it is passed over the molten zinc salt.

TABLE VII.—*Reaction between $ZnCl_2$ and Fe_2O_3, Both Being Thoroughly Dried.*

Drying: 70 hrs. at 150°–210° C. in a Stream of Air which had passed through $CaCl_2$ and P_2O_5.
Heating: 7100 minutes at 475° C.

No.	$ZnCl_2$, grm.	Fe_2O_3, grm.	H_2O, grm.	H_2O, %.	Soluble Iron Found.	
					Grm.	% of Fe Added.
a	6·54	0·076	Dried		0·00004	0·07
b	8·35	0·070	,,		0·00001	0·02
c	7·18	0·076	0·2	2·7	0·00024	0·42
d	5·92	0·064	0·4	6·3	0·00010	0·22

The solvent action of molten flux for iron oxide increases with the ammonium chloride content and to a lesser degree with the moisture content. Owing to the fact that these fluxes are undergoing constant decomposition while molten, results are not easily duplicated, but a tendency for the rate of attack to fall off with time has been observed.

TABLE VIII.—*Solution of Mild Steel in Molten Flux at 475° C.*

Flux.	Time (t). Minutes.	Loss in Weight of Steel. L (grm./m.^{2}).	$L/\sqrt{t}$ (representative).
$ZnCl_2$	0	0	
	15	26·4	7
$ZnCl_2$, 5% NH_4Cl	0	0	
	15	114	
	30	186	
	45	177	29
$ZnCl_2$, 10% NH_4Cl	0	0	
	7½	476	
	15	591	
	30	670	
	45	611, 641	150
$ZnCl_2$, 16·6% NH_4Cl	0	0	
	4	895	
	7½	1126	
	15	1365	375

Note.—For the same steel and molten zinc at 475° C. $L = 10·6\sqrt{t}$.

The results obtained (Table VIII) for the attack of mild steel by molten flux show that the activity of the flux increases with its ammonium chloride content, and that for a given flux the loss in weight is proportional to the square root of the time. For comparison the loss in weight of mild steel in molten zinc at the same temperature equals $10{\cdot}6\sqrt{\text{time}}$. For the flux containing 5 per cent. ammonium chloride the proportionality factor is of the order of 30, so that the attack of steel by flux is greater than by zinc.

Reaction between Flux and Zinc Bath.

The reduction of iron from the flux by molten zinc was determined by heating weighed quantities of zinc, zinc chloride, and ferric chloride in sealed glass tubes at 475° C. followed by analysis of the flux and zinc.

TABLE IX.—*Reaction between Flux and Zinc at* 475° *C.*

Experiment No.	Weight of Zinc Used. Grm.	Weight of Iron added as FeCl$_3$. Grm.	Mol. % FeCl$_3$ in Flux.	Distribution of Iron found after Heating.			
				Weight as FeCl$_3$ in Flux. Grm.	Mol. % FeCl$_3$ in Flux.	Weight of Iron in Zinc. Grm.	Atomic % Fe in Zinc.
RR 2	6·6632	0·0749	3·9	0·0078	0·42	0·0672	1·16
3	5·8246	0·0213	0·83	0·0195	0·76	0·0015	0·034
4	7·5304	0·1112	4·4	0·0209	0·90	0·0890	1·36
6	7·5374	0·0227	0·94	0·0166	0·69	0·0058	0·090
7	7·3396	0·0815	4·8	0·0074	1·06	0·0714	1·13
8	7·9252	0·0297	0·91	0·0284	0·89	0·0010	0·015
12	7·4940	0·0189	0·58	0·0149	0·46	0·0035	0·06
13	6·6918	0·0102	0·31	0·0083	0·25	0·0010	0·017
16	7·2478	0·0894	1·10	0·0157	0·69	0·0737	1·18
15	7·6458	0·0359	3·96	0·0318	0·96	0·0039	0·22
18	7·5498	0·0894	0·86	0·0277	0·79	0·0018	0·028

Table IX shows the results obtained after 2 and 4 hrs. at 475° C. The reduction of the iron salt by the molten zinc is clearly shown. Even with 4 hrs.' heating * equilibrium was not attained, there being a relationship between the concentration of iron initially in the flux and the concentration found in the zinc, owing to the fact that the reaction occurs at the flux-metal interface and is therefore governed to a large extent by the rate of diffusion of iron salt up to that interface. In practice, where the area of contact between flux and zinc is large the reduction of iron from the flux will be more complete and more rapid.

In one test where about 4 grm. zinc were heated for 3 hrs. at 475° C. in a sealed tube with about 2 grm. $FeCl_3$, 17 per cent. of iron was found in the zinc bead, and in another test about 5 grm. of zinc were heated for 18 hrs. at 475° C. with 0·12 grm. of ferric chloride, the metal bead taking up 8·13 per cent. iron.

Micro-examination of zinc which has been melted in contact with flux containing chloride of iron shows it to possess the same structure as "dross," *i.e.* well-defined crystals of $FeZn_7$ in a matrix of zinc.

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* RR 12–18.

THEORY OF THE MECHANISM OF FLUXING IN GALVANIZING.

If a strip of mild steel is cleaned with emery paper and dipped into molten zinc, no coating will be obtained, since there is sufficient oxide on the steel surface to prevent wetting of the steel by the zinc. If a zinc–ammonium chloride flux be used, the steel will be wetted and a coating produced. It is suggested that this flux (which has been shown to turn iron oxide and metallic iron to chloride) replaces the oxygen atoms on the steel surface by chlorine atoms. It has also been shown, however, that molten zinc decomposes iron chloride, so that when the " fluxed " surface enters the molten zinc the chlorine is removed as zinc chloride leaving the steel surface free to alloy with the zinc. This mechanism is not in conflict with the idea usually held that the flux enables clean metal to come in contact with clean metal, but merely shows the steps of the process. The experimental data indicate that, until the flux is actually displaced by the zinc, it is combined with the surface of the steel, and that the zinc itself must play its part in producing the " clean " steel surface by breaking up the compound formed.

This explanation is supported by the fact that, whilst acid potassium sulphate will dissolve iron oxide and solid iron even more readily than zinc–ammonium chloride to give a water-soluble compound (presumably iron sulphate), molten zinc is incapable of reducing the iron from such a flux, and mild steel cannot be galvanized when acid potassium sulphate is used as a flux.

DISCUSSION OF THE GENERAL APPLICATION OF THE THEORY.

The fact that tin is capable of decomposing iron chloride [8] means that a similar mechanism holds for fluxing in tinplate manufacture, and suggests that it might hold generally where a solid metal is being wetted by a liquid metal in the presence of a molten salt or flux. A wide range of cases was accordingly investigated with respect to the reduction by a molten metal of the fluxed oxides of iron, copper, and nickel and as regards the wetting of iron, copper, and nickel by the molten metal using the fluxes in question. The results obtained are given in Table X, a positive sign under the heading " Result of Chemical Test " indicating that reduction did occur, and a similar sign under the heading " Result of Dipping Test " indicating that a hot-dipped coating could be obtained with that particular combination of metals and flux. Negative signs have precisely the opposite significance. With the 34 combinations tested, the signs for each are invariably the same in the two columns, a negative sign never accompanying a positive, thus providing ample confirmation of the general applicability of the mechanism of fluxing de-

PLATE XXXII.

FIG. 1.—Unetched Cd (white) + $FeCd_2$. × 1000.

FIG. 2.—Unetched Pb (black) + $FePb_2$. × 1000.

[*To face p.* 176.

scribed above. It is particularly interesting to note that similar reactions occur in tinning and soft-soldering using such materials as resin and glycerine as fluxes, as occur in galvanizing using the more active chloride fluxes, the difference between the fluxes being merely one of degree of intensity of chemical activity.*

TABLE X.—*Showing Relationship between Fluxing and Coating Formation.*

Solid Metal.	Liquid Metal.	Flux.	Result of Chemical Test.	Result of Dipping Test.
Mild Steel (Fe)	Bi	chloride	—	—
	Sn	,,	+	+
	Pb	,,	+	+
	Cd	,,	+	+
	Zn	,,	+	+
	Sb	,,	+	+
	Al	,,	+	+
Copper (Cu)	Bi	,,	—	—
	Sn	,,	+	+
	Pb	,,	+	+
	Cd	,,	+	+
	Zn	,,	+	+
	Sb	,,	+	+
Nickel (Ni)	Bi	,,	—	—
	Sn	,,	+	+
	Cd	,,	+	+
	Zn	,,	+	+
	Sb	,,	+	+
Mild Steel (Fe)	Pb–Sn solder	resin	+	+
		glycerine	+	+
		lactic acid	+	+
	Sn	resin	+	+
		glycerine	+	+
		lactic acid	+	+
Copper (Cu)	Pb–Sn solder	resin	+	+
		glycerine	+	+
		lactic acid	+	+
	Sn	resin	+	+
		glycerine	+	+
		lactic acid	+	+
Mild Steel (Fe)	Sn	palm oil	+	+
Mild Steel (Fe)	Brazing-solder (Brass)	borax	+	+
Mild Steel	Zn	acid potassium sulphate	—	—
Mild Steel (Fe)	Zn	zinc bromide	+	+

(Total number of combinations, 34.)

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* It is possible, in special cases, that the "flux" may do no more than remove oxide, leaving the solid surface clean without the formation of a compound between flux and metal which must be decomposed by the liquid metal, as for example in the use of hydrogen in the soldering of steel with copper, but where molten salts are used for fluxing the mechanism described above must hold.

It may be concluded that, using a liquid flux, "drossing" will always accompany the formation of a hot-dipped coating, even though, as appears to be generally the case, the alloy layer formed by interaction of liquid metal and the solid metal being coated is perfectly adherent to the work. Within limits, however, drossing can be controlled; for example, by preventing the pickling salts being carried into the flux, by reducing the activity of the flux to the minimum necessary for perfect wetting, and by the addition of special substances to the molten metal or flux (see for example Lorenz [9]). Dross in the galvanizing process can also sometimes arise to a small extent from the breaking up of the $FeZn_7$ layer which forms the base of the coating by the evolution, at galvanizing temperatures, of hydrogen which has been occluded in the pickling operation.

SPECIAL CASES OF COATING BY HOT-DIPPING.

Cadmium Coatings.

G. de Lattre [10] has discussed the advantages of cadmium over zinc for the production of hot-dipped rust-resisting coatings on steel, and considers that, since steel is not attacked by molten cadmium, drossing will not occur. The inactivity of steel in molten cadmium has been confirmed by the author,[1] Ageew and Zamotorin [11] and Isaac and Tammann.[12] It is quite clear, therefore, that molten cadmium and solid iron do not give a "dross," but it is possible that reaction with the flux may do so.

Preliminary experiments having shown that iron definitely entered iron-free cadmium melted in contact with ferric chloride, some cadmium was heated with a large excess of ferric chloride and a little zinc ammonium chloride in a silica basin. After cooling, the flux (which now contained cadmium) was removed by washing with hot water, the basin was cleaned, and the button of metal remelted and poured into a hard-glass tube. A small quantity of metal remained in the basin and was not properly melted until a red heat had been reached. It was then added to the rest in the glass tube, the whole melted and well shaken before being allowed to solidify slowly in the hot tube, which was held undisturbed in a vertical position.

The bottom of the rod so obtained contained 0·006 per cent. of iron, and micro-examination showed the presence of a new constituent, mainly along the grain boundaries. The top of the rod contained 5·3 per cent. of iron and a fairly large amount of grey constituent.

A similar experiment with cadmium–zinc eutectic gave a still more distinct dross segregation at the top (5·08 per cent. iron), the bottom being almost iron free (0·0088 per cent. iron). After heating a small quantity of cadmium for about 15 minutes with a large quantity of ferric chloride in a hard-glass tube, the solidified metal was washed and remelted twice. It was then granulated by pouring into water and heated for some time at a good red heat under a NaCl-KCl flux, in order to boil off the excess cadmium. To obtain still further concentration the metal was again heated under a flux to a good red heat, and two small pieces of metal were obtained. These pieces could be hammered quite thin and were distinctly magnetic, and one piece, weighing 0·05 grm., when examined under the microscope showed about 10 per cent. of cadmium (white) and about 90 per cent. of grey constituent, which was massive in character, as is shown in Fig. 1 (Plate XXXII), at a magnification of 1000. The whole 0·05 grm. was dissolved for analysis, and 17·8 per cent. iron and 81·2 per cent. cadmium were found. Since these total 98 per cent., the grey constituent must be metallic. If it is $FeCd_2$, the 17·8 per cent. iron will be combined with 71·6 per cent. cadmium leaving 10·6 per cent. cadmium free, thus agreeing with the distribution found under the microscope. The microscopic and analytical tests made in the earlier experiments indicated that the compound is, to all intents and purposes, insoluble in molten cadmium.

When properly fluxed mild steel is immersed in molten cadmium reaction immediately takes place, $FeCd_2$ being formed on the steel surface. Since, however, cadmium is insoluble in the compound, the cadmium cannot diffuse to attack the underlying steel and the reaction ceases at once. A similar state of affairs holds for solid magnesium and molten tin.[13] Drossing accompanies the formation of the coating due to reaction between the molten cadmium and the iron salts contained in the flux, and the resulting compound, being infusible at the working temperature and lighter than cadmium, rises to the top of the metal bath.

Hot-Dipping in Pure Lead.

Since, according to Isaac and Tammann,[12] lead and iron have no affinity for each other, it is generally considered that a "bonding" agent, *e.g.* tin, must be added to the lead bath (see, for example, Rawdon [14]). An attempt was made to produce a lap-joint with mild steel, using ammonium chloride as the flux, and pure lead as the solder. On breaking the joint, fracture occurred through the lead, the separated halves being lead-coated. Spectroscopic analysis of the lead used in this and the following experiments showed it to be very pure.

A continuous coating of this lead was obtained on mild steel by hot-dipping using zinc–ammonium chloride as the flux. The formation of the coating was slow, two dips of about 2 minutes each being necessary.

Micro-examination of a button of lead which had been melted in contact with ferric chloride showed the presence of a constituent which was harder than the lead and white in colour. A piece chipped off the top of the button contained 0·15 per cent. of iron. The white constituent was segregated to the top of the button and its appearance is shown in Fig. 2 (Plate XXXII). The reduction of iron from the flux by molten lead is very slow and this is the reason why a longer time is necessary to form a lead coating than to form a zinc or cadmium coating.

By considerably increasing the time of heating and the quantity of ferric chloride used, followed by liquation, an alloy rich in iron was obtained. A small piece (0·75 grm.) was chipped off the top and hammered fairly thin. Micro-examination of both sides showed about 20 per cent. of free lead, the rest being the hard white constituent. This sample was very magnetic and was all dissolved for analysis, 9·22 per cent. iron and 90·62 per cent. lead being found. Since these total 99·82 per cent. the mixture is metallic. If the iron is present as the compound $FePb_2$ the 9·22 per cent. iron will hold 68·26 per cent. lead in combination, leaving 22·52 per cent. free, thus agreeing with the distribution found under the microscope.

The formation of a lead coating by hot-dipping is thus quite normal, a lead–iron compound ($FePb_2$) serving to cement the lead and the steel together. The observed inactivity of molten lead with respect to solid steel is due to the insolubility of lead in the compound which acts as an insulating skin. The slowness of formation of the coating is due, not to the low affinity of iron for lead, but to the slowness of removal of the chlorine layer from the fluxed surface by the molten lead. Additions, such as tin, to the lead, speed up this reaction and so make it easier to obtain a coating.

The Tinning or Soldering of "Aluminium-Bronze."

Cases do exist, however, where wetting of the compound first formed is incomplete, giving an unsatisfactory coating, as for example in the tinning of "aluminium-bronze."

If a strip of "aluminium–bronze" (8 per cent. aluminium) is rubbed clean with emery paper, and a small piece of tin, together with zinc–ammonium chloride, is then placed upon it, and the whole heated, it will be found that the tin melts and flows in the normal way to form a shallow pool. Almost at once, the edges of the pool *recede*, leaving a dirty-white coloured area all round the still molten tin, the whole still being covered with molten flux. This recession after wetting has occurred takes place independently of the composition of the flux used and does not occur with copper as the basis metal.

A strip of bronze was heated for some minutes in molten tin at about 300° C. and, after cooling, the melt was sectioned and polished, when a layer of bright interfacial alloy between the tin and the bronze was clearly visible to the naked eye. A sufficient thickness of this alloy was produced on an accurately machined bronze rod so that turnings of it could be obtained for analysis. The alloy contained

	Per cent.
Tin	46·4
Copper	49·0
Aluminium	3·9
Iron	0·025

The iron was derived from the "bronze" in which it was present as an impurity. The aluminium in this tin alloy is 8 per cent. of the copper content, showing that the solid has reacted as a whole with the tin. From the work of Edwards and Andrews [15] it appears that this alloy is a solid solution of tin and aluminium in Cu_3Sn, thus differing from the alloy formed in the soldering of copper (Cu_3Sn with tin in solid solution) in that it contains aluminium.

By maintaining a deep pool of molten tin on a piece of "aluminium-bronze" strip and then grinding down, a specimen was obtained in which the greater part of the surface was "bronze," with a large area of tin and an area of tin alloy ("compound"). Repeated attempts were made to tin the compound, but all of them failed. It is this lack of complete wetting of the interfacial alloy by tin which makes it impossible to obtain satisfactory lap joints with "aluminium-bronze." If the pool of molten tin is deep enough, the mere weight of the molten metal is sufficient to keep it pressed out to the edge of the fluxed area. The fact that the interfacial alloy grows readily to visible thickness shows that tin dissolves in and diffuses through it, making it more difficult to understand why tin should only partially wet it.

SUMMARY AND CONCLUSIONS.

Quantitative data on the sources of iron salts in galvanizing flux have been presented, and it has been shown how these lead to the formation of "dross."

A theory of the action of fluxes in hot-dipping processes has been advanced and evidence offered in support. It has been concluded that contamination of the liquid metal ("drossing") is a normal accompaniment of hot-dipping processes, and methods for controlling it have been indicated.

The coating of steel with cadmium and lead by hot-dipping has been brought in line with tinning and galvanizing by the discovery that these metals can form compounds, $FeCd_2$ and $FePb_2$, with iron. These compounds are both magnetic, have high melting points, and are lighter than cadmium and lead respectively, so that the drosses rise to the surface of the liquid baths. In both cases the molten metal is insoluble in the compound, so that its formation on the surface of the steel being dipped effectively shields it from further attack.

The action of molten tin on an 8 per cent. "aluminium-bronze" has been shown to result in the formation, on the bronze surface, of a solid solution of tin and aluminium in Cu_3Sn, which is only partially wetted by molten tin, making it impossible to solder the "bronze" successfully.

ACKNOWLEDGMENTS.

The work described in the present paper has arisen out of the galvanizing research of the British Non-Ferrous Metals Research Association, to the Council of which the author is indebted for permission to publish these results. The author's thanks are also due to Professor D. Hanson, D.Sc., of Birmingham University, in whose laboratory part of the experimental work was carried out, and to Mr. D. M. Smith, B.Sc., A.R.C.S., D.I.C., for making the spectroscopic examination of the lead and spelter used.

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DISCUSSION.

Professor R. S. Hutton,* D.Sc. (Vice-President): I feel that this is a paper which is very suitable for discussion at a joint session of the two Institutes, because if ever there was a field on which the ferrous and non-ferrous metals are brought intimately in contact it is surely in the case of coated metals such as galvanized steel and tinplate. In this case the non-ferrous partner is the "top dog," and it is really on that account that the British Non-Ferrous Metals Research Association ventured to initiate some researches in this field of galvanized products.

I think that the general impression is that the production of galvanized products is essentially a ferrous industry, but whilst admitting that some of the most important metallurgical considerations are concerned with the base metal, we feel there is ample scope for further study with regard to the coating itself. Consequently the Research Association has started a number of investigations, the report which the author has given being one of several. Other work has been concerned not only with the process of galvanizing but, more recently, with the products of galvanizing, and work is in progress at Cambridge on the testing of galvanized coatings and on the behaviour of tanks, tubes, and other products in connection with hot-water corrosion—work of very great practical importance.

I hope that the present paper will attract attention, so that we may have some constructive criticism, because the thesis which the author presents really goes a very great deal further than may at first sight seem to be the case, and a whole field of interest in regard to the soldering and jointing of metals is more or less directly affected by his conclusions. Any new knowledge we can gain with regard to the mechanism of fluxing in hot-dipping, soldering, or brazing is likely to be extremely important both to the scientific metallurgist and in particular to the practical craftsman in the application of these methods. I think that the paper deserves very serious study from that point of view, and I hope that some of the bold statements which the author has made and the conclusions that he has reached will be subjected to constructive criticism by the members of both the Iron and Steel Institute and the Institute of Metals.

Lieut.-Commander G. K. Rylands,† R.N. (ret.) (Member): I can only discuss this paper from the severely practical point of view. It must be of very great assistance to industry when an association like the British Non-Ferrous Metals Research Association and a very able investigator like the author give us this help and this lead on various galvanizing problems, but I think that the author takes rather a pessimistic view regarding the coating of metals; he more or less informs us that the production of dross is inevitable.

I am inclined to question that view. I believe that if suitable precautions are taken, and the process is kept under proper control, the amount of dross produced in wire galvanizing—of which alone I speak—should be practically negligible over many months of working. It seems that in some of these tables the author has rather overlooked the practical aspect. For instance, in Tables III and IV he refers to heating times and temperatures which are altogether outside any practical experience. He refers, for instance, to a temperature of drying of from 150° C. So far as wire galvanizing is concerned, the temperature of drying would never exceed the boiling point of the flux, and the time of drying will never be in excess of a few seconds; I cannot say offhand how many seconds, but I think that 5 seconds would be a very liberal estimate. I do not see what is the implication of this "maximum temperature

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at which any given flux can be 'dried-off' consistent with a perfect coating." I do not see the object of finding it. In our experience the minimum temperature that can be worked with, consistent with proper drying and proper cleanliness of surface, is always the one required.

I fail to understand what is meant by "a concentrated zinc chloride solution." That sounds vague; it sounds as if it were a very strong solution, and I personally should hesitate myself, in ordinary wire galvanizing, to work with anything greater than a 5 per cent. zinc chloride solution.

In Table V reference is made to a "saturated zinc chloride solution." That suggests to me, as a purely practical man, without extensive scientific training, a sort of nasty, treacly mass which it would be quite impossible to use for any reasonable form of galvanizing.

Coming to the theory and mechanism of fluxing and galvanizing, the author makes the general statement that "If a strip of mild steel is cleaned with emery paper and dipped into molten zinc, no coating will be obtained." He makes that statement generally and without qualification, but I suggest that it is purely a matter of time. If a strip of mild steel cleaned with emery paper be dipped into zinc and left long enough, a definite coating will be obtained, and if it is left still longer the steel will depart altogether! If the author's general statement were true, it would be very useful for the industry, because we should be able to clean the inside of our galvanizing baths with emery paper and then presumably they would last for ever! I only wish that that were the case.

That brings us to the whole crux of this matter. Our experience does seem to indicate that the principal source of the formation of dross in galvanizing is not the wire itself or the flux or anything else on the wire, but the mass of iron of which the bath is constructed, and the rollers, &c. which are immersed in the zinc, many of which are revolving and causing a certain turbulence, which undoubtedly increases the rate of solution. That is the real source of the largest volume of dross which is formed in a well-controlled galvanizing process.

Mr. W. R. Lysaght,* C.B.E., J.P.: Professor Hutton said that we may regard galvanized iron as partly ferrous and partly non-ferrous. In my young days the ferrous represented 85 per cent. and the non-ferrous 15 per cent., but to-day owing to competition and so on, in some cases the ferrous is 95 per cent. and the non-ferrous 5 per cent. They have got to that now, I believe, in Japan!

Mr. Daniels (*in reply*): I am glad that one speaker has taken to heart Dr. Hutton's desire for criticism. Mr. Rylands seems to consider that dross in a well-conducted galvanizing operation should be negligible, or practically negligible. I have tried to show, by studying very carefully the various factors entering into the galvanizing operation, that dross can be reduced very considerably. I have illustrated the various sources of dross and shown how they can be controlled, and that each time one of these sources is cut out the total amount of dross can be reduced. I feel, however, that the evidence shows that the flux itself is a source of dross which cannot be entirely eliminated. During the last few days I have carried out some experiments, using a flux which has practically no action on steel but which does act quite definitely as a flux; it will clean the material and enable it to be galvanized with a perfectly continuous coating. The dross in that case was cut down to about 0·04 grm. per m.^{2} of sheet surface, whilst the lowest amount of dross quoted in Table V is 0·36 per m.^{2} of sheet surface. It has therefore been cut down very

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considerably compared with the zinc chloride solution, but it has still not disappeared completely.

Mr. Lysaght: How many pounds to the ton is that?

Mr. Daniels: I cannot say offhand.

Mr. Lysaght: That is the only thing most galvanizers are interested in.

Mr. Daniels: The question of heating times and temperatures was investigated because I have seen articles in galvanizing works left open over a coke fire for 20 minutes while the galvanizer was doing something to his bath. In wire galvanizing, where things are carried out much more efficiently, the flux may be dried off at 110° C. and only for a few seconds, but there are cases where the time has been very much longer than that, and I was convinced that time and temperature would have a very bad effect on the flux. The point was therefore investigated to show exactly what the conditions were.

The maximum temperature of preheating of 100° C. seems to be unnecessarily low. If the flux can stand further heating, and the article be heated further after dipping in the flux solution, there is the advantage of putting the articles into the zinc bath at a temperature nearer that of the zinc, and cutting down the heat input into the zinc bath which would be necessary if the articles were cold.

The zinc chloride solution called " concentrated " was saturated at room temperature.

Mr. Rylands' method of galvanizing without a flux, merely by rubbing with emery paper, does not seem to be a very practical proposition.

With regard to the pot itself forming dross, it has been shown * that if the temperature of the zinc in contact with the steel surface never rises above 480° C., the dross compound $FeZn_7$ which is formed as a result of the reaction between the steel and the zinc never leaves the zinc surface and cannot form dross at the bottom of the galvanizing kettle. I have stated in this paper that under normal conditions the reaction between zinc and steel cannot form dross. I maintain that that is quite true, and the abnormal conditions are such as are very rarely met with in galvanizing practice. One is the addition of 1 per cent. of cadmium to the zinc bath, and no practical galvanizer would think of doing that; another is the use of steel containing various alloy elements—for instance, nickel–chromium steel gives a considerable amount of dross when acted on by molten zinc, and I know of a case where a lot of dross was formed from the steel surface by the action of zinc on a steel which was full of slag and rich in phosphorus and sulphur.

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* E. J. Daniels, *J. Inst. Metals*, 1931, **46**, 81–96.

THE DISTORTION OF WIRES ON PASSING THROUGH A DRAW PLATE.*

By PROFESSOR G. I. TAYLOR, F.R.S.,† and H. QUINNEY,‡ M.A., MEMBER.

SYNOPSIS.

Composite copper wires ⅛th in. in diameter, each consisting of two wires of semi-circular section, were pulled through various draw-plates. Photographs are reproduced showing the distortion of the cross-sections. These are treated in a quantitative manner, measurements of the ratio of distortion to increase in length being found for various reductions in area and angle of taper. The principal results are: (1) When an annealed wire is drawn through successive holes in a draw-plate, each of 3° taper, so that it suffers equal proportional reductions in area at each draught, the distortion of the cross-section rapidly diminishes until (in the example of Figs. 1–6) it has ceased to be measurable after four draughts. (2) For any given reduction in area the distortion increases as the angle of taper increases. (3) When the reduction in area is small and the angle of taper large so that the length of wire in contact with the drawhole is small compared with its diameter, the distortion of the central part is independent of the angle of taper, but the distortion in the outer part increases as the angle of taper increases. (4) For a given reduction in area and angle of taper the distortion in the outer part of the wire is greater when the drawing is done in two stages than when the whole operation is done in one draught. The distortion in the central portion is the same in the two cases. (5) The fact that the distortion of the outer part of the wire varies so much with the angle of taper of the draw-hole, whilst the inner part is little affected, seems to explain why different X-ray analysts obtain consistent results for the structure of the inner parts of drawn wire, but widely divergent results for the outer layers.

IN some recent papers § and discussions on the mechanics of wire-drawing, attention was directed to the distortion suffered by planes of particles initially at right angles to the axis of a wire as they pass through the die. It has been suggested to the authors by Mr. W. E. Alkins that members of the Institute of Metals might be interested in some photographs which they took rather more than a year ago and which illustrate this distortion. The authors' experiments were made with annealed copper wire of semi-circular cross-section and ⅛ in. in diameter. The flat face was polished and engraved with fine scratches running

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† Yarrow Research Professor of the Royal Society.

‡ Engineering Laboratory, Cambridge.

§ (*a*) Alkins and Cartwright, *J. Inst. Metals*, 1931, 46, 293–303. (*b* Francis and Thomson, *J. Inst. Metals*, 1931, 46, 313–337.

parallel and perpendicular to the axis of the wire over a length of some 20 or 30 diameters. The wire was then bent double in the middle so that the flat polished faces were in contact. It was then filed sufficiently conical to enable the bend to be pushed far enough through the die for a 3-jaw grip to hold it. The die was then very carefully adjusted until the axis of the conical die hole was vertical. The chuck, which was constrained to move vertically, was then moved downwards at a constant speed. These precautions in regard to centring and setting up were found to be necessary in order to ensure that the two halves pull through the die in an exactly similar manner. Small errors in setting up the die and chuck resulted in unsymmetrical distortion as revealed by the scratches or by a residual curvature of the wire after drawing.

It is evident that the division of the wire into two halves * should not affect the stresses or strains which occur during the process of wire-drawing, because, owing to symmetry, the stress exerted across any axial plane must be entirely normal to the surface, so that the stresses in a split wire should be identical with those in a solid wire. The same considerations do not, of course, apply to rods or wires built up of concentric tubes.

In the first series of experiments the wire was fixed to the slide rest of a lathe, and transverse scratches were made by means of a weighted razor blade of such a depth that they were just visible after passing through five successive draw-holes, so that the length increased 3·7 times. The diameter of the wire was initially 0·1235 in., and the diameters after passing through the five holes were 0·1140 in., 0·0978 in., 0·0842 in., 0·0720 in., and 0·0640 in. The dies used were of the type used in commerce, and were kindly presented to the authors by Mr. W. E. Alkins; their angle of taper was approximately 3° (*i.e.* the

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* This method has been used by Siebel, and it was the appearance of his paper just after the present authors had completed the work here described that made it seem unnecessary for them to publish their results. The fact, however, that their results were obtained with ⅛-in. wires drawn through ordinary die holes, whilst Siebel used large rods, and the fact that they have analyzed their photographs and given quantitative interpretations of them, have made them reconsider their original decision not to publish them. Some of the photographs are not technically so good as Siebel's. This is due chiefly to the small size of the wire as compared with Siebel's, and to the fact that the present authors' method of annealing produced grains which were too large a fraction of the diameter of the wire. E. Siebel, "Die Formänderung bei technischen Formgebungsverfahren," *Naturwiss.*, 1931, **19**, 515.

Note added May 26, 1932—The photographs referred to above are reproduced in Professor Körber's lecture to the Institute on May 11, 1932 (*J. Inst. Metals*, 1932, **48**, 317). Readers may therefore compare the two sets, and will see that there is good qualitative agreement between them. The more quantitative interpretation of the present authors' photographs which are given in the following pages may be regarded as an extension of the work described by Professor Körber.

angle between the surface of the die and the axis of symmetry), but they were not exactly conical.

The successive appearances of the scratches are shown in Figs. 1–6 (Plate XXXIII). It will be seen that they resemble parabolas. The actual forms of the transverse scratches were obtained by measurement of enlarged photographs. They are shown in Fig. 7, which contains 5 curves drawn to scale. No. 1 is the form after one draught, No. 2 after 2 draughts, etc.

The curves show that, in addition to the longitudinal extension and lateral compression, there is a shearing strain parallel to the axis which increases to a maximum value at the surface. Figs. 2–6 (Plate XXXIII) enable the amount of shearing strain to be compared with the extension at each stage. The shearing strain is the small angle through which a transverse line initially straight is bent during the passage through the die.

If x_1, x_2 . . . x_5 are the heights of the centres of the curves of Figs. 2, 3 . . . 6 above their bases, and d_0, d_1, d_2 . . . d_5 the initial diameter and the diameters of the wire after the first, second . . . fifth draughts, the measured values of x_n and d_n (*i.e.* the values of x and d after the nth draught) are given in the second and third columns of Table I. If ε_n is the ratio of the length of wire after the nth draught to its initial length, then, if there is no appreciable change in density, $\varepsilon_n = \left(\frac{0{\cdot}1235}{d_n}\right)^2$, and the values of ε_n are given in column 4.

Assuming as a rough approximation that the curves of Figs. 2–6 are parabolas, the maximum shearing strain occurs at the surface of the wire, and in the case of the first draught it is

$$ds_1 = 4x_1/d_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

To obtain ds_n, the amount of shearing strain which occurs during the nth draught, it is necessary to remember that after the first draught

TABLE I.

1.	2.	3.	4.	5.	6.	7.	8.	Draught.
n.	d_n.	x_n.	ε_n.	$\varepsilon_n/\varepsilon_{n-1}$.	$x_n - x_{n-1}\left(\frac{\varepsilon_n}{\varepsilon_{n-1}}\right)$.	ds_n.	$\frac{ds_n}{\left(\frac{\varepsilon_n}{\varepsilon_{n-1}} - 1\right)}$	
0	0·1235	0	1·00	...	...	...	...	...
1	0·1140	0·0046	1·17	1·17	0·0046	0·16	0·9	first
2	0·0978	0·0111	1·59	1·36	0·0049	0·20	0·5	second
3	0·0842	0·0174	2·15	1·35	0·0024	0·11	0·3	third
4	0·0720	0·024	2·94	1·37	0·00	0	0	fourth
5	0·0640	0·029	3·72	1·27	...	0	0	fifth

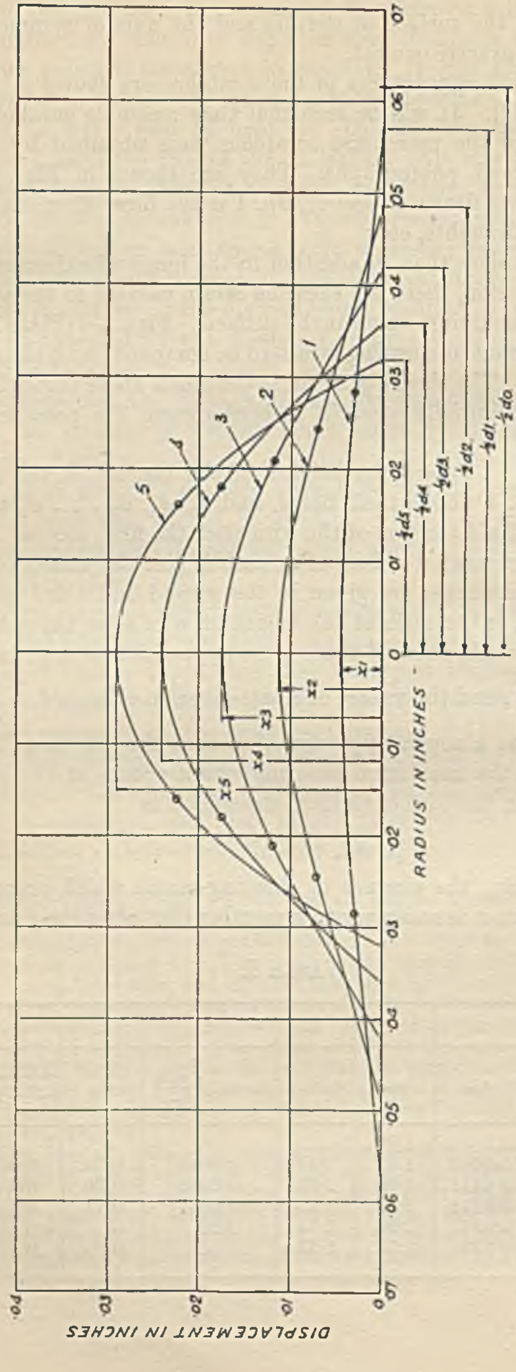
1
2
3
4
5
x1
x2
x3
x4
x5
½d5
½d4
½d3
½d2
½d1
½d0
.07
.06
.05
.04
.03
.02
.01
0
.01
.02
.03
.04
.05
.06
.07
RADIUS IN INCHES
.04
.03
.02
.01
0
DISPLACEMENT IN INCHES

Fig. 7.

the scratched transverse line is no longer straight at the beginning of the operation. Even if no further shearing strain occurred during subsequent draughts, the parabolas would become higher and narrower, owing to the lateral contractions and longitudinal extension of the wire. To allow for this effect, the geometry of the system shows that one must use the expression

$$ds_n = 4\left\{\frac{x_n - x_{n-1}(\varepsilon_n/\varepsilon_{n-1})}{d_n}\right\} \quad . \quad . \quad . \quad . \quad (2)$$

This is, of course, identical with expression (1) for the first draught, because when $n = 1$, $x_{n-1} = 0$. The values of these shearing strains ds_n have been calculated from the figures of columns 2, 3, and 4 of Table I. They are given in column 6 of the same table.

It is clear that at any given stage of the proceedings the shearing strain might be expected to increase with the amount of extension. The percentage extension during the nth draught is $100\left(\frac{\varepsilon_n}{\varepsilon_{n-1}} - 1\right)$. The quantity $\left(\frac{\varepsilon_n}{\varepsilon_{n-1}} - 1\right)$, which is the ratio of the extension of the wire during the nth draught to the length of the wire before the nth draught, may be called the proportional extension, occurring during the nth draught.

The quantity which expresses the ratio of the maximum shearing strain to this extension is evidently $\frac{ds_n}{\left(\frac{\varepsilon_n}{\varepsilon_{n-1}} - 1\right)}$. The values of this have been calculated, and they are given in column 8, Table I.

It will be seen that in the first draught $\frac{ds_n}{\frac{\varepsilon_n}{\varepsilon_{n-1}} - 1} = 0{\cdot}9$, in the second draught it is 0·5, in the third it is 0·3; in the fourth and fifth it is too small to be measurable. These experiments show, therefore, that in drawing copper wire through these dies it was only in the first three draughts, whilst the metal was rapidly hardening, that the distortion was appreciable. During the fourth and fifth draughts no further measurable * distortion occurred, the longitudinal extension and lateral contraction being uniform across the section.

A first glance at Figs. 5 and 6 (Plate XXXIII) would suggest that the distortion is increasing, because the fourth parabola is higher and narrower than the third, and the fifth is higher and narrower than the fourth; but the figures in columns 2 and 3 of Table I show that these

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* *i.e.* measurable by the somewhat insensitive methods here described.

changes in shape are merely due to the lateral contraction and longitudinal extension, for in the absence of shearing strain the height of a parabola would increase in the ratio $\frac{\varepsilon_n}{\varepsilon_{n-1}}$. It will be seen from column 3 that $\frac{x_4}{x_3} = \frac{0{\cdot}024}{0{\cdot}0174} = 1{\cdot}38$, whilst from column 5 $\frac{\varepsilon_4}{\varepsilon_3} = 1{\cdot}35$. For the fifth draught $\frac{x_5}{x_4} = \frac{0{\cdot}29}{0{\cdot}24} = 1{\cdot}21$, whilst $\frac{\varepsilon_5}{\varepsilon_4} = 1{\cdot}27$. Thus in these two draughts $\frac{x_n}{x_{n-1}} = \frac{\varepsilon_n}{\varepsilon_{n-1}}$, so that the whole measurable distortion was an extension without additional shear.

Observations with More Rapidly Tapering Die Holes.

The dies with which the series of observations already described were made had only a small taper of about 3°. With a view to finding out whether a more rapid contraction of the die hole would increase the distortion of cross-sections, three dies were prepared, all designed to draw down from 0·127 in. to 0·1075 in. The first was one of Mr. Alkins' dies with taper 3°, the second had a taper of 15°, and the third had a taper of 30°, and in order to observe the actual distortions occurring everywhere during the process of drawing, the specimens were ruled with four longitudinal and a large number of transverse scratches. The split wire was then drawn through the plate until the middle of the draw plate was approximately in the middle of the engraved area. The draught was then stopped and the specimen was drawn out backwards, special precautions again being taken to ensure that this operation was carried out symmetrically.

With this technique the distortions occurring within the draw plate could be observed, but before any reliable results could be obtained it was necessary to improve on the methods of engraving used in the first series of experiments. To this end an engraving machine was made with an accurate feed screw of 0·5 mm. pitch, and of the quality used in first-class optical instruments. The engraving tool was a safety-razor blade which had been broken across the middle. It was mounted on a pivoted holder so that its cutting edge was at 45° to the horizontal plane of the polished surface of the specimen. The weight of the holder was held by a long and weak spiral spring, and the depth of the cut was controlled by weighting this holder until the knife pressed with a known force on the specimen. The pressure used on the blade varied from 5 to 50 grm., and the scratch made was invisible to the naked eye.

The engraving machine which held the specimen had two perpen-

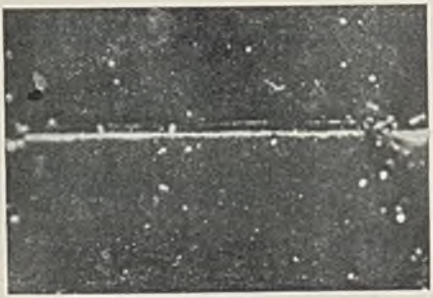

FIG. 1.—Original wire as marked.
Diameter 0·1235 inch.
Magnification 17·7 diameters.

FIG. 2.—First draught: load required to draw through die 115 pounds.
Diameter after drawing 0·114 inch.
Magnification 17·7 diameters.

FIG. 3.—Second draught: load required to draw through die 230 pounds.
Diameter after drawing 0·0978 inch.
Magnification 17·7 diameters.

FIG. 4.—Third draught: load required to draw through die 180 pounds.
Diameter after drawing 0·0842 inch.
Magnification 17·7 diameters.

FIG. 5.—Fourth draught: load required to draw through die 110 pounds.
Diameter after drawing 0·0720 inch.
Magnification 17·7 diameters.

FIG. 6.—Fifth draught: load required to draw through die 58 pounds.
Diameter after drawing 0·0640 inch.
Magnification 17·7 diameters.

[*To face p.* 192.

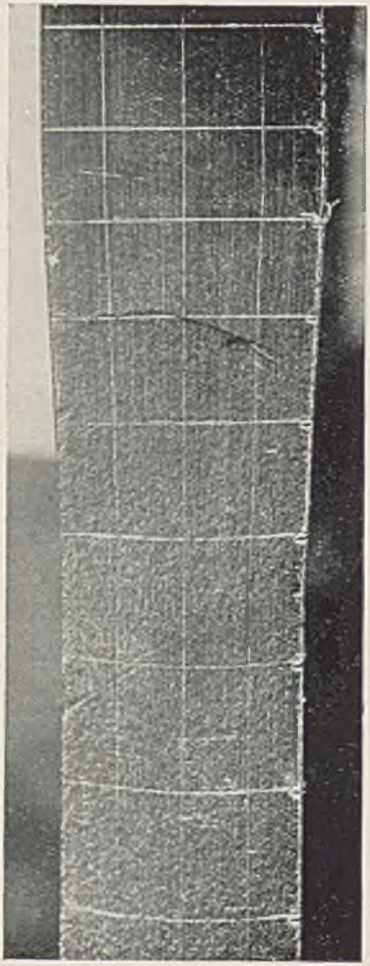

FIG. 8.—3° taper. × 12·1.

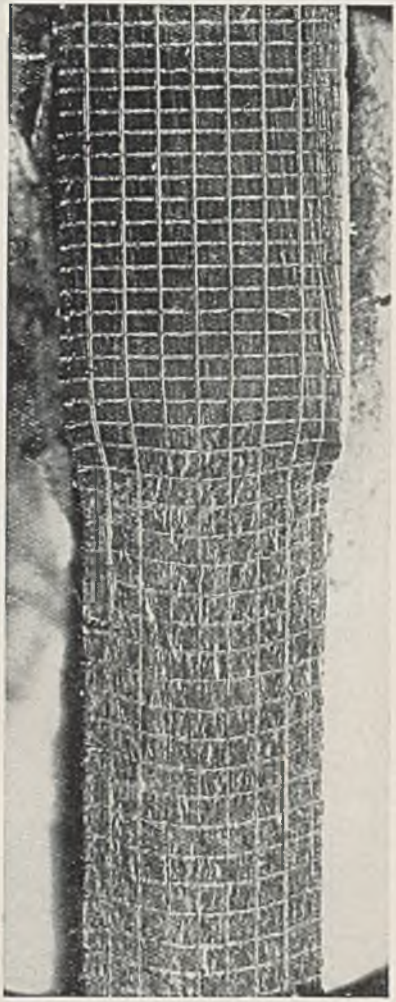

FIG. 9.—15° taper. × 12·1.

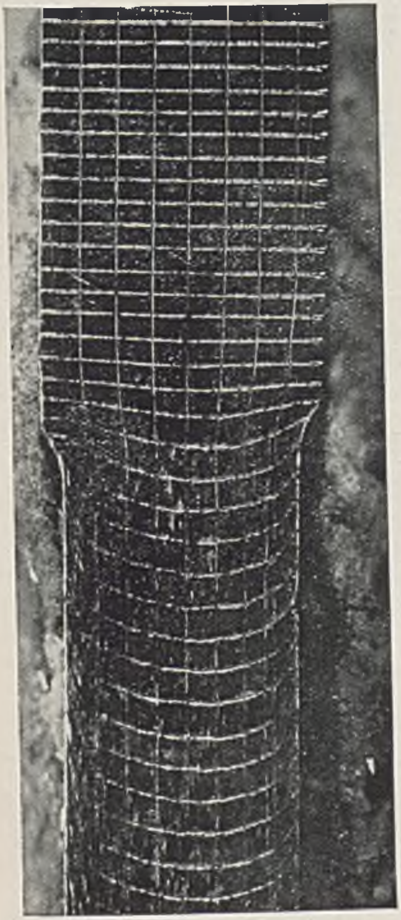

FIG. 10.—30° taper. × 12·1.

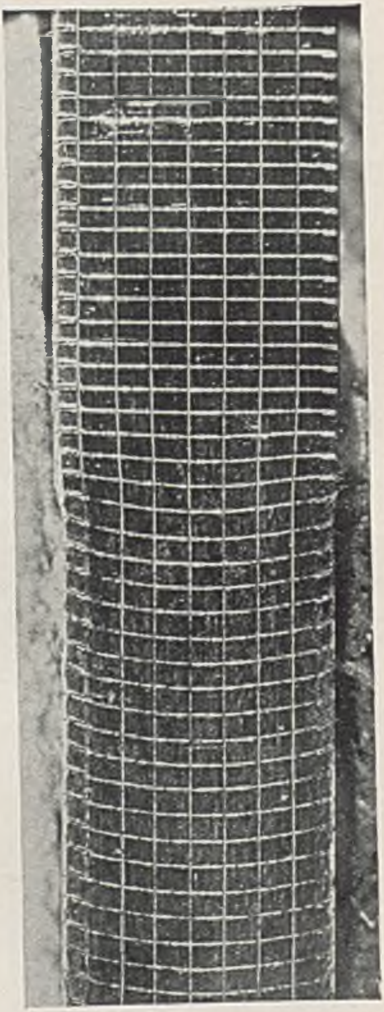

FIG. 11.—15° taper. × 12·1.
2-Stage draught at the first stage.

Plate XXXVI.

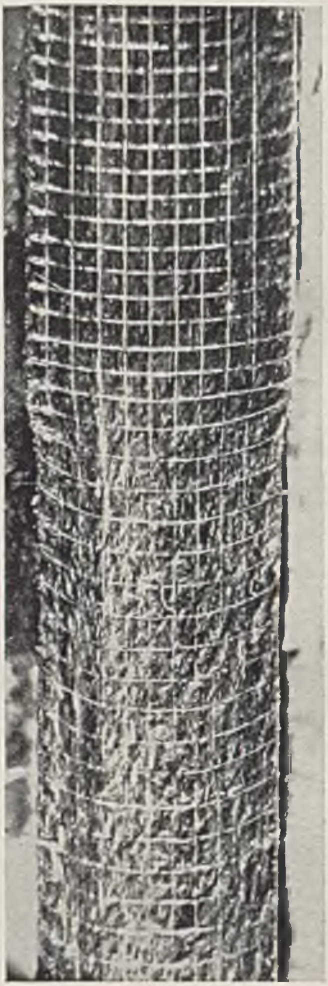

FIG. 12.—15° taper. × 12·1.
2-Stage draught, after second stage.

dicular movements like a slide rest. The transverse marks were made by sliding the specimen by hand under the tool, and, after engraving each line, the feed screw was turned through a given angle so that the lines were equidistant. Although the marks could not be seen by the naked eye in ordinary lights, they could be illuminated by special types of lighting, and enlarged photographs could be taken. Some of these are shown in Figs. 8–12 (Plates XXXIV–XXXVI).

Fig. 8 shows the effect of drawing through a die hole with 3° taper from 0·127 in. to 0·107 in., the reduction area being therefore 29 per cent. The length of wire on contact with the draw plate was $L = \frac{1}{2}\left(\frac{0{\cdot}127 - 0{\cdot}107}{0{\cdot}127}\right)\frac{d_0}{\tan 3^\circ} = 1{\cdot}5d_0$, where d_0 is the diameter of the wire before drawing.

Fig. 9 shows the distortion when the angle of taper is 15°, the reduction in area being the same as before—namely, 29 per cent. The length of wire in contact with the plate was $0{\cdot}29d_0$.

Fig. 10 shows the distortion when the angle of taper is 30°, the reduction in area being 33 per cent. In this case the length of wire in contact with the plate was $L = 0{\cdot}14d$.

Since the reduction in area is nearly the same in all cases, Figs. 8–10 are comparable.

It will be seen that the distortion of the cross-section increases rapidly as the taper increases, and the length of contact consequently decreases. In the case of the 30° taper the precautions taken to ensure symmetry do not seem to have been very successful, the chord joining the ends of the curved transverse line is not perpendicular to the axis. In order to compare the distortion of plane sections for various angles of taper, the transverse lines in each photograph were measured by means of a reading microscope fitted with a stage and measuring screw for moving the photograph under the microscope in a direction at right angles to that of the motion of the microscope. The co-ordinates thus measured of points on any transverse scratch were then set out on a diagram as shown in curve I, Fig. 13. In this diagram the ordinates represent the displacement of the transverse lines parallel to the axis of the wire, whilst the abscissæ represent distances from the central axis of the wire. The scale of the ordinates is increased in the ratio 3 : 1, in order to show up more clearly the principal characteristics of the distortion.

It will be seen that curve I, which represents the distortion of the cross-section after drawing through the die with 30° taper, is noticeably unsymmetrical. In the other cases the asymmetry was scarcely appreciable, but in this case there must have been some accidental want of symmetry in the drawing of the wire. In order to eliminate as far as possible errors due to this cause, and thus make it possible to compare the distortions produced by various draw holes, the curves were shifted in the manner represented in Fig. 13, so that they represent, as in curve II, the displacement of the transverse section relative to the plane through its outer edge.

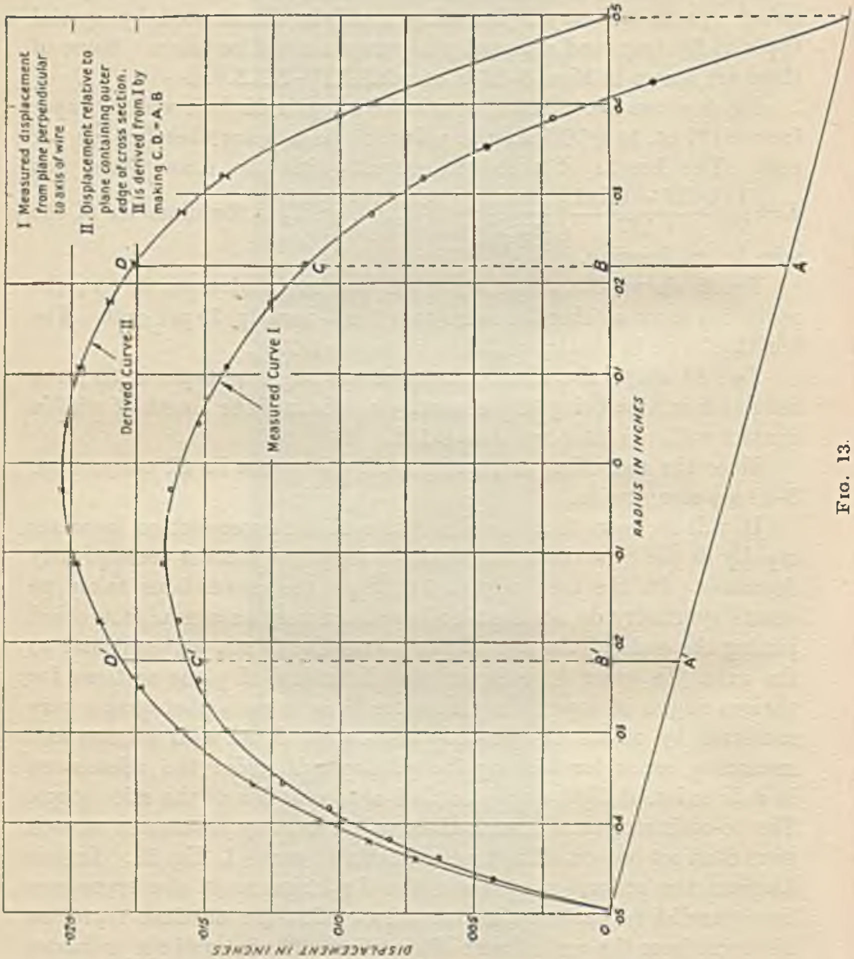

FIG. 13.

The curves derived in this way from Figs. 8, 9, and 10 are shown as *A*, *B*, and *C* in Fig. 14. It will be seen that with the 3° taper

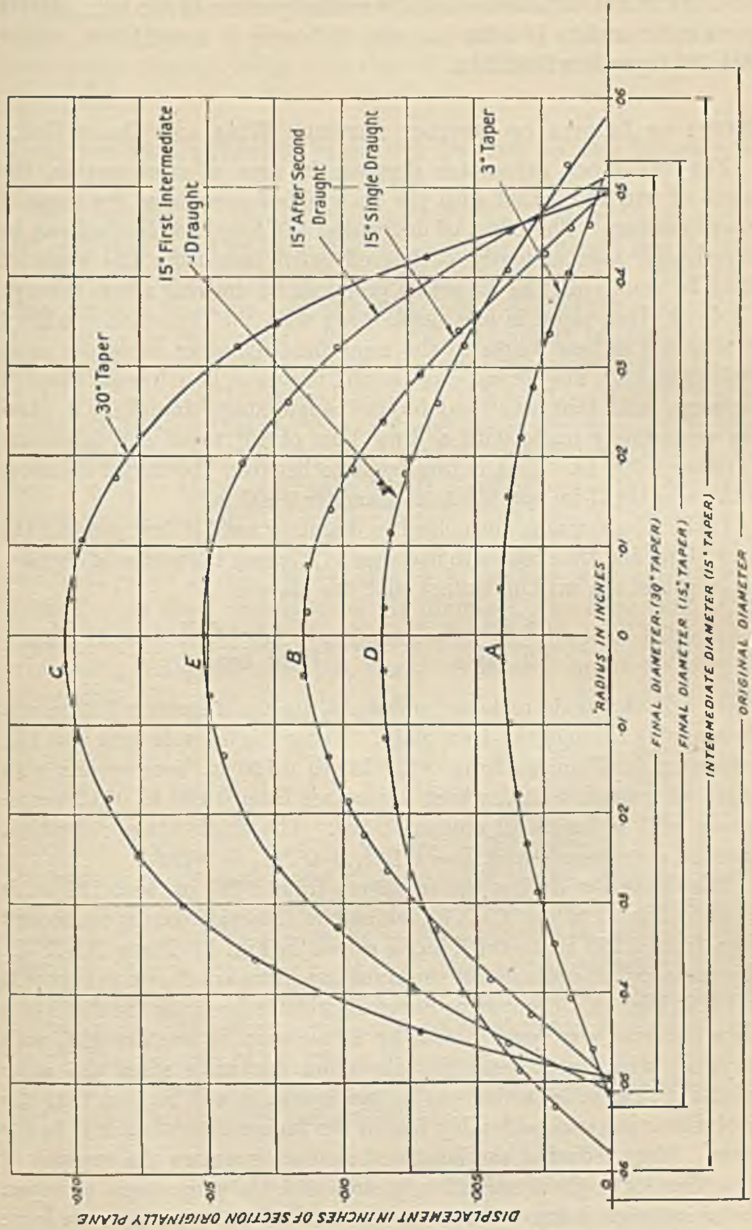
30° Taper
15° First Intermediate Draught
15° After Second Draught
15° Single Draught
3° Taper
C
E
B
D
A
RADIUS IN INCHES
·06
·05
·04
·03
·02
·01
0
·01
·02
·03
·04
·05
·06
FINAL DIAMETER (30° TAPER)
FINAL DIAMETER (15° TAPER)
INTERMEDIATE DIAMETER (15° TAPER)
ORIGINAL DIAMETER
DISPLACEMENT IN INCHES OF SECTION ORIGINALLY PLANE
·020
·015
·010
·005
0

Fig. 14.

the longitudinal displacement of the central portion of the wire relative to its outer surface is 0·004 in., with 15° taper it is 0·0115 in., whilst with 30° taper it is 0·0205 in.

Effect of Length of Contact between Wire and Draw Hole.

For any given percentage decrease in area of cross-section, the length of wire in contact with the draw hole decreases as the angle of taper increases. The effect of decreasing the length of contact can be investigated independently of the effect of increasing the angle of taper, by comparing the distortion produced by drawing a wire through a hole of given taper in one single stage with the distortion produced by drawing in two stages to the same final diameter using the same angle of taper. The second stage would, of course, be a draught through the same hole that was used for the single stage draught. A plate was accordingly made with a draw hole of 15° taper and minimum diameter 0·120 in. This is intermediate between the initial diameter of the wire 0·127 in. and the final diameter 0·107 in.

If the wire remains unchanged in diameter until it first touches the draw plate, and then ceases to decrease as it leaves the region of contact, the length of the wire in contact with the plate is

$$L = \frac{1}{2}\frac{d_1 - d_2}{\tan\alpha} \quad \text{or} \quad L = d_1\left[\frac{d_1 - d_2}{2d_1 \tan\alpha}\right] \quad . \quad . \quad . \quad (3)$$

where α is the angle of taper and d_1, d_2 are the diameters before and after passing through the draw plate. Using this formula with $\alpha = 15°$, a decrease in diameter from 0·127 in. to 0·120 in. corresponds with length of contact $0{\cdot}10d_1$, whilst a decrease from 0·120 to 0·107 corresponds with a length of contact $0{\cdot}19d$. The single stage reduction, however, corresponds with $L = 0{\cdot}10d_1 + 0{\cdot}19d_1 = 0{\cdot}29d_1$.

The distortion during the reduction from 0·127 in. to 0·120 in. is shown in Fig. 11 (Plate XXXV), whilst the distortion during the second stage from 0·120 in. to 0·107 in. is shown in Fig. 12 (Plate XXXVI). The measured co-ordinates of the transverse lines are shown in curves *D* and *E* in Fig. 14. Comparing curve *B*, which represents the distortion when the wire is reduced in area by 29 per cent. in one draught, with curve *E*, which represents the distortion occurring when the same reduction in area is carried out in two stages, it will be seen that the total distortion is considerably less in the former case than it is in the latter. Thus reducing the length of contact increases the amount of distortion for a given reduction in area and the same angle of taper. If, for instance, a draw plate were constructed containing a very large number of holes, each of slightly less diameter than its predecessor, but all having the same angle of taper, this result would lead one to expect that the distortion of the cross-section would be greater if the wire were drawn through every hole than if it were drawn through every other hole.

VARIATION IN DISTORTION FROM THE CENTRE TO THE SURFACE OF THE WIRE.

In comparing the three curves *B*, *C*, *E*, Fig. 14, it will be seen that, although they stand up from their bases to very different heights, they are nearly parallel curves in the middle part of the wire. The differences between them are confined to the outer part of the wire. Curve *A*, however, is flatter than *B*, *C*, or *E* throughout its length. This can be seen more clearly by displacing the curves parallel to the axis of the wire until their vertices coincide. This has been done in Fig. 15, and it will be seen that the curves *B* and *E* are very nearly coincident over three-fifths of their diameter. The curve *C* is slightly steeper than *B* or *E* in the central part, but it must be remembered that the final diameter was slightly smaller in the case of the 30° taper than in the case of the 15° taper. Making due allowance for this, it will be seen that when *L*, the length of wire in contact with the die, is a fraction (less than one-third) of its diameter, the distortion of the central three-fifths of the wire depends only on the total reduction in area, being independent of the actual value of *L* or of the angle of taper of the die. On the other hand, when $L = 1{\cdot}5d_0$, as in the case of curve *A*, the distortion in the central part is considerably less than for curves *B*, *C*, and *E*, where $L = 0{\cdot}29d_0$, $0{\cdot}14d_0$, $0{\cdot}19d_0$, and $0{\cdot}10d_0$.

Comparing curves *B* and *E*, a decrease in *L* from $0{\cdot}29d_0$ for *B* to $0{\cdot}10d_0$ and $0{\cdot}19d_0$ for *E* corresponds with an increase in the amount of distortion in the outer part of the wire. This might be expected, for the regions of greatest stress must be concentrated near the part of the wire where there is contact with the die hole, so that a decrease in *L* may be expected to correspond with an increase in concentration of shearing stress in the outer parts of the wire and a consequent increase in distortion there. On the other hand, the stress distribution in the central part of the wire would scarcely be expected to depend much on the exact length of the region of contact, so that the fact that the distortion in the central part of the wire is the same in the three cases *B*, *C*, and *E* is also quite understandable.

THE STRUCTURE OF DRAWN WIRE.

The structure of drawn wire has been examined by several investigators by means of X-rays, but the results are not in good

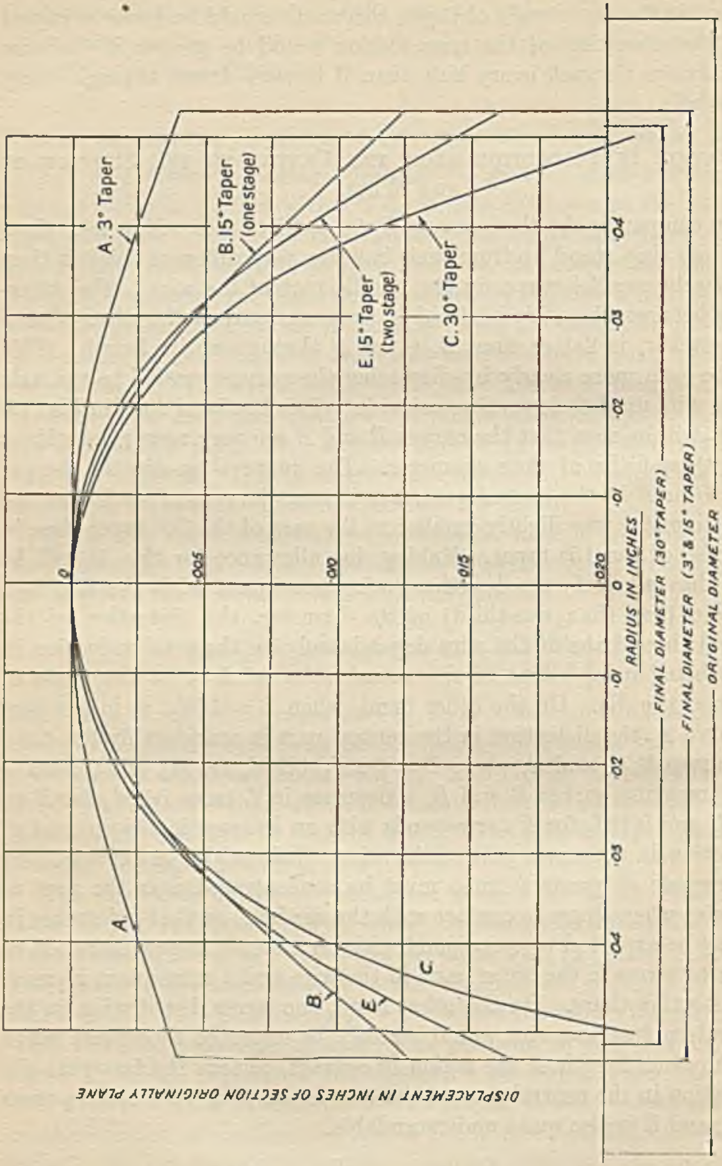

Fig. 15.

agreement. Schmid * found that there is a considerable degree of preferred orientation throughout the wire, but in the central part the orientation is more pronounced than in the outer part. W. A. Wood,†

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* *Z. Metallkunde*, 1928, **20**, 375.

† *Phil. Mag.*, 1931, [vii], **11**, 611.

on the other hand, found preferred orientation only in the central part of the wire in a region extending out to less than half the radius. In the rest of the wire, comprising four-fifths of its total area of cross-section, he found practically no preferred orientation of the crystal axes. Unfortunately, none of the workers with X-rays has given precise descriptions of the exact conditions of drawing. Comparison of the four curves of Fig. 15 which represent the distortions of plane cross-sections under varying conditions of drawing for one given reduction in area, namely 29 per cent., shows that enormous variations in the distortion of the outer layers are likely to occur as the conditions of drawing are varied. On the other hand, the distortion in the central portion of the wire, out to half its radius, is not nearly so sensitive to the conditions of drawing, and in any case the distortion there is small, so that the agreement between various X-ray workers as to the structure of the central parts of the wire and their disagreement as to the structure of the outer part may be due entirely to differences in the manner in which their wires were drawn. It is perhaps significant that the part of the wires B, C, E for which the distortion was unaffected by varying the value of L, extended from the middle to a radius of 0·03 in., *i.e.* to 0·6 of the total radius of the wire. The area over which W. A. Wood found preferred orientation stretched out from the centre to a distance of 0·4 times the radius.

In conclusion, the authors wish to express their thanks to Lord Rutherford and Professor Inglis for permission to carry out this work in their laboratories in Cambridge.

DISCUSSION.

Professor F. C. Thompson,* D.Met. (Member): The honour of initiating this discussion should have been in the hands of Mr. Alkins, for it is perfectly clear that if it had not been for the material that he supplied and for his encouragement to the authors the Institute would not have received this paper.

The authors have more or less apologized for presenting the paper, in view of the similar work brought forward by Professor Körber. I am, I think, voicing the opinion of all those interested in the production of wire or in the investigation of the wire-drawing process when I say that I see no justification for that apology.

The first of the two points which I think worthy of discussion relates to the authors' very interesting observations on the effect of drawing down the wire in two stages, as distinct from one. In the first place, they have shown that drawn down in two stages the distortion is greater than if it is done in one. That can be more or less correlated with the observation that Francis and I made recently, that the work done to effect a given amount of reduction in two stages, is greater than in one. Lubrication losses, of course, come in, but even

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* Professor of Metallurgy, The University, Manchester.

allowing for them, more work has to be done in effecting the reduction in two stages. That is in agreement with the observation the authors have made.

The wire-drawing process is, however, obviously extremely complex, and when the authors attempt an explanation merely on the lines of the length of contact between the metal and the die in each pass, I feel that there is justification for considering an alternative.

What have the authors done? In one case (Fig. A) they have taken the wire down in a single pass, and in the other divided the die and separated the two parts by a distance *L*. From their point of view, *L* has no influence. If the distance between the first and the second draw is then made infinitely small,* so far as the authors' argument goes they should still get the result they have obtained, which seems highly improbable. As a matter of fact, there is a very obvious reason why the length *L* should matter. If the material is drawn down, it is heated; it is allowed to wait, it cools down, with the result that when the second pass is taken one is not dealing with the material in a condition identical with that which left the die first. Further, it is well known that very rapid ageing changes occur, which means that again the material for the second draw is not that which originated at the first. I cannot help feeling that there is a probability that the results which the authors have obtained in contrasting the single with the double draw are to be accounted for, in a large measure at any rate, by the change of temperature and the ageing effects between the first and second pass. It would, therefore, be extremely valuable if they would give us exact details of the time that elapsed between taking the first and the second passes. Even, however, if that time was very small, the changes mentioned are likely to explain a large amount of the difference that the authors have observed.

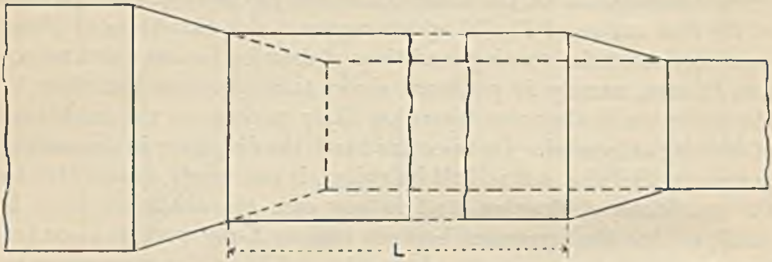

Fig. A.

The other point is this: the authors believe that the "wave front" after drawing becomes at any rate roughly parabolic. With regard to the centre I am in agreement, but I believe that near the surface the curve is something like that shown in Fig. B. For this there is evidence from several directions. That is important, not only theoretically, but also in connection with the troubles which occur in the difficult "casting" problems when the coil ties itself in knots.

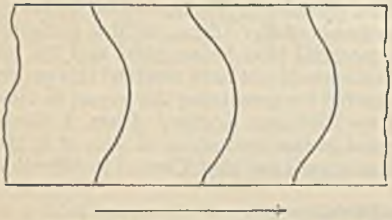

Fig. B.

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* *I.e.* to all intents and purposes a single die is used.

Mr. W. E. Alkins,* M.Sc. (Member): I am pleased to have been instrumental, in a very minor degree, in securing the presentation of this interesting paper to the Institute. The work described differs, in my opinion, quite sufficiently from that of Siebel, brought before the Institute this year by Professor Körber in his admirable May Lecture, fully to justify the authors and the Institute of Metals in publishing it. I feel that we owe a debt of gratitude both to Professor Taylor and Mr. Quinney and to the Institute.

I cannot usefully say much on the paper. I may refer to one small matter, not by way of criticism, but as a warning. On p. 192 the authors describe the drawing of the wire in various dies, and then the drawing of the specimen out backwards. I have never found it possible to draw a wire out backwards without affecting the drawn part to some degree. I think that the ends of the transverse scratches in Figs. 8 and 9 (Plate XXXIV) may show the effect of the withdrawing of the wire. The fact that these wires were so drawn back should be borne in mind in studying the photographs.

The difficulty of drawing back any wire is presumably due to the fact that during drawing the portion just drawn undergoes elastic stretching under the drawing stress, contracting slightly in length when the latter is removed, and at the same time increasing in diameter until it is just too big to pass back through the die.

The conclusion on pp. 191 and 192 of the paper that the whole measurable distortion of transverse planes takes place during the early draughts, while the metal is rapidly hardening, and that afterwards the changes in shape are due merely to lateral contraction and longitudinal extension, so that the later apparent distortion is an extension without additional shear, is clearly important when it is remembered that enormous quantities of wire are drawn on continuous machines, undergoing many successive draughts, all of which are in the same direction.

This brings me to what must be my final point—the usual request for more: it is very distressing to hear that the apparatus has been dismantled. I should like the authors to examine the effect of reversing the direction of drawing after each draught, because methods of drawing which involve such reversal of direction are also of great practical importance.

Dr. H. O'Neill,† M.Met. (Member): I had not intended to discuss the paper, but there are two points which come to mind and seem to confirm parts of the authors' work. The first is that if one takes hardness tests ‡ along the cross-section of increasingly drawn wires, the curve of hardness against diametrical position follows very closely, I think, the curves of displacement which the authors have given in Fig. 7. Secondly, if one measures the rate of hardening or the rate of cold-working by some such thing as the Meyer n-index, one finds during progressive working that the n-index decreases rapidly up to about 20 or 30 per cent. reduction of area, but after that it seems to reach its limiting value of 2·0 and falls no further.§ That appears to bear out the findings of the authors as regards a limiting condition of distortion during drawing.

Lieut.-Commander G. K. Rylands,‖ R.N. (ret.) (Member): There is just one point in connection with parabolic curvature to which Professor Thompson referred. I notice that the authors do state that the die, although approximately conical, was not absolutely conical, but slightly curved. If there were

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† Senior Lecturer, Department of Metallurgy, The University, Manchester.

‡ *Proc. Inst. Mech. Eng.*, **1928**, II, 865.

§ *J. Inst. Metals*, 1926, **35**, 231; 1931, **46**, 273.

‖ General Works Manager, Rylands Brothers, Ltd., Warrington.

a curve near the entrance it is quite conceivable that an effect might be produced like the one to which Professor Thompson has directed attention. Irrespective of other factors, the curved die would give that kind of shape to the transverse scratches described across the section of the wire.

Is it quite right to use the same angle of taper for each draft? Ought it not to be varied so that the length of contact with the bearing is the same for the two successive draughts? If the angle of the die were varied between the two draughts, entirely different forms might be obtained for the successive curves.

Have the authors made any investigations as to the best taper of hole to be used? Is the best taper of hole necessarily the taper which gives the minimum drawing pull? There seems to be a certain amount of doubt about that. I have carried out experiments to get minimum pulls, and have found that low pulls can be obtained with extraordinary tapers and extraordinary shapes of hole, which do not work in practice. It is very difficult to explain. I have also found that there is a succession of minima in plotting pulls against the taper of the "hole." As the taper varies from straight to steep the drawing pull passes through a succession of minima, giving a sort of wave curve. I have found the period of the minima is usually fairly even, but I can conceive of no explanation, and certainly some of the steeper dies and straighter dies are quite impossible to use in practice.

Professor TAYLOR (*in reply*): With regard to Professor Thompson's remarks, I fear there may be a little misunderstanding. I do not think that there is any reason to suppose that if a single die were taken and separated into two parts, the wire being reduced in one operation by pulling through both dies, one would get the same result as by drawing in two operations through each die separately. The stresses would be quite different in the two cases.

I cannot speak as to the actual reason for the differences between the effects of different angles of taper. Professor Thompson may be perfectly right when he says that it may be due to temperature. On the other hand the rise of temperature in these wire drawings is never very great. One knows that it cannot be greater than a few degrees.

As for Professor Thompson's second point, in which he said that we described the transverse marks as parabolas, we only mention parabolas in connection with our first set of wire drawings—that is to say those with very small tapers. In this case the curves were very approximately parabolas.

The distorted transverse lines in our second set of measurements which were made with larger tapers were not parabolas. If reference is made to the curves shown in Fig. 15, it will be seen that those for different tapers nearly coincide in the middle, but differ at the extremities. If they were parabolas and coincided in the middle they would coincide all the way across the sections.

With regard to the question of the little bend back in the parabola form—referred to by Mr. Alkins as well as by Professor Thompson—if the illustrations in the paper are examined, this will be seen most clearly in Fig. 9 (Plate XXXIV). It occurs at the point where the wire is actually passing through the die. It does not seem to extend into the part where the wire has left the die, although if it does Mr. Alkins's explanation may account for it.

I have only to say that I have noted Mr. Alkins's suggestion that it would be interesting to carry out the reversal of wire-drawing for the second draught, and that if we have time I hope that we shall carry it out. We will also bear in mind the suggestions of the other speakers, but I am not really in a position to reply to them, because my knowledge of the technical side of wire-drawing is not extensive.

MOULD MATERIALS FOR NON-FERROUS STRIP INGOT CASTING.*

By G. L. BAILEY,† M.Sc., Member.

(Communication from the Research Department, Woolwich.)

Synopsis.

Grey cast-iron is the material most generally used for moulds for the casting of non-ferrous strip ingots. Cast-iron moulds are subject to two particular defects: (*a*) gas evolution from the face of the mould when this is overheated during pouring ("blowing"); and (*b*) transverse cracking of the working faces. The conditions producing "blowing" have been studied and the gas has been found to originate in a reaction between the carbon of the iron and a superficial oxide film.

Transverse cracking of the cast-iron mould surface is due to stresses resulting from a high-temperature gradient in the mould wall immediately after casting. Mild steel moulds, which are free from "blowing" and cracking, are liable to serious distortion resulting from such stresses.

Copper is considered the most satisfactory material for strip ingot moulds. Its high thermal conductivity prevents serious temperature gradients and consequent distortion. For high melting-point materials copper moulds are water-cooled with advantage, but for alloys such as brass they can be used under certain conditions without any special cooling.

Introduction.

The work to be described in this paper formed a portion of a comprehensive research on the casting of 70 : 30 brass strip ingots which has been in progress for some years in the Research Department, Woolwich, for the British Non-Ferrous Metals Research Association.

The experimental work in this section of the research was carried out almost entirely in the years 1927 and 1928, and enabled certain general conclusions to be drawn as to the characteristics desirable in a mould material for this type of work. More fundamental work on the heat transfer across the metal-mould interface was planned but has not yet been carried out.

Previous Work.

Early records of the casting of brass strip ingots indicate that the moulds originally used were of stone. The weakness of this material

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† Development Officer, British Non-Ferrous Metals Research Association; formerly of the Research Department, Woolwich.

led to its replacement by grey cast-iron, which has been in almost universal use for many years. Cast-iron offers the great advantages of durability, cheapness, and ease of casting to shape with a smooth surface; the average life of good quality moulds is stated to be 2000 to 2500 heats. The readiness with which cracks are formed on the inner working faces of the mould, frequently at an early stage of its life, and certain other properties indicate that cast-iron is not an ideal mould material.

Little scientific work has been carried out on ingot moulds and the most suitable materials for their construction. Some attention has, however, been paid in recent years to the use, particularly for brass, of water-cooled copper-faced moulds, and to the behaviour of cast-iron moulds for steel casting.

Matuschka * has studied the thermal changes during the cooling of a steel ingot in the mould and has determined the temperature at different positions in the wall of a mould of commercial size. The fourth report of the Heterogeneity Committee of the Iron and Steel Institute, published in 1932, includes work on the thermal properties of ingot mould irons by Pearce and Morgan and by Donaldson.

In recent years a copper-faced water-cooled mould has been introduced and widely adopted for brass ingot casting.† In this mould a copper plate about 0·75 in. in thickness is provided with a jacket through which a continuous supply of water is run. It is claimed that such moulds have a long life, and facilitate production, since they can be rapidly filled and evacuated.

Rohn ‡ has also used, with considerable success, copper-faced water-cooled moulds of special design, for the casting of nickel alloys of high melting point, and claims a long life for these moulds even when surface dressings are entirely dispensed with.

Roth § has discussed in general terms the application of water-cooled moulds to brass casting. He made some measurements of the temperature gradient within the ingot using a water-cooled billet mould, and within the ingot and mould wall with cast-iron moulds.

Erichsen ‖ has more recently developed water-cooled moulds with Invar plates, which have been successfully used for brass casting.¶

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* Matuschka, *Arch. Eisenhüttenwesen*, 1929, **7**, 405; and *J. Iron Steel Inst.*, 1931, **124**, 361.

† Junker, *Z. Metallkunde*, 1926, **18**, 312; *Metallwirtschaft*, 1930, **9**, 406.

‡ Rohn, *Z. Metallkunde*, 1927, **19**, 473–478.

§ Dr.-Ing. Dissertation, Aachen, 1929.

‖ British Patents Nos. 358,697, October 1931; and 299,850, May 1929.

¶ The British Non-Ferrous Metals Research Association has made a special study of these developments, and has prepared translations and reports thereon for its members.

SCOPE OF PRESENT WORK.

The present work comprises a detailed study of the cause and avoidance of certain types of defect which are encountered in brass strip ingots when cast-iron moulds are used, and an examination of the properties of a variety of alternative mould materials.

At the outset information was sought as to the moulds used and service obtained by a considerable number of manufacturers in this country. Cast-iron moulds were found to be almost universal, but in addition to their liability to cracking they are subject to another disadvantage—the evolution of gas from the mould face where the dressing is too thin or on account of local overheating, and the consequent formation of an ingot surface defect commonly termed "blowing." An example of this defect in an ingot of 70 : 30 brass is illustrated in Fig. 1 (Plate XXXVII). This gas evolution occurs in particular at the point of impingement of the stream on the mould face, and while not generally serious in casting brasses by the ordinary methods, it is more common with high-temperature alloys, such as nickel–brasses and cupro-nickel. The general commercial practice of dressing the mould heavily with a volatile carbonaceous dressing prevents this local overheating to a great extent, but during this research the disadvantages, from other points of view, of heavy volatile mould dressings have been demonstrated. Alternative casting methods which were developed, however, increased the severity of the conditions at the mould surface and intensified this "blowing" effect.

A careful investigation of the origin of this gas evolution from cast-iron and other mould materials was therefore undertaken. The liability of cast-iron to cracking, and of other suggested materials to distortion was also examined in detail. Finally, the influence of mould materials on the structure and soundness of the cast ingot also came under consideration. It should be emphasized that throughout this work the mould materials were examined with special reference to the casting of 1-in. thick strip ingots of 70 : 30 brass, but it is considered that many of the conclusions arrived at are directly applicable to the casting of other materials.

I.—THE OCCURRENCE AND CAUSE OF "BLOWING" OF CAST-IRON MOULDS.

In the course of earlier experimental work, the following tentative conclusions had been drawn concerning the occurrence of "blowing" :—

(1) Grey cast-iron and semi-steel are liable to evolve gases, while

dead mild steel under ordinary conditions of service does not show this property.

(2) Gas evolution occurs only where the mould surface is overheated either by impingement of the stream of metal or the use of an initially high mould temperature.

It was found that even when using thin mould coatings small ingots could be produced satisfactorily in cast-iron moulds if the stream of metal was central and the mould vertical, but where the stream was allowed to impinge on the mould face localized "blowing" usually occurred. When casting long ingots the avoidance of impact of the stream on the mould face was more difficult and in general rapid pouring with a heavier flow of metal greatly increased the extent of blowing.

Standard Small Scale Test of Mould Materials for Liability to "Blowing."

In order to obtain a rapid test of the "blowing" tendencies of mould materials the small-scale apparatus shown in Fig. 2 was devised. An electrically-heated carborundum crucible, arranged for bottom-pouring, was supported at a fixed height above a base plate which carried a slab (4 in. × 4 in. × 0·5 in.) of the mould material to be tested. A wire-wound heater recessed in the base plate, provided control of the temperature of the mould material. A machined block of 70 : 30 brass weighing 180 grm. was melted, heated to 1050° C., and poured in a smooth stream on to the plate of mould material. A disc of brass about 3 in. in diameter was obtained, the under surface of which showed characteristic "blowing" if the mould material was one liable to produce this defect (see Fig. 3, Plate XXXVIII). Measurement of the volume of the cavities in the underside of the disc by filling with wax gave a roughly quantitative comparison of the blowing tendencies of different materials.

Examination of Typical Samples of Commercial Mould Materials.

Information concerning the quality of the cast-iron normally used for commercial ingot moulds was obtained by the examination of samples of worn-out ingot moulds obtained from the works of sixteen members of the British Non-Ferrous Metals Research Association.

Table I.—*Range of Composition of Commercial Cast-Iron Ingot Moulds.*

	Per Cent.
Graphitic carbon .	2·5 to 3·1
Combined carbon .	nil to 0·8
Silicon . . .	1·5 to 4·0
Manganese . .	0·3 to 1·0
Sulphur . . .	0·04 to 0·13
Phosphorus . .	0·14 to 1·2

Analysis showed that the compositions of these specimens varied between wide limits (see Table I) while the specific gravities covered the range 6·80 to 7·15.

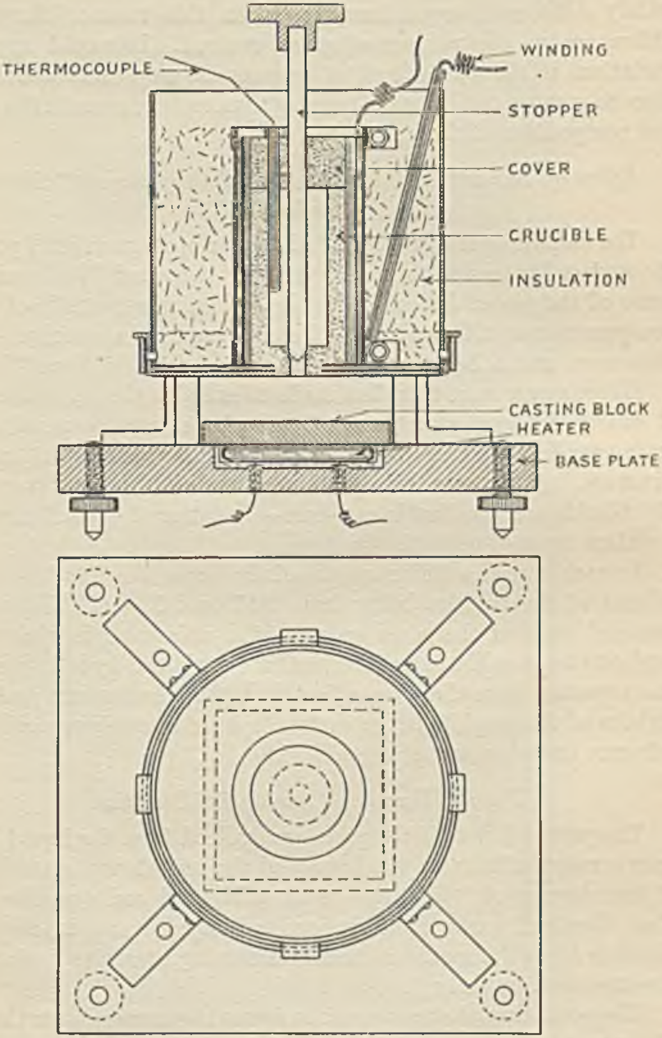

Fig. 2.

The samples supplied had been in service for periods varying from 4 months to 10 years before failure—generally by cracking—but the information given was not sufficiently detailed to permit any correlation of life with composition. Where the size of the sample permitted, plates bearing the original inner surface of the mould were tested for "blowing" in the small-scale apparatus. Seven plates, of widely differing compositions, tested in this manner showed small differences in the volume of gases evolved. It would appear that variations in the "blowing" of commercial grey iron moulds are due more to varying conditions of pouring than to differences in the structure and composition of the iron.

Effect of Amount and Distribution of Graphite on "Blowing" Tendencies.

The cast-irons tested were all of similar open grain, and porosity of the surface layers due to loss of graphite suggested itself as a possible cause of the gas evolution on heating. Preliminary trials of plates of non-porous materials such as mild steel, copper, "aluminium–bronze," Nichrome, and Acheson graphite all showed freedom from "blowing."

Experiments were therefore made to examine the behaviour of irons of widely different structures. Small plates were prepared of open-grain grey-irons, white iron, and irons of intermediate or "mottled" structure. At the same time tests were made of "perlit" iron and also of "Blackheart" malleable cast-iron—the latter after machining, giving a surface layer of pearlitic structure.

In each case the under surface of the brass disc was "blown," the volume of the cavities being from 0·15 to 0·25 c.c. The variations obtained were of the same order as the differences in the results of duplicate tests on the same slabs, and are explained by later results. It was apparent from these tests, however, that the amount and state of division of the graphite in the surface layer of a cast-iron mould did not influence its behaviour as regards "blowing."

Possible Reactions Causing Gas Evolution.

The probability that the gases are evolved from the liquid brass, or from a reaction between the brass and the mould face is small in view of the absence of "blowing" with mild steel and graphite moulds. That dissolved gases could be evolved rapidly and in considerable amounts from the mould material on heating at atmospheric pressure also appeared unlikely.

The possibility that gas could be formed by a reaction in the surface of the cast-iron, involving a superficial oxide film and the carbon of the iron, was then considered. The surface of the cast-irons previously tested were oxidized in varying degrees, and the reduction of this oxide by carbon when the mould surface was heated to a high temperature would be expected to result in considerable evolution of oxides of carbon.

PLATE XXXVII.

FIG. 1.—70 : 30 Brass Ingot Cast in Grey Iron Mould, Showing Extensive "Blowing" Defects. × ⅔.

[*To face p.* 208.

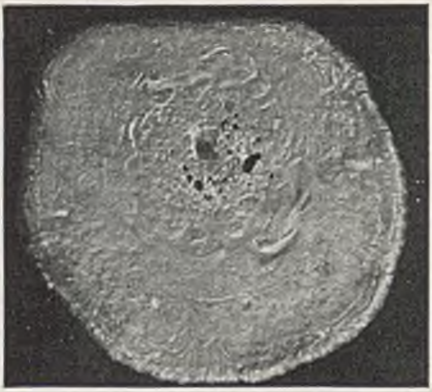

FIG. 3.—Under Surface of Small Brass Disc Poured on Cast-Iron Plate, Showing "Blowing." × ½.

FIG. 4.—Surface Layer of Decarburized White Iron Plate. × 100.

FIG. 5.—Original Structure of Grey Cast-Iron Cylinder. × 250.

Fig. 6.—Centre of Grey Iron Cylinder after Treatments *in Vacuo*, Showing Deposition of Graphite. × 250.

Fig. 7.—Edge of Cylinder shown in Fig. 6, Showing Decarburization of Pearlite. × 250.

Fig. 8.—Structure of Non-Pearlitic Cast-Iron × 100.

PLATE XI

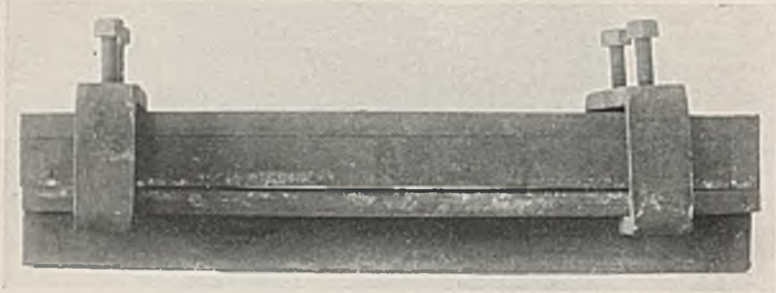

FIG. 10.—Mild Steel Ingot Mould after 6 Heats. × ⅙.

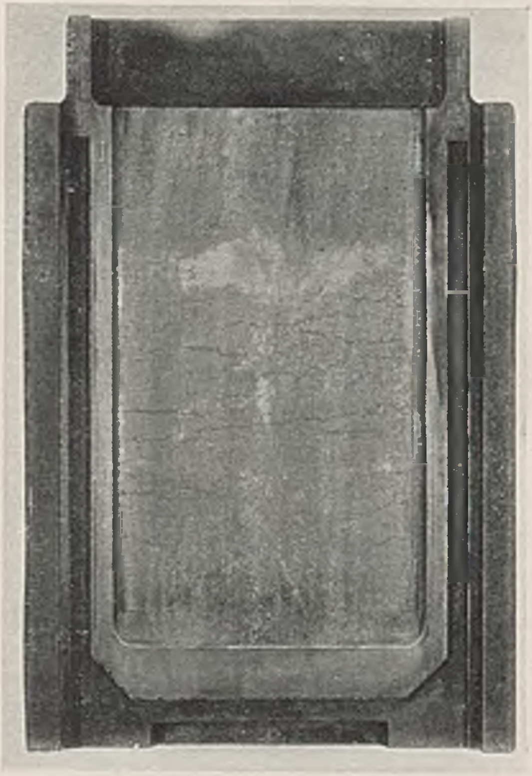

FIG. 16.—Inner Face of Grey Cast-Iron Ingot Mould after Approximately 100 Heats. × ⅓.

PLATE XLI.

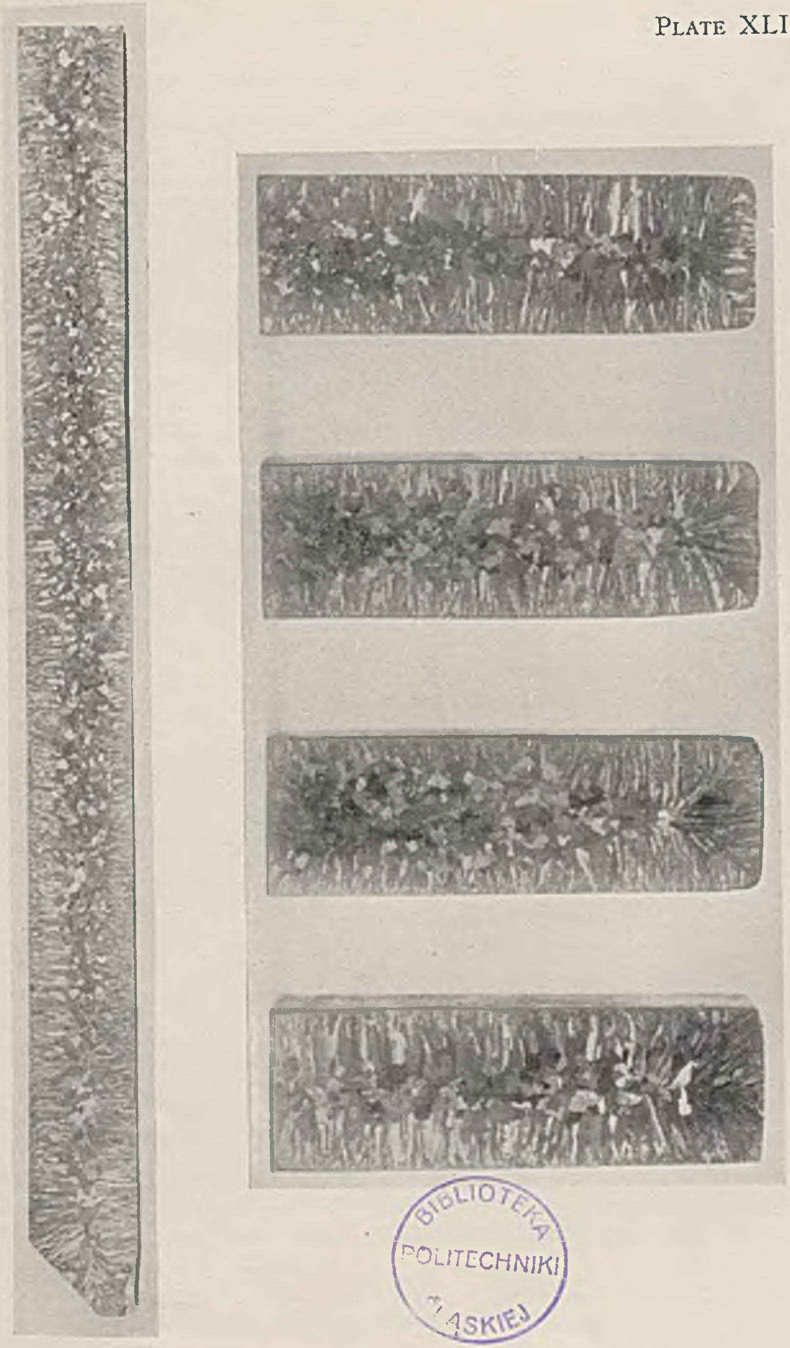

FIG. 17.—Structure of 70 : 30 Brass Ingot Cast in Grey Iron Mould Coated with Lampblack.

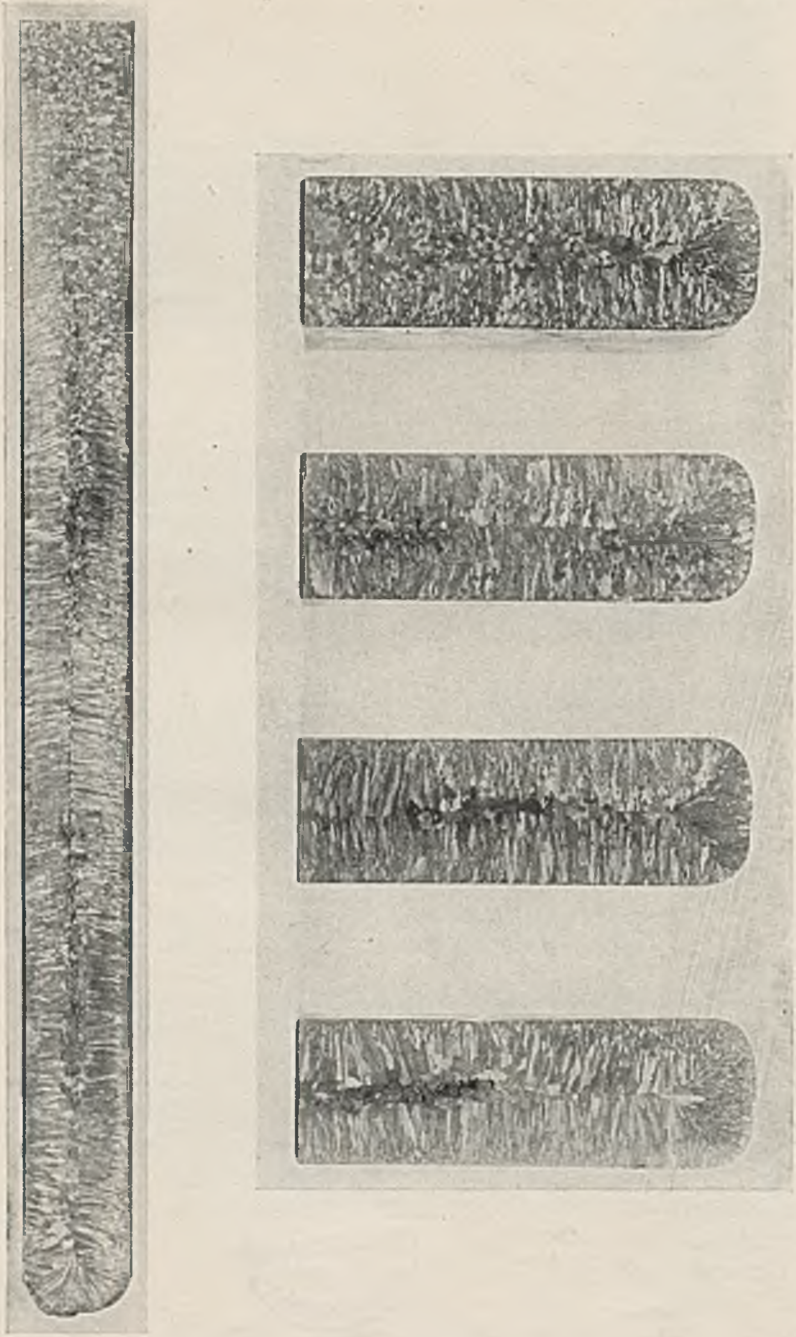

FIG. 18.—Structure of 70 : 30 Brass Ingot Cast in Water-Cooled Copper Mould Coated with Lampblack.

To test this hypothesis experiments were made to determine :—

(*a*) the influence of varying degrees of surface oxidation of ferrous materials of varying carbon content;
(*b*) the temperature necessary for the surface reaction;
(*c*) the temperature attained by the mould face during pouring.

The Influence of the Degree of Oxidation and Carburization on Liability to "Blowing."

Small-scale tests were made of the effect of varying degrees of oxidation on a variety of ferrous alloys of different carbon contents. The results obtained are shown in Table II.

TABLE II.—*The Influence of Different Degrees of Oxidation and Carbon Content on the "Blowing" of Iron–Carbon Alloys.*

Plate.	Treatment of Plate.	Temperature of Testing, ° C.	Degree of Oxidation.	Volume of Gas Holes in Brass Disc. C.c.
Grey cast-iron . .	machined	100	nil	0·17
		320	blue	0·29
		650	black	0·65
Mild steel 0·1% C . .	machined	100	brown	0·01
		400	deep blue	0·01
		700	black	nil
High-carbon steel 1% C .	machined and ground	100	nil	nil
		100	pale straw	0·04
		350	straw	0·10
		350	deep blue	0·20
White cast-iron . .	as cast	350	straw	0·09
		350	deep blue	0·14

The white iron plate used for these tests was subsequently packed in iron oxide and annealed at 950° C. for 7 hrs. The surface layer after this treatment showed considerable decarburization (see Fig. 4, Plate XXXVIII) and on re-testing gave only 0·03 c.c. of gas.

These results confirm the suggestion that "blowing" is due to a reaction between oxide and carbon in the surface layer of the ingot mould. Where the carbon content of the surface layer of the mould material was high, the amount of gas evolved varied, in each case, in the same direction as the degree of oxidation. In the case of mild steel, which gave a mere trace of gas at ordinary temperatures, the absence of "blowing" at 700° C. was probably due to the thick layer of surface oxide. When for other reasons an ingot of the dimensions 12 in. × 6 in. × 1 in. was cast in a mild-steel mould at an initial temperature of 700° C., the longer time of solidification permitted sufficient gas evolution at the steel–oxide face to cause some of the superficial oxide on the mould to be pressed into the ingot surface.

The Temperature Necessary for the Surface Reaction.

In order to determine the reaction temperature between oxide and carbide, samples of grey and white iron were heated *in vacuo* after various treatments and the volumes of gas evolved at different temperatures were measured. The specimen was heated in a silica tube in an electric furnace, with a thermocouple in contact with the specimen. The end of the tube was connected through drying towers and a mercury manometer to a vacuum pump. The specimen was inserted in the cold and the apparatus evacuated. Heating was then commenced and the volume of gas in the apparatus measured by the increase in pressure recorded. This gave the approximate volume, at room temperature, of the gas evolved, as the hot furnace tube comprised only a small proportion of the total volume of the apparatus.

Annealings of Grey Cast-Iron.

Two cylinders each 4 in. long × 0·75 in. in diameter were cut from a 1-in. diameter sand-cast bar of grey iron containing:

	Per cent.
Graphite carbon	2·85
Combined carbon	0·55
Silicon	2·25
Manganese	0·54
Sulphur	0·01
Phosphorus	0·02

The first cylinder, " A," in the " as machined " condition was heated to 800° C. in 2·5 hrs. Evolution of gas commenced at 700° C. and became rapid at 750° to 800° C. After maintaining at 800° C. for 2 hrs. evolution practically ceased, when 95 c.c. of gas had been evolved.

After several heats *in vacuo* a satisfactory blank was obtained. Removal of the specimen to a desiccator for several days resulted in the evolution of 48 c.c. of gas on reheating—again between 700° and 800° C. Removal of the specimen from the tube and exposure to air for some hours was always followed by a gas evolution on reheating, while no gas was evolved after standing *in vacuo.*

The specimen was then allowed to remain for some hours in the cold in the furnace tube in different gas atmospheres before reheating. Cylinder nitrogen (partially purified with alkaline pyrogallol), air, and oxygen were tested in turn, each gas being dried. The volumes of gas evolved by the specimen after each treatment are shown in Table III.

The second cylinder, " B," from the same cast-iron was subjected

TABLE III.—*Gas Evolved from Grey Cast-Iron Cylinder " A " on Annealing in Vacuo After Various Treatments.*

Treatment of Sample.	Gas Evolved on Annealing for 2 hrs. at 800° C. C.c.
As cast and machined	95
In vacuo for 18 hrs.	23
In air in desiccator for several days	48
In vacuo for 18 hrs.	2
In dry air in furnace tube for 48 hrs. in the cold . . .	20
In vacuo for 18 hrs.	nil
In partially purified nitrogen in furnace tube for 19 hrs. in the cold	7
In dry air in furnace tube for 46 hrs. in the cold . . .	18
In dry oxygen in furnace tube for 18 hrs. in the cold . .	20

to similar treatments in different atmospheres. Purified nitrogen, air, and oxygen were in this case admitted when the cooling specimen was at 400° C., and were left in contact with the cast-iron for 18 hrs. in each case. The results obtained are shown in Table IV.

TABLE IV.—*Gas Evolved from Grey Cast-Iron Cylinder " B."*

Treatment of Sample.	Gas Evolved on Annealing for 2 hrs. at 800° C. C.c.
As cast, machined and superficially oxidized . . .	101
In vacuo for 18 hrs.	13
In air in desiccator for several days	51
In vacuo for 60 hrs.	10
In dry air in furnace tube at 400° C. and for 18 hrs. in the cold	28
In pure nitrogen in furnace tube at 400° C. and for 18 hrs. in the cold	6
In dry oxygen in furnace tube at 400° C. and for 18 hrs. in the cold	51

It is apparent from these results that the " blowing " of grey cast-iron which has been exposed to the atmosphere after the extraction of dissolved gases *in vacuo* is connected with the absorption of oxygen by the specimen.

White iron cylinders subjected to similar treatments gave off appreciable volumes of gas, again at 700°–800° C., only when oxidation between annealings was permitted.

Influence of Annealings in Vacuo on the Structure and Composition of the Iron.

The original pearlite–graphite structure of the grey-iron bar " A " is shown in Fig. 5 (Plate XXXVIII). After the various annealings *in vacuo* there was found to be a considerable deposition of graphite from the carbide throughout the bar, giving a structure in the central areas of graphite plus pearlite and ferrite (see Fig. 6, Plate XXXIX). In the surface layers, however, no pearlite was visible, the structure being entirely ferrite plus graphite (see Fig. 7, Plate XXXIX).

Analysis of the bar after the treatment was carried out both on the surface layer from which 0·01 in. was turned and on drillings from the centre of the bar.

	Centre of Bar.	Surface Layer.
Graphitic carbon, % . .	3·01	2·99
Combined carbon, % . .	0·43	0·10

Comparing these figures with the original analysis of the material, it is apparent that throughout the thickness of the bar an additional 0·15 per cent. of graphite had been deposited from the combined carbon. No diminution of total carbon had occurred in the centre of the bar but the outer surface layer was decarburized by approximately 0·30 per cent. at the expense, apparently, of the combined carbon only.

To supplement these results other cylinders from the same grey cast-iron were annealed : (1) 5 heatings to 800° C. under constant vacuum and (2) 5 heatings to 800° C. with intermediate oxidation. Micro-examination of the first of these bars showed some deposition of graphite from the carbide, and considerable residual pearlite, the structure being uniform throughout the section. The structure of the central portion of the second bar was similar to that of the first, but in this case the surface layers were free from pearlite.

Summary of Results of Vacuum Annealings of Cast-Irons.

The following facts are apparent from the above experiments :

(1) On exposure to the atmosphere, a cast-iron absorbs oxygen which causes evolution of gases on heating.

(2) This gas evolution commences at 700° C. and becomes rapid at 750° to 800° C.

(3) Gas evolution is accompanied by the decarburization of the pearlite in the surface layer of the iron.

Behaviour of Non-Pearlitic Iron.

In view of the fact that pearlite appears to be the main constituent reacting with superficial oxide, tests were made of a small plate of non-pearlitic iron, prepared by cooling a high-silicon iron slowly from 900° C. The structure of the plate was almost entirely ferrite and graphite (Fig. 8, Plate XXXIX). The volume of gas evolved on testing was

0·04 c.c. on the first cast and 0·08 c.c. on the second. These amounts are much less than those obtained from normal grey irons, but are sufficient to indicate a small effect due to the presence of graphite—due either to reaction with oxide where contact with the graphite flakes is sufficiently good or to the retention of air in the mould surface, particularly where graphite is mechanically removed from the surface layers.

The Temperature Attained by the Mould Face during Pouring.

In experiments described in a later section of this report, measurements were made of the temperature gradients in the walls of a grey cast-iron ingot mould during and immediately after pouring a 12 in. × 6 in. × 1 in. ingot of 70 : 30 brass. Two series of measurements were made, one in which the stream of metal did not touch the mould face and a second in which the stream struck the portion of the mould carrying thermocouples. In each case the temperature of the inner face of the mould reached a maximum in 12 seconds after pouring. Extrapolation of the curves obtained (Fig. 9) showed that these maximum surface temperatures were approximately 520° C. and 800° C. respectively, indicating that the mould surface is sufficiently overheated by impingement of the molten stream to permit a rapid evolution of gas due to the reaction discussed above.

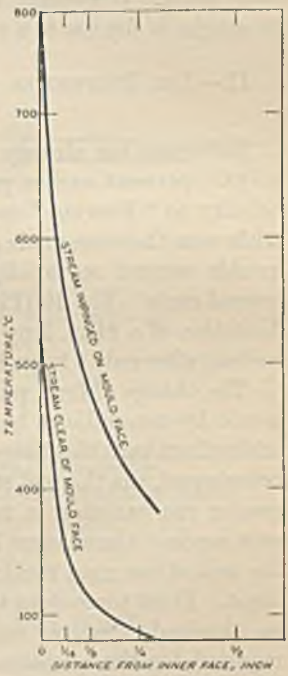

Fig. 9.—Maximum Temperature Gradient in Cast-Iron Mould Wall.

Discussion of Results.

Examination of various possible causes of the "blowing" of cast-iron ingot moulds has indicated that this occurs only when pearlitic irons are superficially oxidized. Graphite alone produces only a small amount of "blowing," but this phenomenon is liable to occur with a wide variety of ferrous alloys in which the content of combined carbon is high.

The presence of an oxide film on the surface of a cast-iron ingot mould is very difficult to avoid entirely. In ordinary works practice the thickness and nature of the usual type of mould dressing provide some protection against oxidation and against local overheating during pouring, but a thin mould dressing is relatively ineffective in this direction. In the small-scale experiments described, cast-iron was found to oxidize sufficiently on free exposure to air at atmospheric temperatures to produce "blowing" on reheating, and experimental trials of cast-iron ingot moulds under conditions designed to minimize oxidation failed to reduce "blowing" to any great extent. Freedom from "blowing" could be secured by the application to the mould surface of a thick metallic coating, but such coatings showed the disadvantage of flaking or blistering with continued use owing to the difference between the coefficients of thermal expansion of the coating and the basis metal. It appears, therefore, that a remedy for this defect must be sought in the use of a carbide-free mould material.

II.—THE PROPERTIES OF MOULD MATERIALS AFFECTING THEIR PERMANENCE.

Reference has already been made to the fact that steel containing only 0·1 per cent. carbon proved free, under normal conditions, from the liability to "blowing" to which cast-iron is subject, and preliminary trials were therefore made of steel ingot moulds. It was found that such moulds warped so rapidly and seriously as to become useless after several casts. Fig. 10 (Plate XL) shows the nature and amount of the distortion of a 24-in. long strip ingot mould of mild steel (0·1 per cent. carbon) after only 6 heats had been poured in it.

The change of form produced in a mass of material such as an ingot mould by non-uniform heating and cooling, is due to thermal stresses arising from variable changes in volume through the section. Other factors being equal, the thermal stresses and resulting distortion are higher the greater the variation in temperature in the specimen. Measurements were made of the changes in temperature at different points throughout the wall of the ingot mould during and subsequent to the casting of the ingot. From these data the temperature gradients at any stage could be obtained. Several materials were so tested, and the properties required for the avoidance of warping were deduced. Confirmatory tests were made using a small-scale mould and these were finally extended to the casting of brass in larger moulds of promising materials.

The Temperature Gradients in the Wall of a Mild Steel Ingot Mould During and After Pouring.

Measurements were made of the variations in temperature of thermocouples set into the wall of a mild steel mould at distances of $\frac{1}{16}$ in., $\frac{1}{4}$ in., and $\frac{1}{2}$ in. from the inner surface. The mould used was of the usual type for 12 in. × 6 in. × 1 in. ingots, with walls $1\frac{1}{8}$ in. thick, and $\frac{1}{8}$-in. diameter holes were drilled for the thermocouples near the centre of one face. To ensure rapidity in recording, platinum/platinum–rhodium thermocouple wires of only 0·2 mm. diameter were used with the bare welded junction in contact with the bottom of the hole. The mould, preheated to 100° C. and dressed with lampblack, was filled with 70 : 30 brass by pouring at 1100° C. in a time of 10 seconds. Readings of the temperatures of the thermocouples were taken simultaneously at 5-second intervals.

The time–temperature curves obtained for the three positions are shown in Fig. 11. From these results curves were plotted showing the temperature gradients in the mould wall at various intervals of time after pouring (Fig. 12).

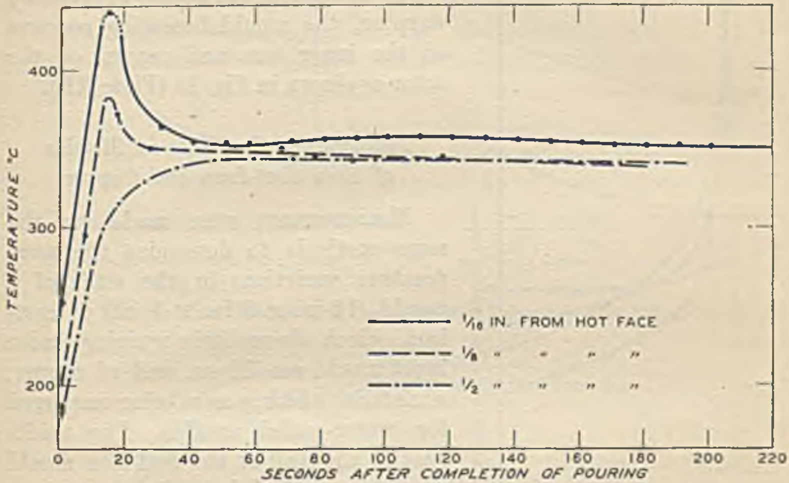

FIG. 11.—Temperature Variations in Wall of Mild Steel Ingot Mould.

The Thermal Stresses in a Mild Steel Mould.

The rapid changes in temperature of the inner surface layer cause large and rapidly changing stresses in this portion of the mould wall. The inner face expands rapidly during the 10 seconds immediately after pouring. The mould tends to open at top and bottom to accommodate this increase in length, but is held by the clamps and by the rigidity of the thick mass of cold metal at the back. In the hot layers of the mould a severe compressive stress is thus set up which is largely relieved by plastic flow.

After 10 seconds from the completion of pouring the conduction of heat through the mould wall exceeds the rate at which heat is supplied to the inner face by the ingot. The inner surface layers then cool somewhat while the main body of the mould is heating up. The stresses at this point are reversed and a tensile stress is set up on the inner face and a compressive stress in the outer layers. In the initial stages some stress may be relieved by permanent extension of the inner face, but as temperature gradient diminishes considerable stresses are set up below the elastic limit and the mould wall reaches an approximately uniform temperature with a tensile stress on the inner surface and compressive stress on the outer.

These stresses are largely relieved by warping, the mould becoming concave on the inner face and convex on the outer as shown in Fig. 10 (Plate XL).

FIG. 12.—Temperature Gradients in Mild Steel Mould Wall.

Temperature Gradients in Moulds of Grey Cast-Iron and Copper.

Measurements were made by the same methods to determine the temperature variations in the walls of a mould (12 in. × 6 in. × 1 in.) of cast-iron, which shows little warping under ingot mould conditions, and of copper, a material which is now being employed for water-cooled moulds. The thickness of the wall of the cast-iron mould was $1\frac{1}{8}$ in. and of the copper 1 in.

The temperature gradients in the mould wall at various intervals of time after pouring are shown in Figs. 13 and 14. Curves showing the variations in temperature in the wall of the cast-iron mould were similar to those shown in Fig. 13, and those for the copper mould are shown in Fig. 15. The maximum temperature reached by the inner face of the cast-iron mould was about 100° C. below that for mild steel. This temperature is probably affected by slight variations in the distance of the stream of metal from the mould face. To ascertain the maximum temperature to which the cast-iron mould face can be heated by the stream of metal, a second experiment was carried out in which the stream of 70 : 30 brass was allowed to impinge fully on the portion of the mould wall on which measurements were being made. The approximate maximum temperature gradient produced under these conditions in cast-iron is shown in Fig. 9 together with the curve of the average gradient reproduced from Fig. 13.

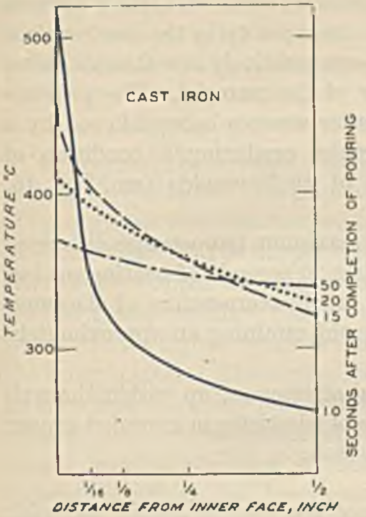

Fig. 13.

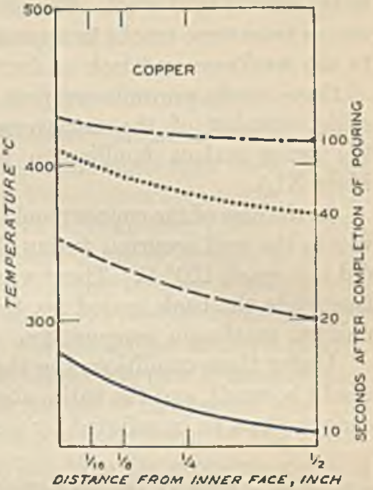

Fig. 14.

Temperature Gradients in Cast-Iron and Copper Mould Walls.

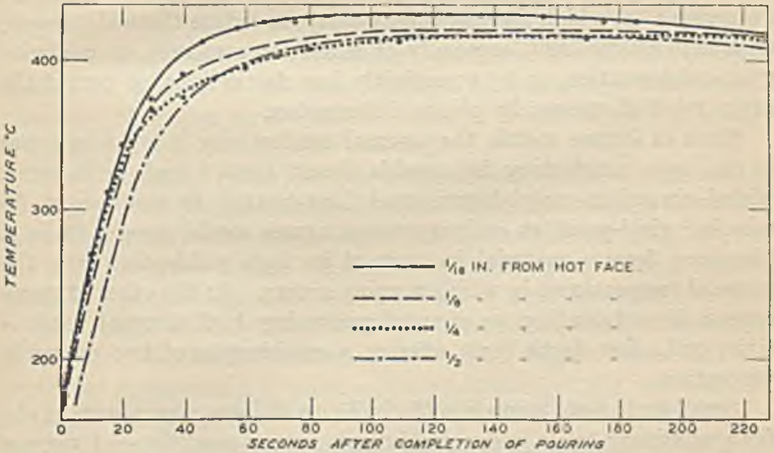

Fig. 15.—Temperature Variations in Wall of Copper Ingot Mould.

Thermal Stresses in Moulds of Grey Cast-Iron and Copper.

The thermal stresses set up in the wall of a grey cast-iron mould are of the same order as those in a steel mould, and the absence of warping is due to the different mechanical properties of the cast-iron. The initial expansion of the inner layers causes a small permanent deformation by compression, followed by a reversal of stress on cooling down as in the case of mild steel. The tensile stress set up in the inner surface causes transverse cracks to appear at comparatively low stresses owing to the weakness and lack of ductility of the material. The presence of these cracks prevents warping, further stresses being relieved by a slight opening of the transverse cracks, producing a condition of the inner surface familiar to users of such moulds (see Fig. 16, Plate XL).

In the case of the copper mould the maximum temperature difference within the wall occurred during the first 20 seconds of heating up but did not reach 100° C. There was no fall in temperature of the inner face while the back heated up, the mould attaining an approximately uniform maximum temperature.

Under these conditions the thermal stresses set up within the wall would be small, and the entire absence of elasticity in annealed copper enables them to be relieved by plastic flow.

Properties Necessary for the Avoidance of Warping in Ductile Material.

From a consideration of the foregoing results the following properties would appear to be necessary in a mould material to minimize distortion : (*a*) a high thermal conductivity, to reduce thermal stresses; (*b*) a high elastic limit, especially at raised temperatures, to minimize plastic deformation, or (*c*) a negligibly low elastic limit, to permit the entire relief of stresses by plastic deformation.

Since in ferrous metals the thermal conductivity is low a material of this type satisfactory for moulds should have a high yield-point. Nickel–chromium–molybdenum steel heat-treated to give about 55 tons/in.^{2} yield-point at ordinary temperatures would appear to be a promising ferrous material in view of its high yield-point over the range of temperatures in which warping occurs. At the other extreme copper is outstanding as a metal possessing high thermal conductivity and a low elastic limit, offering a combination of two desirable properties.

Small-scale tests using moulds built up of loose plates were made for preliminary trials under particularly severe conditions of various materials selected on these considerations. 70 : 30 brass was cast into these moulds, and mild steel, included for comparative purposes, was found to warp considerably in either thick or thin sections after a single heat. Copper plates showed negligible distortion after 13 heats, while heat-treated nickel–chromium–molybdenum steel warped only slightly after 25 heats. A pure aluminium plate was tested in view of its intermediate thermal conductivity between steels and copper, and was actually found to warp only slightly after 5 heats. This material, however, was unsuitable for casting brass owing to a slight tendency to fusion at the point of impact of the stream.

Testing of Ingot Moulds of Selected Materials.

Copper and heat-treated nickel–chromium–molybdenum steel having proved comparatively free from warping in the small-scale tests, moulds of these metals were constructed to give brass ingots 24 in. × 6 in. × 1½ in. of 70 lb. weight. The copper mould was built up from plates of rolled electrolytic copper 1·5 in. thick. Using a heavy stream of metal (70 : 30 brass) the alloy steel mould was found to show a tendency to weld on to the ingot—which tendency was only overcome by aluminizing the inner surface. The copper mould was not subject to this difficulty. In each case a considerable number of ingots was cast in these moulds without any serious distortion. This success of the special steel and copper moulds provided an interesting confirmation of the earlier conclusions which had been reached, but from the economic point of view the copper alone constitutes a practicable proposition, as the aluminized and heat-treated special steel mould is somewhat costly.

Discussion of Results.

Determinations of the temperature gradients in the walls of ingot moulds for casting 70 : 30 brass strips have shown that with ferrous materials, the inner surface of the mould is heated rapidly to a high temperature immediately after pouring.

About 10 seconds after the completion of pouring, *i.e.* approximately the stage of complete solidification of the ingots dealt with in this work, the temperature of the surface layer falls again while the main body of the mould becomes hotter. A similar maximum temperature, rapidly attained and maintained for a short space of time, has been observed in ingot mould walls by other workers. The Heterogeneity Committee of the Iron and Steel Institute in its Fourth Report shows that the inner face of the mould in which a 38-cwt. steel ingot was cast attained a maximum temperature 7–10 minutes after casting. Matuschka similarly gives evidence of a small peak in the temperature of the inner layers of the mould wall some 2–3 minutes after pouring. The explanation of this peak accepted by these workers is that it corresponds to the point at which the ingot shrinks away from the mould face, and the sudden change in the direction of the curves in the present work may be due to the same cause.

In few observations of previous workers are the rapid rise and fall of the temperature of the inner surface layer of a cast-iron mould shown so clearly as in the present work. This is considered to be due to the fact that measurements have not been made sufficiently closely to the inner face of the mould. Roth, for instance, measuring the variations in temperature in iron moulds when casting brass, obtained slight evidence of this change in direction of the heating curves in only one instance, as his measurements were made no nearer than 5 mm. to the inner face of the mould.

The rapid fluctuations in temperature of the mould wall cause considerable stresses to be set up, which result in serious distortion of mild steels and transverse cracking of the inner faces of cast-iron. Such distortion can be largely overcome in materials of low thermal conductivity by the use of alloys of high yield-point, but such a procedure is uneconomic for strip casting.

Copper as a mould material has been found to give successful results—its high thermal conductivity prevents the formation of steep temperature gradients and serious thermal stresses are therefore avoided. When pouring 70 : 30 brass at 1100° C. into a solid copper mould with walls equal in thickness to that of the cast strip, the maximum temperature recorded in the mould wall was of the order of 400° C. This is of importance in considering the question of the welding of the ingot on to the mould. With ferrous alloys increasing the thickness of the wall does not affect the initial temperature of the inner face and will not therefore diminish welding tendencies. With copper, however, the uniformity of the temperature throughout the mould wall means that, under the conditions of these experiments, conduction of heat through the mould keeps pace with the rate of heat input. Increasing the thickness of the mould wall therefore would be expected, other things being equal, to decrease the maximum temperature attained. These experiments with copper moulds have been made with a vertical stream of brass. Pouring in such a manner that the stream impinges on the mould wall may be expected to cause a higher local temperature and with alloys of higher melting point may cause adhesion to the solid copper mould.

Water-cooling of a copper mould is also successful in preventing adhesion, the effect being to maintain the temperature throughout at a comparatively low level. It is clear that, from the point of view of maintaining a low temperature on the inner face of the mould, water cooling can be advantageously applied only to a material of high thermal conductivity such as copper, and would be of little use if applied to steel.

III.—THE INFLUENCE OF THE MOULD MATERIAL ON THE PROPERTIES OF THE CAST INGOT.

Ingots of 70 : 30 brass were poured under standard conditions in each of the following moulds and examined for surface quality, structure, and soundness :

	Size of Ingot. In.	Mould Walls. Thickness, In.
Grey cast-iron	12 × 6 × 1	1¼
Water-cooled copper . . .	12 × 6 × 1	⅜
Heat-treated Ni–Cr–Mo steel . .	24 × 6 × 1½	1¼
Solid copper	24 × 6 × 1½	1½

Both inert and volatile (graphite and oil) mould dressings were used, other conditions of pouring being the same. In each casting the metal was poured at 1100° C. in a single stream giving a rate of rise of metal in the mould of 1·2 to 1·5 in. per second. The mould was pre-heated to 80°–100° C. and was used vertically.

Ingot Surface.

Little variation was observed in the surface qualities of the ingots with different moulds apart from small amounts of blowing from the cast-iron mould when using inert dressings. Where mould dressings were thin the surface chill with the copper moulds was somewhat greater than with the others, resulting in fine laps on the ingot surfaces. These, however, were avoided when a moderately thick mould coating was used.

Soundness.

Density determinations were made on representative whole 12 in. × 6 in. × 1 in. ingots and on longitudinal half sections of each large ingot. The results calculated to percentage cavities in the whole ingot are given in Table V.

TABLE V.—*Influence of Mould Material on Soundness of 70 : 30 Brass Ingots.*

Ingot Mould.	Size of Ingot. In.	Percentage Cavities in Whole Ingot.	
		Non-Volatile Dressing.	Volatile Dressing.
Grey cast-iron . . .	12 × 6 × 1	0·38	0·31
Water-cooled copper . .	do.	0·27	0·29
Ni–Cr–Mo steel . . .	24 × 6 × 1½	0·63	...
Solid copper . . .	do.	0·69	...

The figures show little variation for any one size of ingot except that the water-cooled copper mould castings are slightly sounder than castings of the same size in the cast-iron moulds.

Ingot Structure.

The structure of ingots cast in the different moulds under comparative conditions varied but little. Where an inert mould dressing was used, the crystals were mainly columnar with only a small central zone of equiaxed structure. In the small ingots the water-cooled copper mould appeared to increase somewhat the length of the columnar crystals (cf. Figs. 17 and 18, Plates XLI and XLII), but little difference was observable between the structures of the large ingots cast in solid copper or alloy steel moulds. The use of a volatile mould dressing produced an altogether different structure with all types of ingot mould—the ingots consisting almost entirely of fine equiaxed crystals. This effect, which has been previously noted by Genders,* is due to the turbulence set up during the initial period of solidification by the volatilization of the dressing, and is of far greater magnitude than the differences due to the material of the mould.

Reviewing these results it would appear that, from the point of view of ingot surface, moulds of solid copper, water-cooled copper, and alloy steel, give brass of higher quality than moulds of cast-iron. None of these alternative materials showed liability to produce defects in the ingot by "blowing" or warping. The effect of the mould material on the ingot structure was slight, water-cooled copper producing only a slight increase in columnar crystallization compared with cast-iron.

Effect of Nature of Mould on the Speed of Solidification of the Ingot.

In connection with this work it is of interest to refer briefly to some small-scale measurements that were made on the speed of solidification of 70 : 30 brass in small moulds of different types.† The ingots used were (*a*) a small truncated cone 4 in. long × 2 in. in diameter at the top, and (*b*) a cylinder 6 in. long × 1·5 in. in diameter. In each case measurements of the solidification period of the centre of the ingot were made using moulds of different materials and wall thicknesses. Some typical results are given in Table VI.

Measurements were also made of the effect of the initial temperature of the thick-walled steel mould on the solidification period. The results are shown in Fig. 19.

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* *J. Inst. Metals*, 1930, **43**, 187.

† "The Influence of Dissolved Gases on the Soundness of 70 : 30 Brass Ingots," *J. Inst. Metals*, 1928, **39**, 191.

TABLE VI.—*Solidification Speed of* 70 : 30 *Brass Ingots Poured in Different Moulds.*

Mould.	Dressing.	Mould Temperature. ° C.	Solidification Period. Seconds.
Conical Ingots.			
Thick cast-iron . .	lampblack	150	17
Thick copper . .	do.	125	14
Thick steel . . .	do.	180	15
do. . . .	oxidized	180	16
Thin cast-iron . .	lampblack	260	22
Dry sand . . .	nil	100	153
Cylindrical Ingots.			
Thick copper . .	lampblack	120	16
Thin cast-iron . .	do.	120	22
Thick steel . . .	oxidized	810	145
Dry sand . . .	nil	120	310

The results obtained with these small castings provide a guide to the influence of the mould on the solidification of small brass ingots which is helpful in considering the major results obtained with strip ingot moulds.

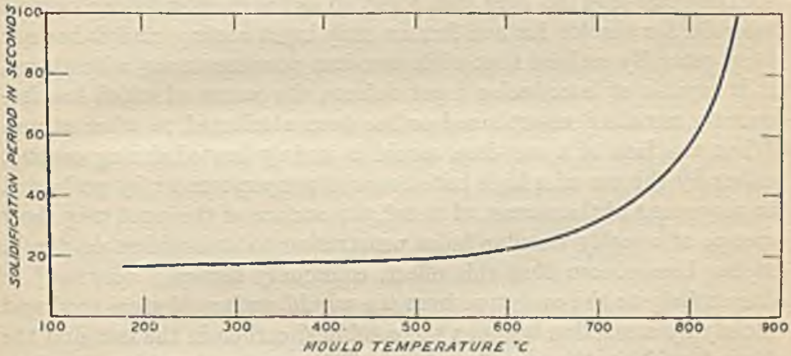

FIG. 19.—Variation of Solidification Period with Mould Temperature.

That the use of a copper mould does not give a greatly increased speed of solidification as compared with cast-iron is in agreement with the small influence on ingot quality noted in considering the larger strip moulds. It is evident that heat transfer from metal to mould is dependent on other factors than thermal conductivity of the mould, such as the interference offered by the discontinuity at the metal–mould interface.

Decreasing the thickness of mould wall in cast-iron moulds from an area ratio of 4 : 1 to 1 : 1 also had little effect on the time of solidification. Cast-iron moulds ordinarily used in brass strip casting are of the order of 1·5 in. in thickness, but this thickness is necessary, as thin-walled moulds quickly deteriorate in use. Any increase in thickness beyond about ½ in. may be regarded almost entirely as having the purpose of increasing the life of the mould. Variation of the temperature of the mould within the practicable limits similarly has no noticeable effect on the solidification period of the ingot. It is interesting to note in this connection that Courty * investigating the "flowability" of aluminium alloys in a metal spiral mould found that variations in the temperature of the mould had little effect on the length of spiral until the melting point of the metal was approached. His curve for length of spiral : mould temperature was similar in type to that shown in Fig. 19.

It must be emphasized that these remarks apply solely to ingots of about 1 in. in thickness, cast in moulds of the usual size, and that when considering ingots of appreciably different type or size great care must be employed in utilizing these results.

GENERAL SUMMARY AND CONCLUSIONS.

Grey cast-iron has long been regarded as the most suitable available material for moulds for non-ferrous strip ingot casting, and it has not been generally realized that while cast-iron possesses many advantages, it is capable of introducing ingot defects, the source of which has frequently remained unexplained or has been attributed to other causes. When the face of a cast-iron mould is unduly heated during casting, either by the use of a high initial mould temperature or by prolonged impingement of the stream of metal, the surface of the ingot may show groups of roughly circular holes penetrating to a considerable depth. It has been shown that this effect, commonly termed "blowing," is due entirely to the evolution from the mould surface of gases produced mainly by a reaction between the combined carbon in the iron and the film of oxide in the mould surface. This reaction has been found to occur readily above 700° C., a temperature frequently reached by some portions of the face of an iron mould immediately after casting. Blowing may also be produced to a slight extent by reaction of the graphite of the cast-iron with oxide or by the expansion of air either absorbed by the graphite, or in cavities in the metal. Other ferrous alloys, such as steels of high carbon content, may evolve gases in a manner similar to that of cast-iron owing to the same oxide–carbide reaction. While surface protections such as refractory washes or electrodeposited

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* *Compt. rend.*, 1930, 190, 936.

coatings are capable of avoiding the production of "blowing," such measures are not a sufficiently permanent remedy for general adoption in practice.

It would appear, therefore, that to eliminate the risk of "blowing," a mould material is required containing very little carbon, and from this point of view, low carbon steel and certain non-ferrous metals have proved suitable materials for moulds.

A further source of defects in brass ingots made in moulds of cast-iron is the transverse cracking which inevitably occurs on the face of the mould at a certain stage, frequently early, in its life. The cracks eventually develop to an extent entailing the scrapping of the mould. This is due to the stresses arising from the repeated unequal heating and cooling of the mould and probably occurs more readily in low quality cast-iron of high phosphorus content than in high quality hæmatite irons and "semi-steel" or other special close-grained irons.

Mild steel, while not possessing the disadvantages of "blowing" and cracking, has been found to be unsuitable as a mould material, since, after brief use, the mould becomes permanently deformed. This effect is due to thermal stresses arising from a steep temperature gradient in the wall and is therefore similar in origin to the cracking of cast-iron moulds. With a material of high thermal conductivity such as copper, the temperature gradient through the mould wall during casting remains relatively small, and warping is not found to occur to any appreciable extent. No other metal possesses more favourable properties in this respect than copper except pure silver. Aluminium, while having a fairly high thermal conductivity, has too low a melting point to be suitable for brass casting moulds. For the casting of metals of low melting point, however, such as alloys of aluminium and of zinc, aluminium may be a satisfactory material for moulds.

The successful use of copper for non-ferrous ingot casting moulds will depend on the provision of means for preventing the mould from rising in temperature during casting to a point involving risk of the welding on of the ingot. Accordingly the mould may be one of small thickness, water-cooled on the outer faces, or may be of solid copper of adequately large section. For brass a solid mould is satisfactory—a copper mould giving a brass ingot 24 in. × 6 in. × 1½ in. dimensions should have a minimum wall thickness of 1·5 in. For alloys of high melting point water-cooled moulds are necessary—in some cases special design of the mould is essential to avoid adhesion (cf. Rohn). It has been confirmed experimentally that in a copper mould the rate of solidification of a brass ingot of thin section and its consequent structure and properties are not appreciably affected whatever method is adopted for the absorption of heat conducted from the mould faces; water-cooling may therefore be considered to have little relation to the quality of the ingot, its function being to prevent over-heating of the mould and to facilitate rapid production.

Ingot moulds free from warping can be made from a material having a sufficiently high elastic limit (at both low and raised temperatures) to avoid plastic deformation under the thermal stresses induced during casting. Experimental trials have shown that a mould of nickel–chromium–molybdenum steel, suitably heat-treated, is satisfactory in this respect, but is subject to other disadvantages and is somewhat costly.

From all points of view, therefore, it is considered that copper is the most suitable material for brass strip ingot moulds, either as a solid mould of slightly greater thickness than the cast-iron moulds at present in use, or as a thinner water-cooled mould. The use of copper moulds obviates the surface difficulties associated with cast-iron, while affecting the structure and soundness of the ingots but little.

ACKNOWLEDGMENTS.

In conclusion the author wishes to thank the Council of the British Non-Ferrous Metals Research Association for granting its permission for the publication of this paper, and Dr. L. Northcott for much assistance in the experimental work.

DISCUSSION.

Dr. W. Rosenhain,* F.Inst.Met., F.R.S. (Past-President): I have read this paper with great interest, and I have also had the advantage of having seen something of the progress of the research and of some of its other ramifications. I think that the results which have been obtained are exceedingly interesting and are likely to prove of practical importance.

Whether or not, so far as strip ingot casting is concerned, the use of copper moulds is the only or the best solution remains to be seen, because there are certain difficulties; the cost of the moulds in works where there have to be a great many of them is a serious item with normal prices for copper.

The most interesting feature of these results is, perhaps, the author's explanation of the warping of ordinary steel moulds and the non-warping of cast iron, owing to internal cracking. This is a plausible explanation, but it seems almost too easy to be accepted as the whole story; if it really is the whole story, then it seems to me there are mechanical ways of overcoming the trouble. For instance—I do not suggest this as a practical solution, but it indicates the direction in which we may look for it—if we made, on the inside of a steel plate used for a mould, a number of saw-cuts, or, in other words, robbed the inner face of tensile strength in that or some other way, then surely such a plate must behave like a cast-iron mould cracked on the inside, and

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* London.

could scarcely warp. It may be objected that a mould so treated would be spoilt, but it might be feasible to fill those cracks with suitable material, either once and for all (with copper, for instance) or provisionally (with some form of dressing which did not cause trouble in the metal). There would be many advantages if that made it possible to use steel moulds.

One of the troubles with a mould made of a soft material like copper is that it must either be made very thick and heavy, to render it sufficiently strong and rigid to stand the handling these things generally receive, or else one must be prepared for the occurrence of mechanical distortion. I know of one instance where a mould, usually made of cast iron, was made instead of a special alloy iron which is ductile. It did not warp, but it was bent in handling; the ordinary methods of taking the mould apart and putting it together were too vigorous for a ductile material. That perhaps applies more to copper than it would to steel.

The other question which interested me concerns the "blowing" phenomenon and the suggestion—probably a sound one—that it is due to the reaction between an oxide film on the molten metal entering the mould and the carbon of the mould itself. It seems to me, if that were the most serious trouble there would be two ways of overcoming it. One, which I believe the author and his friends have attempted, is to prevent oxidation and the formation of that surface oxide film; and I think that considerable success can be obtained in that way. The other is to remove the carbon from the surface of the mould; in other words, to use a material the surface of which has been decarburized. I should like to see the results of experiments made with cast-iron moulds the inner faces of which had been deliberately decarburized by suitable annealing. In that way the "blowing" trouble might perhaps be overcome to a large extent.

This whole question of mould materials, mould design, and mould use is of fundamental importance, and I think that the importance extends to the fields of both ferrous and non-ferrous metallurgy. I have heard in this room, on more than one occasion, the problem of the steel ingot mould discussed and referred to as difficult and not entirely solved. On the other hand, I know very well that the moulds used for the majority of non-ferrous metals are regarded at the present time as being far from finally satisfactory. I feel that the work which the author has described and the results that he has obtained will assist us to make improvements, perhaps in both fields.

Professor R. S. HUTTON,* D.Sc. (Vice-President): I think that it is particularly fitting that Mr. Bailey's paper should be presented at a joint session of the Iron and Steel Institute and the Institute of Metals, because those in the steel industry who wish to know what is the practice of the non-ferrous industry with regard to casting ingots will no doubt turn to the excellent book by Mr. Harry Brearley, who had some rather scathing remarks to make on the casting of ingots of brass and other non-ferrous metals. I think that the work described in the present paper shows that those in the non-ferrous metal industry are thinking very seriously about their problems, because this particular investigation—which, as the author points out, is part of a very extensive programme—was initiated at the express wish of the members of the brass ingot casting section of the British Non-Ferrous Metals Research Association.

The author has pointed out very clearly that two of the major problems are reactions at the interface between the ingot mould and the casting and that of the thermal conditions of the mould wall and the solidifying metal. On that point I cannot help feeling—and I think that the author shares this

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* Professor of Metallurgy, The University, Cambridge.

feeling with me—that this work, so far as it has gone, has by no means closed the book, and that we need to know a very great deal more about these thermal conditions. The somewhat useful but still primitive method of merely relying on the intrinsic conductivity of copper, cast iron, or whatever the mould material may be, does not give us anything like the complete control we desire to have and which we must have if we are to secure the best conditions.

In that connection I think that we ought to remember that a great deal of most interesting work has been carried out in Germany by Dr. Rohn, and more recently by the Vereinigte Aluminiumwerke A.G., in which the ingots are cast with very complete control of the withdrawal of heat, and the very interesting results which Dr. Rohn has already published, and others which will no doubt be published in due course, are most encouraging to us in this country.

The author has referred to copper moulds. I do not know whether he refers in this paper to the sort of copper which should be used, but it is rather important that those who are using copper for mould purposes should realize the need for seeing that they get the best high-conductivity copper. In this country we are apt to employ engineering copper, therefore it may be specified as a mould material; but it should be noted that the conductivity of the British Standard copper is only about 50 per cent. of that of high-conductivity copper.

Dr.-phil. W. J. P. ROHN * (Member): As this problem is of very special interest to the members of both Institutes, perhaps I may be allowed to say a few words with regard to the suggestions made by Dr. Rosenhain. Some years ago we tried to follow his ideas by saw-cutting the inner surface of steel moulds. If the saw-cuts are very close to each other, the method is a success; but, as Dr. Rosenhain points out, the saw-cuts must be filled with some material to prevent the liquid metal entering these small slots, and, if these slots are filled with some non-metallic material, it immediately leads to the development of the " blowing " which has been described in detail by the author in this paper. Even if the slots are filled with metallic strips, however, small spaces are usually left for a little air, and very often these are afterwards filled with dirt or something similar, which also leads to " blowing." Our experience, therefore, seems to show, I regret to say, that this way of improving steel moulds is not very suitable.

On the other hand, an ingot mould made of pure copper is certainly a fairly expensive proposition. If the mould is made so that there is a surrounding made of steel or cast iron, and if it is provided with certain guides for leading the cooling water in the right way, then one can use simply a very thin wall of copper for the mould itself. We have found it very suitable, in our experiments, to have a wall thickness of only about 0·25 in. If a mould is constructed in this way, even the first outlay on it is less than is usually required for a grey iron mould, and even with materials such as nickel or steel we find that such moulds are suitable for more than three or four thousand castings with one copper tube. Moreover, to replace the copper lining of such a mould is a question of only a few shillings. In addition, since all the outer part of it is made of steel or cast iron a very strong type of mould is produced. In this way, therefore, I think that even the objection that copper moulds are usually too weak for the rough treatment they undergo in metallurgical work may be met.

Mr. A. J. G. SMOUT † (Member of Council): I am naturally interested in

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† Delegate Director and Production Manager, I.C.I. Metals, Ltd., Birmingham.

the author's conclusion that copper is considered to be the most suitable material for moulds for non-ferrous strip ingot casting, for modern works practice is definitely turning in that direction. I believe that the iron mould will become, or rather is, as obsolete as the old stone mould of the eighteenth century. Real progress will be made only by getting right away from iron of all types, and the brass trade will do well to turn its attention entirely to copper moulds.

At the present time one of the largest works in this country is casting several hundreds of tons per week of both brass and copper from copper moulds, so one may rest assured that the matter is now quite out of the experimental stage. Twenty-five years ago, when I first came into contact with the industry, copper refiners were already beginning to realize the advantage of the high thermal conductivity properties of copper, and were even then casting their cakes on copper bottoms; to-day they are casting copper more and more extensively on copper bottoms and in copper moulds.

A considerable time elapsed before the brass strip casters took a leaf from the copper refiners' book, and it was not until about eight years ago that we in this country—I think that my own company introduced the first mould—began to experiment with copper moulds for brass strip casting, and we have been so satisfied with this experience that we are now turning over to them entirely. We have tried the author's white cast-iron mould, but find it too soft for practical purposes, although it must be admitted that, perhaps because we were already very strongly in favour of copper, it was not given as prolonged a trial as it might otherwise have been given.

Reference has been made to one or two interesting points in connection with copper moulds. I do not think that there need be for one moment any fear of distortion, such difficulties can be entirely overcome by proper mould design, and need not cause the slightest worry. If the moulds are cooled properly there will be no trouble in that direction.

Professor Hutton has mentioned an important point—namely, the quality of the copper used, which must have high thermal conductivity properties. If, in addition, the copper is capable of being welded, the mould will have a much longer life; I therefore strongly urge that this factor be borne in mind. We have patched up many moulds successfully and increased their life considerably by resorting to simple methods of welding.

Reference has also been made to the rough treatment which moulds receive and the need to take this into account. With this I cannot agree. Non-ferrous metallurgy is changing rapidly in this country; we are getting away from "sledge-hammer" methods and changing over to engineering technique. The water-cooled copper-lined moulds of to-day are not subjected to rough treatment, and there is no reason why they should be. Cranes are available, and cranes must be used. Our work-people must be trained, and the managerial staff, whom we represent, must see that the old sledge-hammer methods are scrapped and rigidly stamped out. We certainly must not design down to those methods. That is a statement which, I suggest, not only applies to moulds, but which the non-ferrous industry as a whole should keep always in the forefront.

Finally, as a member of the industry engaged in production, I wish most sincerely to pay a tribute to the author and to his co-workers at Woolwich for the excellent work which has been done over a number of years, under the ægis of the British Non-Ferrous Metals Research Association, in connection with methods of strip ingot casting. The brass industry has learned a great deal from these researches, and I should like to acknowledge that fact publicly. I am afraid that there is a tendency to think that although many researches are conducted and papers published before the Institute and elsewhere, nothing is done in the works; that definitely is not so. Obviously we cannot broadcast what is done, but I wish most emphatically to say that this work is appreciated by those of us who are, as it were, in "the firing line" and up against production problems. Such work gives us a new viewpoint and, what is more important, a fresh inspiration, and an urge to get out of the rut.

Dr. C. H. **Desch**,* F.R.S. (Vice-President): The author has mentioned that comparatively little has been done in connection with the exact determination of the temperature gradient within the mould wall, a matter of great importance in the designing of moulds. As this is a joint meeting of our two Institutes, it is worth while to point out that much more has been done in this matter on the steel side, particularly in Germany. The author referred to the work of the Heterogeneity Committee and made a reference to one paper read by Matuschka in Germany. Since that first paper the German workers have carried the subject much further, and have made exact determinations of the temperature gradient within mould walls of different materials, including copper even for the purpose of casting steel ingots.

It is very interesting to hear from Mr. Smout how far this has been carried in industry. So far as laboratory work is concerned, we make frequent use of water-cooled copper moulds to obtain clean ingots for experimental work.

Mr. W. R. **Barclay**,† O.B.E. (Vice-President): There are just one or two points to which I desire to refer in connection with this paper. In the first place, I wish most cordially to support the statement that, so far as the future is concerned, the greater promise is undoubtedly with the copper mould. The experience we have had in casting nickel alloys from copper moulds is extremely encouraging. One of the real difficulties with the ordinary hematite iron mould is that the "blowing" effects are even more pronounced when the mould is new than when it is slightly worn. I was led some years ago to a study of the behaviour of copper moulds mainly by that very serious difficulty, particularly with the casting of ordinary nickel-brasses with a nickel content of up to 25 or 30 per cent.

The behaviour of the ordinary cast-iron mould is that during the first day's work one gets an enormous number—relatively—of surface cracks, sometimes so serious that the mould is useless. For some years I tried the method of taking moulds out of service at frequent intervals and putting them under a simple milling type of grinding machine, using a carborundum tool to get the surface as smooth as possible, and then putting them back into service. That met with some success in so far as it lengthened the life of the moulds, but it was by no means the success we have had with water-cooled copper moulds. It might be of interest if I say that not only are such moulds used for brass and nickel-brass, but in at least one works similar moulds are regularly used for the casting of pure nickel itself, which involves a temperature in the region of 1550°–1600° C.

Finally, I should like to support the very pithy remarks of Dr. Rohn with regard to cost. I am sure that anyone who has had experience with water-cooled copper moulds will agree that they really do work out definitely cheaper than the ordinary cast-iron moulds, when consideration is given to their enormously increased life.

Dr. **Rosenhain**: I should like, if I may, to make one explanatory remark. What I had to say about copper moulds did not refer to water-cooled moulds, but to solid moulds, which is quite a different matter.

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

Dr. J. C. Hudson * (Member): The author has published some interesting curves showing the temperature gradient in the walls of mild steel and cast-iron moulds. It is obvious that the problem is not solely one of thermal conductivity; but, on the other hand, I am not sure that these curves for 0·1 carbon steel and cast iron represent the best results that could be obtained with regard to thermal conductivity from ferrous materials. I should estimate that, taking into consideration the manganese and other elements present in 0·1 carbon steel, the iron content will be about 99·5 per cent. It should be possible, by using ingot iron and choosing the metal from the outer rim of the ingot, to provide a commercial material with an iron content of 99·9 per cent. or even higher, and I would suggest to the author that it might be of interest to try some experiments on a mould of this material, because it might be found to have a rather better thermal conductivity than mild steel or cast iron.

[*Note Added since the Meeting.*

The various data given in the International Critical Tables are rather conflicting, especially as the thermal conductivity varies with the temperature. I am indebted to the Armco International Corporation for the following data calculated from a report of the U.S. Bureau of Standards:

Thermal Conductivity at *Room Temperature* in B.T.U. per hr. per ft.^{2} per in. thickness per ° F. of Temperature Difference:—

Ingot iron	464
Mild steel	406
Cast iron	377

It will be seen that the data refer to room temperature. It must be admitted that the order may be reversed at mould temperatures, and, further, that the difference in the thermal conductivity of the three materials is small compared with that between any one of them and copper. The practical step is clearly to try out an actual ingot iron mould.]

CORRESPONDENCE.

The Author (*in reply to the discussion at the meeting*): The information which has been given by Mr. Smout and Mr. Barclay as to their practical experience with copper as a mould material is particularly valuable, and Mr. Smout's appreciative remarks concerning the value to industry of research work of this type are extremely encouraging to investigators.

Dr. Rosenhain made some interesting suggestions as to possible methods for treating steel moulds in order to prevent the warping trouble. One would have anticipated that the method of saw cutting the internal faces would perhaps give rise to some difficulties with the filling material, and the evidence of Dr. Rohn appears conclusive in confirming the reality of this difficulty from his practical experience of an identical method.

The second practical suggestion put forward by Dr. Rosenhain that "blowing" of cast iron may be largely reduced by a suitable decarburizing anneal has been tried with considerable, but not complete, success. The results of these experiments were omitted from the paper because of considerations of space. A machined grey cast-iron plate similar to that referred to in Table II, was annealed at 950° C. for 7 hrs. in oxide and the surface largely decarburized. On re-testing on the small-scale apparatus, the volume of gas evolved was only 0·06 c.c. This is a considerable improvement, but

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

it was found impossible to eliminate the "blowing" entirely, presumably owing to some porosity associated with the graphite, and it was felt, therefore, that further investigation was scarcely justified. The non-pearlitic iron to which Mr. Smout refers as having been too soft for practical purposes was included with a view to confirm or otherwise our theories as to the influence of pearlite, and was not put forward as a suggested material for use as an actual mould.

Dr. J. C. Hudson has suggested that I have not been fair to ferrous materials, in that I have tried only alloys with a comparatively low conductivity, and not a pure ingot iron. The figures for conductivity which he quotes show quite clearly, to my mind, such a small improvement in the conductivity of the ingot iron that practical trials of such a material would obviously not be worth while. In any case, one must remember that thermal conductivity and mould distortion are not the only considerations affecting the suitability of a mould material. I have referred to the difficulties of adhesion of brass to a special alloy steel mould, and this would apply likewise to ingot iron.

Professor Hutton mentioned two points which I should like, in conclusion, to emphasize. First, the fact that high-conductivity copper should be employed is of considerable importance, and it is a defect in the paper that this point is not more emphasized. Secondly, I agree with him entirely as to the finality or otherwise of this work. There is obviously a great deal more to be done, and I would not for one moment suggest that anything approaching the last word on the matter has been said in this paper.

Mr. I. E. GORSHKOV, Met.Eng.[*] (Member): Mr. Bailey's very interesting paper deals *inter alia* with the problems of formation of "blowing" in non-ferrous strip ingots and with the behaviour of the moulds during casting. Similar questions were touched on in our study carried out in 1927–28, the results of which were published early in 1932.[†]

Mr. Bailey associates the origin of "blowing" with a reaction between the carbon of the cast iron and oxides, whereas in our practice the occurrence of "blowing" was often observed when both cast-iron and copper moulds were used. Single observations, as well as a number of special experiments, have made us come to the conclusion that the above-mentioned reaction plays a secondary rôle.

The amounts of the gas adsorbed, the rate of its escape when heated, the speed of rise of the level of the metal during casting, properties of coating, &c., seem to be of greater importance in connection with the occurrence of "blowing."

By regulating the rate of rise of the level of the metal, with the coating chosen and other conditions of casting being constant, it is possible, without particular difficulty, to obtain sound ingots when casting even into cast-iron moulds. Many more difficulties are brought about on account of the liability of the latter to cracking on their inner surfaces. The coating matter, or simply air, accumulate in these cracks and give rise to "blowing" (see Fig. A, Plate XLIII).

The tendency of the moulds to deform readily when heated on one side only involves during casting a selective cooling of the middle portion of the ingot which causes the formation of an undershrinkage cavity and the retention of various oxide, slag, and gas inclusions in the lower part of the

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[†] "Moulds for Casting Non-Ferrous Ingots" (in Russian), *Metallurg (The Metallurgist)*, 1932, (1), 67–83.

FIG. A.

FIG. B.

[*To face p.* 232.

ingot. The upward exit of these inclusions is prevented by a previously crystallized metal "bridge," which is formed in the middle portion of the ingot. A photograph of such a shrinkage cavity has been given by Genders * for an ingot fixed in a state when a continuous "bridge" had not yet been formed. (Fig. B, Plate XLIII.)

As is generally known, the deformation of the ingot moulds during casting can be reduced by the use of alloys having low coefficients of thermal expansion, as well as by rational design of the moulds.

I regret that these two questions have not been considered by the author. It would be of great interest if some light could be cast on the question of the temperature gradients for moulds made of Invar. I should also like to have the author's considered opinion as to the design of the moulds for the production of sound strip ingots in the best way. As, however, this question is outside the scope of Mr. Bailey's present work, I hope that he will be able to express his opinion about it at a later date.

Herr OTTO JUNKER † (Member): As a manufacturer of moulds I should like to say how much I appreciate the comprehensive and profound research described in this paper. It will be most helpful in fighting the still numerous and widespread prejudices as to the effect of mould materials and mould construction on castings.

Speaking especially with regard to brass, the research has been carried out exclusively with small ingot sizes and weights, which may perhaps still be considered as the present standard of British and American ingots. On the Continent the brass ingot of 700–1400 lb. weight and 3–4 in. in thickness has become standard, and there is also a growing tendency to adopt these heavier weights in Great Britain and America, mostly in connection with the hot-rolling process. For these heavier ingots and for mass production the use of a *water-cooled* thin-walled copper-lined mould appears to be indispensable, for the following *practical* reasons:

(1) With uncooled copper moulds there is always the danger of warping of a split mould, if used for very long, thin ingots (as known in the U.S.A.) or for the standard 700–1400 lb. Continental brass ingot. This would be a serious drawback in a mass production foundry, requiring a high state of reliability for every part of the outfit.

(2) For larger casting units, uncooled copper moulds would get too warm to be used in the normal intervals of casting from the induction melting furnace. The temperature of 400° C. as indicated in Fig. 15 would be prohibitive for the usual types of dressing grease. It would not even be possible to use one mould per furnace, not to speak of the custom of using one mould per 2 or 3 furnaces, which is quite usual with water-cooled copper-lined moulds. An outstanding advantage of the cooled mould, *e.g.* to give the foundrymen freedom from heat radiation, would also be lost.

(3) For larger casting units solid copper moulds would be of considerable weight, which would make them difficult to handle.

(4) The danger of welding on to a wall of solid copper is not to be underrated even for brass. The temperature of a solid copper mould depends on the proportion, weight of hot-metal : weight of mould, which has practical limits for large casting units.

(5) It is much easier for the foundryman always to maintain exactly the same conditions for every casting with a water-cooled thin-walled mould than with a solid copper mould.

These are some practical conclusions which are not contradictory to Mr.

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* *J. Inst. Metals*, 1926, 35, Fig. 10, Plate XXXIII.

† Otto Junker G.m.b.H., Lammersdorf, Germany.

Bailey's conclusions, but which have been arrived at in accordance with his statements, which I can confirm so far as my own experience goes.

With regard to the casting of steel in water-cooled thin-walled copper moulds, I would cite the publications of Ortel,* and Hessenbruch and Bottenberg.†

Mr. J. G. PEARCE ‡ (Member): This paper is an interesting example of the value of direct attack on a problem created by new demands on material made by a long-established process. The demonstration that "blowing" arises from a carbide-oxide reaction is of particular interest, and appears quite sound. It is confirmed in a general way in, and indeed might have been predicted from, the malleable annealing process. It does not, however, explain the comparative immunity of white iron from "blowing," for it is probable that the white iron tested (Table II) was about half pearlite, although the analysis is not given.

The British Cast Iron Research Association, knowing that the present investigation was in progress, has not risked duplication by working on moulds for non-ferrous ingots. It appears, however, that justice has scarcely been done to the possibilities of cast-iron moulds. The material has various advantages referred to in the paper, and attempts to produce an improved cast iron might have yielded results much more satisfactory than those obtained from the types of ingot mould being made prior to 1927. This suggestion is strengthened by the disadvantage of greatly increased cost of copper and the complication in a melting shop of water cooling. Furthermore, it is clear that the copper mould has little influence on the structure and soundness of the ingots or on the time of solidification.

From other considerations it has been obvious for some time to the British Cast Iron Research Association that ingot moulds should have a structure as uniform and homogeneous as possible, such, for instance, as is offered by an all-pearlitic structure. In view of the small amounts of "blowing" arising from a ferrite/coarse-graphite iron such as is shown in Fig. 8, a logical extension of the author's argument would suggest the desirability of trying a ferrite/fine-graphite iron. The heat-resisting iron developed by the British Cast Iron Research Association known as Silal ‖ has this structure, although for ingot mould purposes it would be desirable to obtain a similar structure with a lower silicon content than is used in commercially made Silal. This material is wholly ferrite/fine-graphite. It has practically no elastic properties, but a further development of this, known as Nicrosilal,§ has an appreciable measure of ductility in the cold. This iron is austenitic, and would be likely to obviate troubles experienced due to the presence of carbide and to the presence of a pearlitic constitutional change point. The thermal conductivity of these irons is slightly less than that of ordinary grey iron, but the resistance offered to breakdown due to heat would probably more than offset this disadvantage.

The author mentions that information at his disposal did not permit correlation of life with composition. It is well known that there is no correlation between mould life and composition for ingot moulds, and this explains the range of compositions used in ingot mould practice.

The AUTHOR (*in reply*): With Herr Junker's remarks I am, in general, in

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* *Stahl u. Eisen*, 1929, **49**, 696–700.

† *Mitt. K.-W. Inst. Eisenforschung*, 1931, **13**, 205–213.

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

‖ Norbury and Morgan, "The Effect of Carbon and Silicon on the Growth and Scaling of Grey Cast Iron," *J. Iron Steel Inst.*, 1931, **123**, 413.

§ Norbury and Morgan, "Nickel-Chromium-Silicon Cast Irons," *J. Iron Steel Inst.*, 1932, **125**, 393–424.

agreement. I have, however, rather deliberately avoided in this paper a consideration of the relative merits of solid and water-cooled moulds. I have been endeavouring rather to investigate the actual properties of particular metals with a view to their application to the manufacture of ingot moulds. I have avoided discussion as to methods of application, not because I do not realize the importance of this question, but because each particular case needs consideration on its merits, and the question is rather a mechanical than a metallurgical one.

I was interested to read Mr. Pearce's communication, realizing fully that it is wise to examine new materials as they are put forward. Through the courtesy of the British Cast Iron Research Association, I have, since presenting the paper, had the opportunity of testing the " blowing " characteristics of some small samples of the special irons to which he refers. Nicrosilal is promising, but even if it proves satisfactory in this respect, the temperature gradients in such materials will be at least as serious as with ordinary grey iron, and this may still have an adverse influence on their suitability. This matter again, however, is one we shall be glad to investigate. I can scarcely agree with Mr. Pearce's remark that my figures in Table II show the comparative immunity of white iron from " blowing." Certainly under equivalent conditions the volume of gas holes in the brass disc was for the white iron only about half that for grey iron, but this method of measurement is admittedly rough, and the amount of gas evolved from the white iron was considerable and serious from the point of view in question.

I am interested in Mr. Gorshkov's remarks, and agree with him up to the point that the reaction I suggest is not the sole cause of " blowing." I do consider it the primary cause, but feel quite certain, with Mr. Gorshkov, that cavities in the ingot surface such as cracks, &c., which are full of gas before casting, will produce a similar defect. The question of the design of moulds is quite outside the scope of the present work. The use of materials such as Invar does not appear to me to be promising. The thermal conductivity of Invar is extremely low, and the higher temperature gradients would to a great extent neutralise possible advantages resulting from its low coefficient of thermal expansion. In any case, Invar has a low coefficient of expansion only at low temperatures—above about 400° C. its expansion is actually somewhat greater than that of grey cast irons.

THE PROPERTIES OF COMMERCIAL VARIETIES OF COPPER AT HIGH TEMPERATURES.*

By T. G. BAMFORD,† M.Sc., MEMBER.

SYNOPSIS.

Certain properties of five typical commercial varieties of copper have been investigated at elevated temperatures. It is shown that although there is a decline in resistance to alternating stresses, at 200°–300° C., there is no brittle range of temperature in copper. Of the varieties tested deoxidized nickel–copper has the best resistance to alternating stresses and has exceptionally good properties in this respect at 560° C.

WHILST much work has been published dealing with the tensile properties of copper at elevated temperatures,[1, 2, 3, 4, 5] little information is available regarding the impact strength, the resistance to alternating stresses, and the hardness [6] at high temperatures of commercial coppers of known composition. These properties are, however, of importance not only as influencing the service value of the metal, but also as affecting its susceptibility to damage when being handled in the mill. It has been stated that there is a black brittle range in copper. Instances were quoted to the author of copper tubes which after annealing had broken up if hammered when cooling through a black heat. If a particular variety of copper develops brittleness when cooling through a range of temperature, then a low impact strength would be anticipated at this temperature. If plastic deformation at a certain temperature be productive of brittleness, then it seems likely that alternating stresses exceeding the elastic limit would cause fracture within a short space of time. It was decided, therefore, in the present research to carry out alternating stress tests up to temperatures as high as might be permitted by the behaviour of the metal. Izod impact tests of copper frequently result in bent but unfractured test-pieces, making it difficult to compare the amount of energy absorbed in breaking coppers at various temperatures. The Charpy test was

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* Manuscript received May 18, 1932. Presented at the Annual Autumn Meeting, London, September 14, 1932.

† Principal, County Technical College, Wednesbury.

used instead of the Izod test. Hardness measurements were taken on the Herbert Pendulum hardness testing machine. It was not found possible to obtain consistent values at temperatures much above 325° C., but as this is stated by Hudson, Ball, and Bucknall [7] to be the maximum surface temperature attained by stayheads in the locomotive firebox, it was thought that the information obtained would be of value.

EXPERIMENTAL WORK.

The metal tested was all supplied in the form of rods 0·700 in. in diameter, made as described in a previous paper,[8] except that lot B was extruded to ¾ in. and lots A, C, D, and E to ⅞ in. All lots were drawn cold to 0·73 in., annealed at 600° C. for 20 minutes, and then drawn cold to 0·70 in. in diameter. The analyses are given in Table I. The microstructures were quite normal in each case.

TABLE I.—*Analyses of the Copper Rods used in the Research.*

Variety of Copper Tested.	Lot.	Arsenic. Per cent.	Nickel. Per cent.	Oxygen. Per cent.	Phosphorus. Per cent.	Iron. Per cent.	Bismuth. Per cent.	Lead. Per cent.	Tin. Per cent.
Deoxidized non-arsenical	A	nil	nil	0·004	0·04	trace	nil	trace	nil
Deoxidized arsenical .	B	0·43	0·05	0·002	0·04	nil	nil	0·01	nil
Nickel–copper	C	trace	1·72	0·010	0·03	trace	0·0005	trace	nil
Tough-pitch arsenical .	D	0·46	0·02	0·060	nil	nil	0·0005	0·04	nil
Tough-pitch non-arsenical	E	nil	nil	0·063	nil	trace	0·0005	trace	nil

Alternating Stress Tests.

The alternating stress tests were carried out on the Amsler rotary bend testing machine, a photograph of which is shown in Fig. 12 of the previous paper.[8] The test-pieces were, however, lengthened so that the load acted at a distance of 5·375 in. from the section of fracture where the diameter was 0·517 in. A small silica tube electrical furnace 4 in. long was used for heating the test-bars, the temperature of which was measured by means of a platinum/platinum–rhodium thermocouple attached very loosely to them by means of fine iron hair wires, so that the bars could rotate freely without damaging the couple. Using a constant voltage of electricity from large accumulators, it was possible to maintain temperatures which varied less than ± 10° C. throughout any test.

The large ball races of the machine were lubricated by a gravity oil feed and the test-bars were gripped in special spring grips made of high-speed steel.

Preliminary tests were carried out at room temperature and also at high temperatures in order to select for each variety of copper a suitable stress which could be used over the range of temperature investigated. Details of the preliminary experiments at 20° C. are given in Table II.

TABLE II.—*Wöhler Tests Carried Out on the Amsler Machine at 20° C.*

Speed of Revolution of Bars, 1760 r.p.m. Test-Bars 10 in. long, turned over a length of 4 in. to a Diameter of 0·517 in.

Lot A.		Lot B.		Lot C.		Lot D.		Lot E.	
Stress. Tons/in.^{2}.	Revolutions to Fracture. $\times 10^3$.	Stress. Tons/in.^{2}.	Revolutions to Fracture. $\times 10^3$.	Stress. Tons/in.^{2}.	Revolutions to Fracture. $\times 10^3$.	Stress. Tons/in.^{2}.	Revolutions to Fracture. $\times 10^3$.	Stress. Tons/in.^{2}.	Revolutions to Fracture. $\times 10^3$.
7·81	234	7·03	2,104	8·02	769				
7·03	531	7·03	2,170	7·81	2,442	7·03	2,540	7·81	1,467
6·86	771	6·64	6,404	7·81	3,673	7·03	2,540	6·42	3,073
6·64	1,895					6·64	9,761	5·64	4,913
6·64	1,455					6·64	9,200	5·25	10,190
6·57	4,368								

The results of the constant stress tests at higher temperatures are given in Table III and are plotted in Fig. 1.

The author was appointed to another post while the research was in progress, and this section of the work had to be discontinued before sufficient results could be obtained to enable general conclusions to be reached regarding the behaviour of copper throughout the entire range of temperature under investigation. It is with some diffidence that the curves are plotted, as it is realized that more evidence must be obtained before it can be decided how far their shape may be regarded as characteristic of the particular varieties tested. It is felt, however, that sufficient evidence has been obtained to enable certain conclusions of importance to be reached from them, and as no similar work has been published elsewhere, it was thought desirable that they should be included in the paper. They provide qualitative data regarding the resistance to rapidly applied alternating stresses, but do not, of course, necessarily indicate the relative changes in the fatigue limits of the materials.

The stresses used in the tests are of equal values in the case of the two non-arsenical coppers; they are of equal but higher values in the case of the two arsenical varieties. For Lot C a still greater stress

TABLE III.—*Wöhler Tests Carried Out on the Amsler Machine at High Temperatures at Constant Stresses for Each Lot.*

Lot A.		Lot B.		Lot C.		Lot D.		Lot E.	
Stress 6·57 tons/in.².		Stress 7·03 tons/in.².		Stress 7·81 tons/in.².		Stress 7·03 tons/in.².		Stress 6·57 tons/in.²	
Temperature. ° C.	Revolutions to Fracture. × 10³.	Temperature. ° C.	Revolutions to Fracture. × 10³.	Temperature. ° C.	Revolutions to Fracture. × 10³.	Temperature. ° C.	Revolutions to Fracture. × 10³.	Temperature. ° C.	Revolutions to Fracture. × 10³.
20	4367	20	2104	20	3673	20	2340	20	
115	842	180	1225	130	357	190	1814	125	657
130	566	230	786	130	501	250	648	180	472
130	456	250	647	140	379	300	283	225	177
130	454	280	332	180	3037	350	673	255	324
				190	892				
130	458	310	367	210	231	400	660	310	149
170	594	375	403	250	321	470	202	470	227
180	293	470*	60	290	642	550	440	550	118
250	521	510	390	340	1732	600	35		
275	739			380	1270				
340	2408			480	314				
360	1100			480	316				
				530	1059				
380	740			540	2045				
				550	2600				
470	315			560	9600				
540	232			620	230				
580	248								
615	112								

* See p. 241.

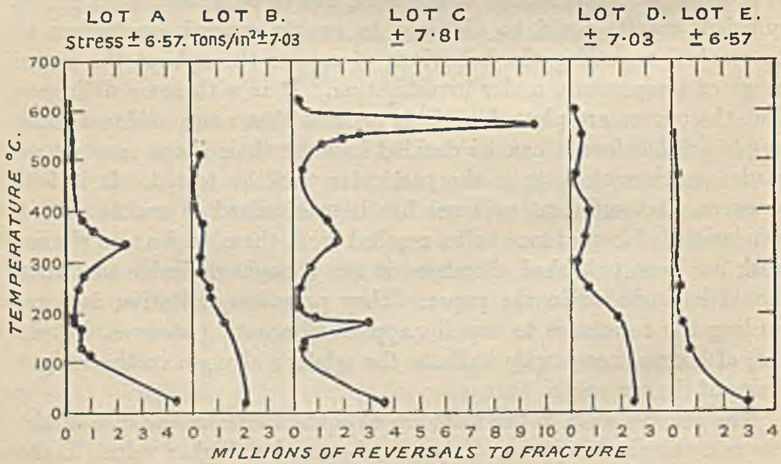

FIG. 1.—Wöhler Tests at High Temperatures.

PLATE XLIV.

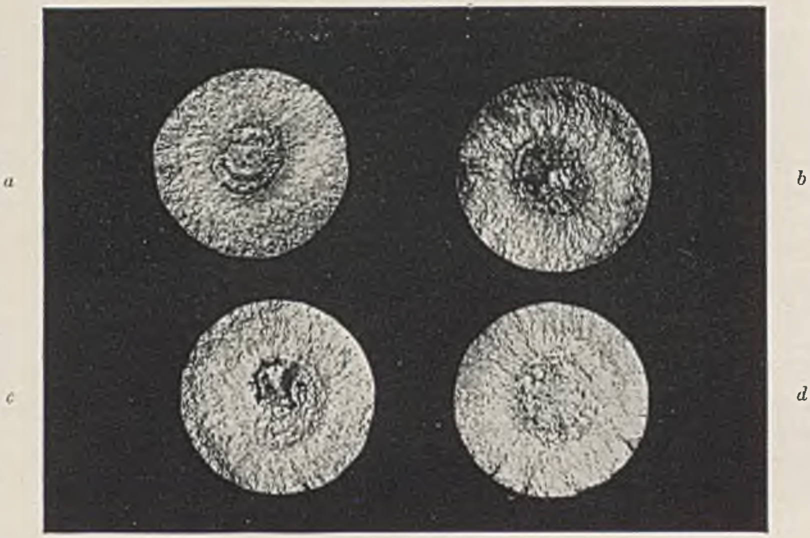

FIG. 2.—(*a*) Deoxidized Non-Arsenical–Copper at 180° C. (*b*) Nickel–Copper at 210° C. (*c*) Nickel–Copper at 480° C. (*d*) Nickel–Copper at 530° C.

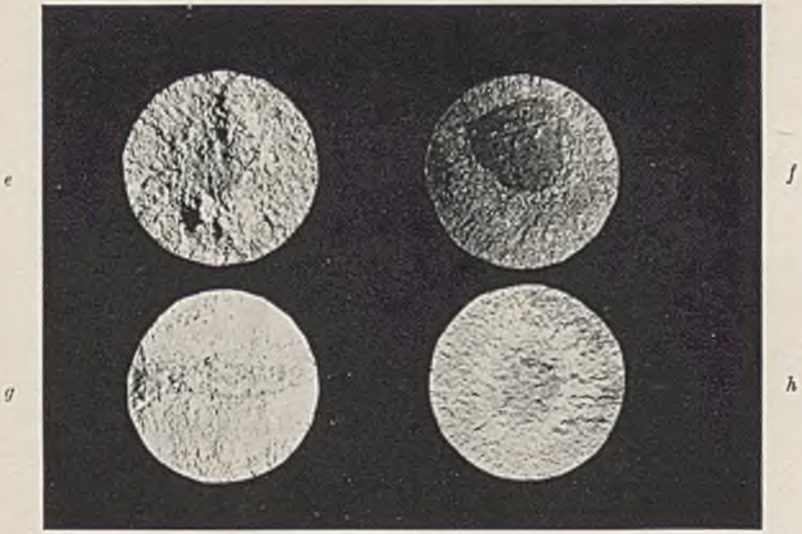

FIG. 3.—Tough-Pitch Arsenical-Copper at 600° C. (*e*) Stress, 6·64 tons/in.^{2}. (*f*) Stress, 6·25 tons/in.^{2}. (*g*) Stress, 5·47 tons/in.^{2}. (*h*) Stress, 4·69 tons/in.^{2}.

Fractured Surfaces of Test-Bars used in Amsler Machine. × 2.

[*To face p.* 240.

was used. These stresses are, of course, in all cases in excess of the endurance limits, and will exceed these limits by amounts which differ from lot to lot. It is, however, a characteristic feature of all the curves that in the neighbourhood of 200°–300° C. the number of revolutions to fracture is much less than at room temperature. It can therefore be regarded as established that, in this temperature range, under stresses exceeding the endurance limit, commercial copper develops a reduced resistance to alternating stresses.

Lot C shows a marked recovery at higher temperatures, and with the exception of the single point at 340° C. obtained with the A series the nickel–copper at all temperatures above 300° C. shows more revolutions to fracture than do the other varieties. As the stress applied to the C bars is some 10 per cent. greater than that used in the B and D tests, and is nearly 20 per cent. greater than that applied to the A and E series, it may be concluded that at all temperatures above 300° C. the nickel–copper is more capable of withstanding alternating stresses than are the other varieties tested.

At 560° C. the nickel–copper withstands 9,600,000 revolutions to fracture. This compares with 3,673,000 revolutions at room temperatures. A Lot C test at 550° C. withstood 2,600,000 revolutions, which is a greater number than that obtaining with any other variety at any temperature above atmospheric.

In the neighbourhood of 560° C., clearly, nickel–copper is remarkably resistant to alternating stresses.

At the highest temperature at which each variety of copper was tested difficulty was experienced in preserving continuous smooth running. In certain cases the bars developed a tendency to oscillate violently for short periods. In one case—that of Lot B tested at 470° C.—the bar bent over considerably, but apparently was able to yield readily to the stress reversals, as it ran quite smoothly until fracture occurred.

Violent oscillation was particularly noticeable with Lot D, tested at 600° C. A series of tests was run at this temperature at successively reduced stresses. The results are detailed in Table IV. They serve to show that, under the reduced but still quite reasonably high stress of 4·69 tons/in.^{2}, smooth running is possible and the metal has very considerable resistance to alternating stresses.

The various coppers used in the research were examined under the microscope both before and after etching. The results revealed were normal, and are not, therefore, reproduced. After fracture in the Amsler machine no change in general structure was noticed in rods the fractured surfaces of which were polished and etched. The fractured

Table IV.—*Wöhler Tests at* 600° *C. on Lot D.*

Stress. Tons/in.^{2}.	Number of Revolutions.	Remarks
7·03	35,000	Bar shook badly before breaking.
6·64	177,200	,, ,, ,, ,, ,,
6·25	155,000	,, ,, ,, ,, ,,
5·47	416,600	Bar broke after steady running.
5·08	235,500	Bar developed periodical vibrationary periods.
4·69	442,400	Bar unbroken, but ran steadily.
4·69	1,085,300	Bar broke after steady running.

surfaces themselves, however, differed considerably according to the temperature of test.

There is a quite definite correlation between the deductions which follow from an examination of the curves shown in Fig. 1 and of the surfaces of the broken test-bars.

A temperature of minimum endurance is evidenced by the existence of torn-out pieces of metal in the centre of the bars. This point is illustrated in Fig. 2, a, b, c (Plate XLIV). At 530° C. the curve is well past the minimum point (Fig. 1, Lot C), and the character of the fracture shows a marked change. The smoother central area and fine radial cracks characteristic of the bars tested at 20° C. are again discernible. The “ tough-pitch ” arsenical–copper, Lot D, tested at 600° C. under a stress of 6·64 tons/in.^{2}, is very badly torn indeed—(Fig. 3 *e*, Plate XLIV), but as the testing load is decreased the fracture becomes smoother. The bar tested at 600° C. under a stress of 4·69 tons/in.^{2} broke with a fracture (Fig. 3 *h*) again more closely resembling the normal fatigue fracture.

Charpy Tests.

The test-pieces, which were of the standard size for the smaller machine which was available for this research, were heated in an electric furnace to slightly above the temperature required for the test. They were then placed on the anvil and their temperature was noted at the time of fracture. The temperature was determined by the use of a fine Chromel–Alumel thermocouple inserted in the slot of the test-pieces which were covered with asbestos sleeves, to reduce chilling effect from the anvil. The results obtained are plotted in Fig. 4.

No decline in impact strength corresponding with the reduction in resistance to alternating stresses takes place at temperatures below 300° C. Except in case of Lot A—deoxidized non-arsenical copper—which has the highest impact value at room temperature, the strength rises sharply to maxima points in the neighbourhood of 300° C.

In all cases the Charpy figure decreases, rapidly for about 100° C. in the region commencing at 300°–350° C., and remains thereafter substantially constant until 600° C., subsequently falling to less than 30 ft.-lb., above this temperature. The two "tough-pitch" varieties Lots D and E are both weaker throughout the entire range of temperature than the three deoxidized lots, and Lot D—"tough-pitch" arsenical copper—has very low impact strength at all temperatures above 350° C.

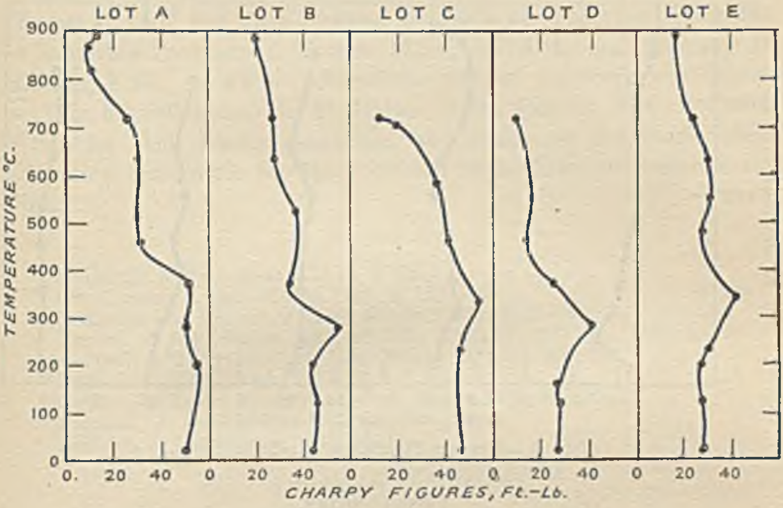

Fig. 4.—Charpy Tests at High Temperatures.

Hardness Tests.

The tests were carried out on the Herbert Pendulum hardness tester described by Sandifer in a recent paper.[9] The 1-mm. steel ball was used, the oscillations with the diamond proving unsuitable by reason of the softness of the metal tested. In every case the standard time test was taken, and the values given represent the time for ten swings of the pendulum. The machine was standardized on glass, which is assumed to have the value 100—readings on glass being taken after every test on the copper. In this way, in each lot tested, the upper limit of temperature for which reliable figures could be obtained, was found. The formation of oxide scale was the chief factor which interfered with the value of tests above about 350° C., although the softening of the ball began to evidence itself above this temperature. The values obtained are plotted in Fig. 5. The total time taken in heating the specimen during a test was about 90 minutes. After recooling, check hardness determinations were taken. In all cases the specimens returned to the hardness figures prevailing before testing.

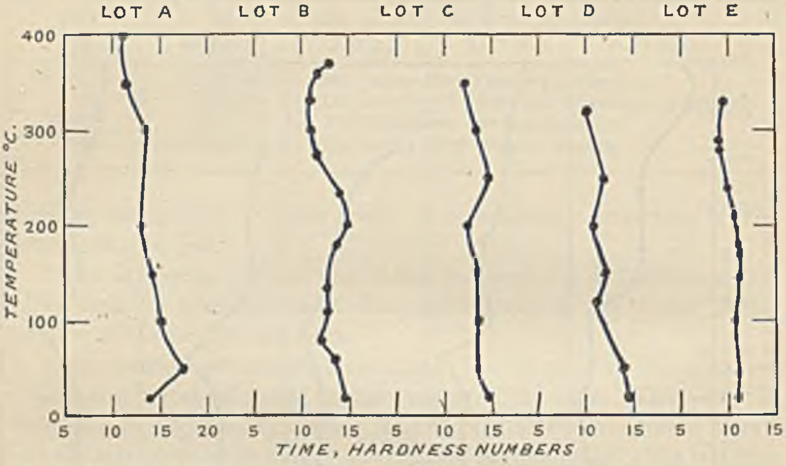

Fig. 5.—Herbert Pendulum Hardness Tests.

Conclusions.

The following conclusions are reached regarding the properties of typical varieties of copper tested at high temperatures:

(1) There is no evidence of the existence of a black brittle range below 600° C.

(2) The impact strength as shown by the Charpy test, develops maximum values in the region 200°–340° C., after which it declines sharply.

Except in the case of the "tough-pitch" arsenical-copper, which is weak at all temperatures above 400° C., quite good impact strength is, however, maintained at all temperatures up to 600° C.

(3) Under alternating stresses exceeding the endurance limit generally speaking the nickel–copper has the greatest, and the "tough pitch" non-arsenical copper the least, endurance. There is in all cases a lowering of endurance in the region of 200°–300° C. The nickel–copper shows a marked recovery at higher temperatures, and is much superior to other varieties in this respect at all temperatures tested above 300° C. It shows an exceptionally high resistance to such stresses at 560° C.

(4) The "tough-pitch" non-arsenical copper is, throughout the temperature range investigated, much softer than the other varieties of copper. The hardness of the deoxidized non-arsenical–copper first

increases with rise of temperature and between 50° C. and 150° C. it is harder than any one of the other varieties.

ACKNOWLEDGMENTS.

The author desires to express his thanks to Messrs. Elliott's Metal Company, Ltd., for their renewed courtesy in supplying the metal, to Emeritus Professor T. Turner, M.Sc., A.R.S.M., and Professor D. Hanson, D.Sc., in whose laboratories part of the work was carried out; to his colleagues, Mr. H. Harris, M.Sc., and Mr. E. C. Rollason, M.Sc., for their kindly assistance, and finally to the Staffordshire Education Committee for the provision of facilities to complete the work.

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CORRESPONDENCE.

DR. F. JOHNSON* (Member): I have read Mr. Bamford's paper with much interest and appreciation. I wish to congratulate the author on having made complete analyses of the materials examined in the research. The determination of the oxygen content is particularly important. I should be glad if the author would cite the reference in support of the quoted statement that "there is a black brittle range in copper."

It would also add to the value of the paper if he would describe the method which he adopted for carrying out alternating tests at high temperatures, and also indicate how many tests were made at each temperature. Other points on which further information would be welcomed are (*a*) the structural appearance and distribution of cuprous oxide in the arsenical and non-arsenical copper used; (*b*) the reason for preferring Charpy to Izod impact tests, in view of the greater discrimination claimed for the latter; (*c*) the variation in grain-size shown by the different materials tested; and (*d*) the degree of segregation, if any, of cuprous oxide in the materials tested.

The AUTHOR (*in reply*): I thank Dr. Johnson for his courteous and helpful contribution. The statements regarding a brittle range in copper were private ones made to me by the late Sir Gerard Muntz and others. It is interesting to note, however, that at a joint meeting of the Manchester Metallurgical Society and of the Institute of Metals held in Manchester on October 19, 1932, both Mr. N. S. F. Hubbard and Mr. C. Davies quoted instances of black brittleness in copper. In those cases no connection could be traced between composition and brittleness. Detailed analyses of three lots

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of nickel–copper locomotive tubes found to be brittle in black-hot flattening showed no analytical feature to distinguish them from three others that stood up satisfactorily to the test.

Mr. C. A. Davies in his observations at Manchester stated that "rate of cooling" was the factor which promoted this black brittleness. He had noticed that, in a bundle of annealed sheets, those near the outside, which were cooled rapidly, became quite brittle at a black heat, whilst the others that cooled more slowly were quite normal.

Regarding Dr. Johnson's second point—the tests were carried out by means of the Amsler machine previously described.* The test-bars were, however, gripped at the ends in a collet made of tungsten steel supported at one end of the machine. In this way it was possible to lengthen the test-pieces and to provide room for the small 4-in. silica tube electric furnace. Regarding the number of alternating stress tests at each temperature—whilst the quantity of metal available did not permit of duplication throughout, important points were generally confirmed often by triplicate tests or by successive tests at nearby temperatures. Charpy tests were preferred for the reason stated on page 237 of the paper.

With regard to microstructure—the grain-size was quite normal and similar for all the lots. The oxide was rather finer than usual and very little segregation could be detected. In the non-arsenical "tough-pitch" variety it was remarkably uniform both in size and distribution.

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* *J. Inst. Metals*, 1925, 33, 167.

THE EFFECT OF DIFFERENT ELEMENTS ON THE ANNEALING AND GRAIN-GROWTH CHARACTERISTICS OF ALPHA BRASS.*

By MAURICE COOK,† M.Sc., Ph.D., Member, and HERBERT J. MILLER,‡ M.Sc., Member.

Synopsis.

An examination has been made of the effect of additions of iron, phosphorus, manganese, and aluminium separately and of aluminium with nickel, and aluminium with silicon, on the annealing characteristics of alpha brass by determining diamond pyramid hardness values and making grain-size measurements on cold-rolled alloys annealed at various temperatures, while the tensile properties on a number of alloys representative of the various series investigated have also been studied. Some of the elements added have the effect of increasing the intrinsic hardness of brass and of raising the temperature of softening and recrystallization, but all exert a retarding influence on the annealing process subsequent to the initial softening, the extent of which varies with the nature and amount of the addition. This retarding influence, which markedly affects grain-growth as well as the physical properties, is shown as a deflection on curves connecting hardness values and tensile properties with annealing temperature.

Introduction.

The changes which take place in hard-worked metals on heating at various temperatures for different periods of time have been the subject of a considerable amount of study, and many investigations have been published dealing with these changes in a wide variety of alloys. Recrystallization and grain-growth phenomena in brasses have been studied more especially by C. H. Mathewson and A. Phillips,[1] A. Phillips and G. C. Gerner,[2] W. H. Bassett and C. H. Davies,[3] F. G. Smith,[4] C. Upthegrove and W. G. Harbert,[5] A. Bass and R. Glocker,[6] A. Wittneben,[7] F. Ostermann,[8] R. Glocker and O. Weinbaum,[9] and F. Eugène.[10] In these several investigations the effect of the various factors influencing the temperature of recrystallization and resulting hardness and grain-size has been very comprehensively studied. The annealing or softening

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curve of a pure alloy derived from hardness values obtained after annealing for some predetermined time at different temperatures is comparatively simple and is of a common type for many pure metals and homogeneous solid solution alloys. Up to the temperature at which recrystallization commences the hardness values change but little, although in some cases there appears to be a slight increase in hardness after heating to temperatures below the recrystallization temperature. When recrystallization commences the softening proceeds and the hardness curve falls very steeply, after which it again flattens out and the decrease in hardness with increased annealing temperature becomes relatively slight.

In the course of investigations, with which the authors have been associated over a period of several years, involving a study of the effect of additions of different alloying elements to brasses of various types, but more especially α-brasses, it has been observed that the simple form of softening curve of the straight brasses was appreciably modified by many of these additions. Whilst the peculiarities which have been noted in this connection have not been exhaustively investigated, they appear to be of sufficient interest to justify description. During the course of the investigations different properties and various characteristics of a wide range of alloys have been studied, but the present paper deals exclusively with the annealing characteristics of a few only of the alloys examined. Alloys containing additions of the following have been studied :—

(*a*) Iron.
(*b*) Phosphorus.
(*c*) Manganese.
(*d*) Aluminium.
(*e*) Aluminium and nickel.
(*f*) Aluminium and silicon.

EXPERIMENTAL PROCEDURE.

The alloys used were cast in the form of commercial strip ingots, cold-rolled in accordance with normal manufacturing operations and finished to a final thickness of 0·125 in. by 50 per cent. reduction in thickness subsequent to the last anneal. From strips of this thickness small square specimens were cut and annealed in an electric resistance muffle for 30-minute periods. After annealing, the specimens were withdrawn from the furnace, allowed to cool in air, and their diamond pyramid hardnesses determined using a 10-kg. load and the standard 136° diamond indenting tool. The microstructures of the annealed samples were also examined and grain-size values recorded. For obtaining data to show the effect of annealing temperature on tensile strength and elongation values larger specimens cut from the same strips were used. The compositions of a number of representative alloys which have been examined in detail are given in Table I (Appendix). The specially added elements produced, to varying degrees, the abnormality in the softening curve which has been referred to, but only the results obtained with one element—namely, iron—will be described in detail as an example.

EFFECT OF IRON.

The effect of the addition of iron to 70 : 30 brass was studied on a series of six alloys, Nos. F7 to F12, in which the iron content varied from 0·01 to 0·49 per cent. The grain-size and hardness of samples of different members of this series at a thickness of 0·125 in. and after annealing for half-hour periods at various temperatures from 220° up to 800° C. are detailed in Table II (Appendix) and illustrated in Fig. 1. It will be seen from this figure that as the iron content increases the annealing or softening curve progressively differs in form from that which characterizes the straight 70 : 30 alloy. Instead of the hardness falling away progressively after softening has once commenced, the addition of iron results in a breaking of the continuity of this slope, producing a bulge which corresponds with a delayed softening. In four of the alloys—that is, with an iron content of up to 0·24 per cent.—the softening effected by annealing at 800° C. is substantially the same in all cases, but with the last member of the series containing 0·49 per cent. of iron the hardness reached on this annealing is appreciably higher. It will further be noted from Fig. 1 that whilst the addition of iron produces a marked retardation in softening on annealing of 70 : 30 brass, the initial softening temperature is not notably altered. In addition to the effect on the hardness, the presence of iron retards grain-growth. The curves connecting grain-size and annealing temperature for different members of the iron series are illustrated in Fig. 1.

In the softening curve for the alloy containing 0·49 per cent. of iron (see Fig. 1) a bulge occurs between temperatures of approximately 400° and 700° C. If from 400° C. the curve were continued normally downwards until it met the remaining portion at about 700° C. a typically smooth softening curve would result. In this range of temperature the grain-growth of "straight" brass is quite progressive. On the other hand, in the brass containing iron the grain-size at 400° C. is much smaller than in the "straight" brass, and moreover when the annealing is carried out at 500° C. and 610° C. the extent of grain-growth is almost negligible. Afterwards, however, at higher temperatures when the curve becomes normal, grain-growth proceeds. This effect of iron, which is typical of the other elements also, on grain-size and growth, is shown effectively by a comparison of Figs. 2, 4, 6, and 8, with Figs. 3, 5, 7, and 9 (Plates XLV and XLVI), which illustrate the microstructures of a straight 70 : 30 brass and brass containing 0·49 per cent. of iron after annealing for half-hour periods at 400°, 500°, 610°, and 700° C. After cold-working and complete annealing 70 : 30 brass containing this amount of iron appeared microscopically to be a homogeneous solid solution.

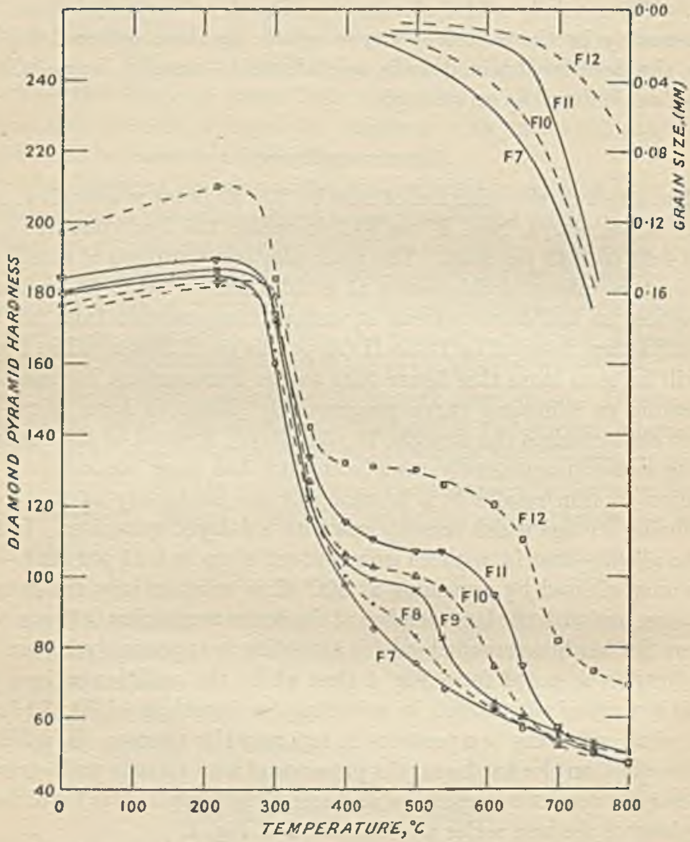

FIG. 1.—Annealing and Grain-Growth Curves of Brasses containing Additions of Iron.

EFFECT OF OTHER ELEMENTS.

Additions of phosphorus, manganese, aluminium, aluminium plus nickel, and aluminium plus silicon, all effect retardation of the softening and grain-growth and also raise the initial softening temperature. In many instances the intrinsic hardness of the alloy is also increased. In

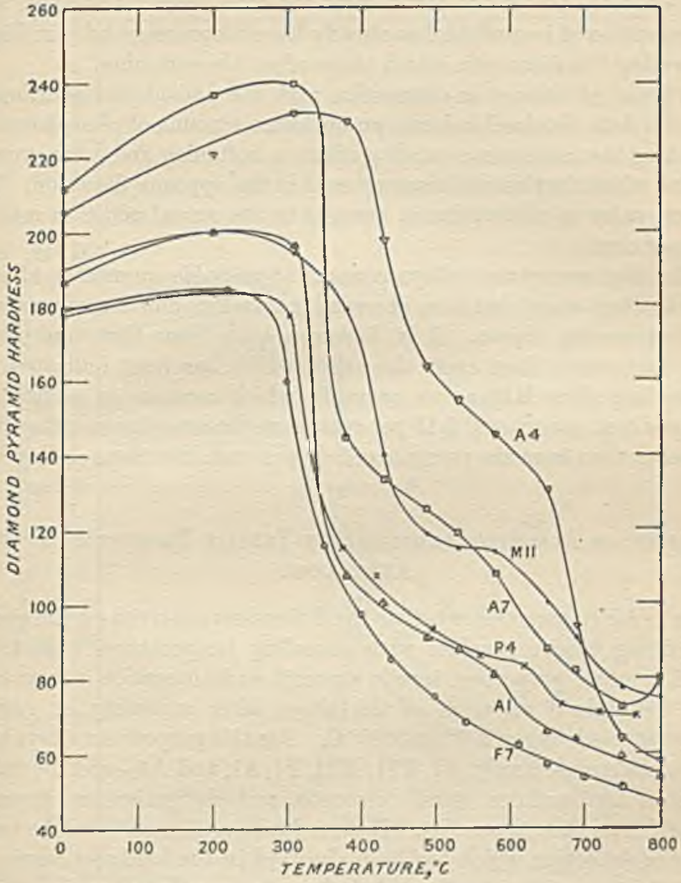

FIG. 10.—Annealing Curves of Brasses containing Additions of Various Elements.

F7. Straight 70 : 30 Brass.
P4. Brass containing 0·04% Phosphorus.
M11. Brass containing 9·00% Manganese.
A1. Brass containing 2·45% Aluminium.
A4. Brass containing 1·62% Aluminium and 2·15% Nickel.
A7. Brass containing 2·38% Aluminium and 1·18% Silicon.

Tables III–VI (Appendix) are given the results obtained with some brasses containing additions of these elements. With any of the elements considered the effect increases in extent with the amount of the addition, as in the case of iron. In Fig. 10 are shown curves of one alloy only of each of the series containing the special additions, with the exception of iron which has already been shown more fully in Fig. 1, illustrating the manner in which these affect the softening.

A point of interest in connection with the phosphorus additions is that the data obtained indicate an optimum amount of phosphorus for obtaining the maximum retarding effect on softening and grain-growth, beyond which further additions operate in the opposite direction. The nearest value to this optimum amount in the actual addition made is 0·04 per cent.

The high-manganese alloys contain appreciable quantities of iron, and the effect which has been observed is therefore due in some measure to the presence of iron. It is, however, quite clear that, apart from iron, manganese does exert the effect which has been indicated, for taking the alloy M10 as an example, which contains in addition to 4·95 per cent. manganese 0·15 per cent. iron, the retardation of hardness is greater than from the presence of 0·15 per cent. iron alone—alloy F10.

EFFECT OF ALLOYING ADDITIONS ON TENSILE PROPERTIES AFTER ANNEALING.

In order to ascertain whether the deflections observed on the curves correlating hardness values with annealing temperatures were to be found in other properties, tensile strength and elongation values have been determined on some of the alloys after annealing at various temperatures between 200° and 800° C. For this purpose six alloys have been examined—namely, F7, F11, M11, P4, A1, and A4—and the values obtained for hardness, tensile strength, and elongation are given in Table VII (p. 260, Appendix). If these data are plotted, it will be noted that the deflection which has been observed in the hardness curve due to the presence of specially added elements is reflected in the curves connecting both tensile strength and elongation values with annealing temperature. This is a result which from a consideration of the nature of the annealing curves would be expected. In Fig. 11 are shown curves connecting tensile strength, elongation, and hardness values with annealing for a "straight" 70 : 30 brass and a 70 : 30 brass containing 0·24 per cent. iron. The retarding effect of the iron addition in the annealing process is clearly shown by a direct comparison of the two series of curves.

GENERAL CONSIDERATIONS.

The results which have been obtained do not of themselves indicate the cause or causes which have given rise to the effects which have been noted. The increase in intrinsic hardness of brass caused by some of the additions does not call for any special comment, for this is quite a common effect, which is met with in many alloys. The raising of the softening temperature is not an uncommon result. The outstanding point of interest is the deflection from the normal shape of the annealing

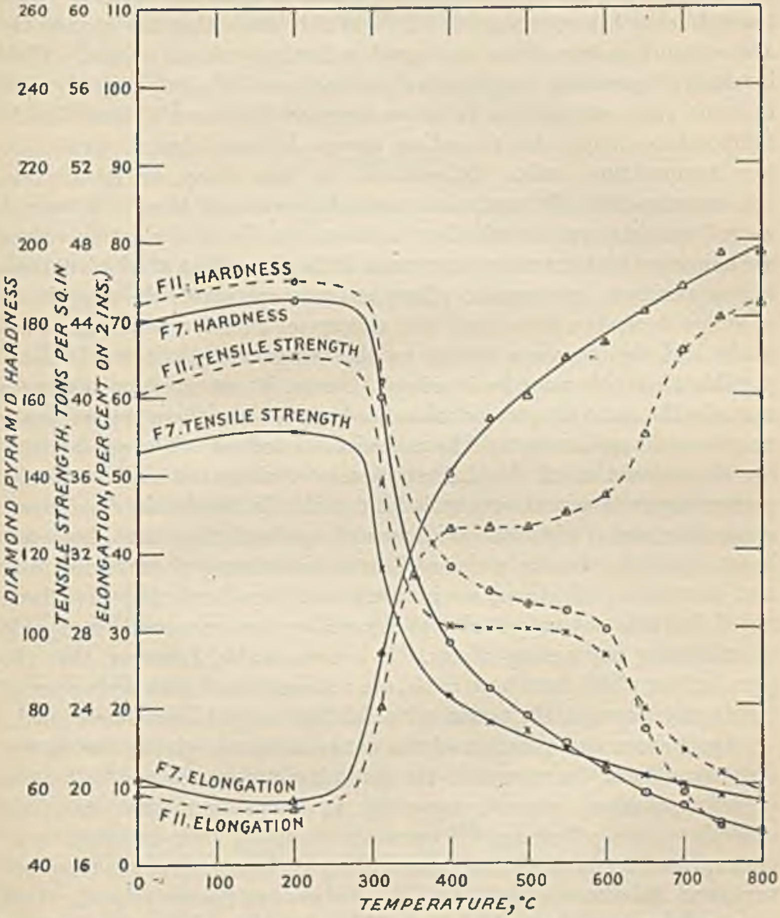

FIG. 11.—Tensile and Hardness Values of Straight 70 : 30 Brass (F7) and Brass containing 0·24% Iron (F11) Annealed 30 Minutes at Different Temperatures.

curves, whether they relate to hardness or tensile strength, after initial softening and recrystallization have commenced. Consideration of these curves shows that apart, as already indicated, from possibly increased intrinsic hardness and also somewhat raised softening temperature, all the alloys have behaved similarly up to the point at which the softening has commenced. It is at this stage that the apparently abnormal departure from the usual softening process occurs. With increase in annealing temperature the hardness falls only slightly, and in some cases retardation is so pronounced that over a considerable temperature range the annealing curves become almost parallel to the temperature axis. Subsequent to this delay or retardation the curves generally assume a normal downward trend. It would seem from these curves, whether hardness, tensile, or elongation values are considered, that at temperatures a little above that at which softening commences, an opposite effect becomes operative, the magnitude of which depends on the kind and amount of addition which has been made and also to some extent on the temperature. It would seem possible that this may be in effect akin to, if not in some instances actually the same as, precipitation hardening, since there is apparently no phase change in any of the materials examined. The age-hardening characteristics of the different series of alloys referred to in the present paper have not been studied in detail. In the aluminium–brasses containing nickel additions evidences of age-hardening have, however, been obtained. In the series of brasses containing phosphorus, iron, and manganese additions, no indications of age-hardening have been noted, but it is not suggested that these alloys are necessarily incapable of exhibiting any ageing effects. It is conceivable, however, that the peculiarities which have been noted are not associated with ageing *per se*, but to other causes, the nature of which has not yet been ascertained.

Apart from the question of the cause or causes giving rise to the deviations from the normal in the softening curves, the results have a directly practical interest, especially in connection with annealing operations. In a "straight" brass the resulting grain-size and hardness values for any fixed time of annealing are functions of the temperature, and it is known that these two values are closely related. One result arising out of the deviation of the softening or annealing curves from the normal consequent on the addition of special elements such as iron, phosphorus, manganese, aluminium, nickel, and silicon, is that of the breaking down of the simple connection between grain-size and hardness on annealing.

It is known in a general way that the presence of relatively small amounts of such elements as phosphorus and iron in brass, hardens the alloy and renders it more difficult to anneal, or, in other words, raises its softening temperature. No previous data, however, would appear to have been published in which quantitative indications have been given of the extent of this effect which is of interest in the commercial annealing of brass. Apart therefore from its theoretical aspects, it is hoped that the data will be found to be of use in showing the effect of additions of iron, phosphorus, manganese, aluminium, nickel, and silicon on the intrinsic hardness, initial softening temperature, the softening curve, and grain-growth characteristics of hard-rolled α-brasses.

SUMMARY.

The effects on the annealing characteristics of 70 : 30 brass of additions of iron, phosphorus, manganese, and aluminium separately and of aluminium with nickel and aluminium with silicon have been studied with special reference to an abnormality which they produce on the softening curves.

These elements have been found to exert a retarding influence on the annealing process subsequent to the initial softening, the extent of which varies with the amount and nature of the addition. The effect is shown as a deflection in the smooth hardness-annealing temperature curve which is characteristic for a "straight" brass after the commencement of recrystallization. Subsequent to the deflection, the annealing curves of brasses containing the specially added elements tend to resume the normal form. The retardation of softening is also accompanied by a retardation in grain-growth.

The different elements which have been considered also raise the intrinsic hardness of brass, and in most cases increase the temperature of initial softening on annealing.

The deflections in the softening curves corresponding with delayed or retarded softening subsequent to the commencement of recrystallization, which have been found to characterize the brasses containing the various additions considered, have also been observed in curves connecting tensile strength and elongation values with annealing temperatures. It is possible that the delayed softening, the extent of which depends on the quantity and nature of the addition made to the brass, may, in the case of some of the alloys at least, be a manifestation of age-hardening properties, but it cannot be assumed that the effect in all the alloys examined is necessarily due to the same cause.

ACKNOWLEDGMENTS.

In conclusion, the authors desire to express their thanks to Dr. H. W. Brownsdon, M.Sc., for his very valuable advice and helpful criticism in

connection with extended investigations of which the results detailed in the paper constitute but a small part. Their thanks are also due to the Management Board of I.C.I. Metals, Limited, for permission to publish the results.

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APPENDIX

TABLE I.—*Compositions of Brasses Investigated.*

Alloy No.	Copper, %.	Tin, %.	Lead, %.	Iron, %.	Manganese, %.	Nickel, %.	Silicon, %.	Aluminium, %.	Phosphorus, %.	Zinc (diff.), %.
F7	70·04	...	0·01	0·01	...	...	...	...	...	29·94
F8	69·70	...	0·01	0·07	...	...	...	...	...	30·22
F9	69·62	...	0·01	0·11	...	...	...	...	...	30·26
F10	69·70	...	0·01	0·15	...	...	...	...	...	30·14
F11	69·69	...	0·02	0·24	...	...	...	...	...	30·05
F12	69·49	...	0·02	0·49	...	...	...	...	...	30·00
P1	69·38	0·01	0·01	0·03	...	...	...	...	...	30·57
P3	69·85	0·01	0·02	0·03	...	...	...	...	0·008	30·08
P4	69·72	0·01	0·02	0·03	...	...	...	...	0·04	30·18
P6	69·25	0·01	0·02	0·02	...	...	...	...	0·135	30·56
M8	68·43	...	0·01	0·03	...	...	...	...	...	31·53
M9	70·60	...	0·01	0·03	1·05	...	...	...	...	28·31
M10	69·24	0·02	0·08	0·15	4·95	0·10	0·02	...	...	25·44
M11	68·06	0·02	0·06	0·21	9·00	...	0·05	...	...	22·60
M12	68·70	...	0·04	0·21	13·85	...	0·06	...	...	17·14
M8	68·43	...	0·01	0·03	...	...	...	...	...	31·53
A1	77·28	...	0·01	0·01	...	...	...	2·45	...	20·25
A2	77·18	...	0·01	0·01	...	0·55	...	1·63	...	20·62
A3	76·08	...	0·01	0·01	...	1·10	0·01	2·34	...	20·45
A4	76·76	...	0·01	0·01	...	2·15	0·01	1·62	...	19·44
A5	72·25	...	0·01	0·02	...	5·17	0·01	1·71	...	20·83
M8	68·43	...	0·01	0·03	...	...	...	...	...	31·53
A1	77·28	...	0·01	0·01	...	...	...	2·45	...	20·25
A6	75·00	...	0·01	0·01	...	...	0·55	2·38	...	22·05
A7	77·40	...	0·01	0·01	...	...	1·18	2·38	...	19·02

PLATE XLV.

Straight 70 : 30 Brass.

FIG. 2.—Annealed ½ hr. at 400° C. × 100.

FIG. 4.—Annealed ½ hr. at 500° C. × 100.

70 : 30 Brass containing 0·49 per cent. Iron.

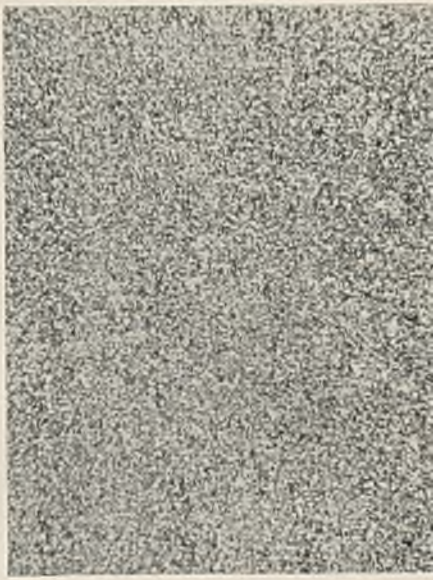

FIG. 3.—Annealed ½ hr. at 400° C. × 100.

FIG. 5.—Annealed ½ hr. at 500° C. × 100.

[*To face p.*

Straight 70 : 30 Brass.

70 : 30 Brass containing 0·49 per cent. Iron.

FIG. 6.—Annealed ½ hr. at 610° C. × 100.

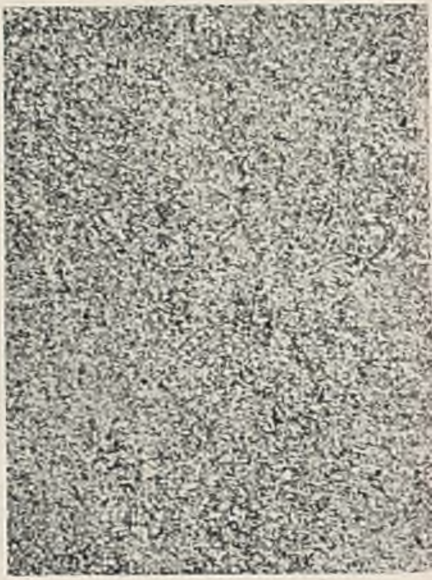

FIG. 7.—Annealed ½ hr. at 610° C. × 100.

FIG. 8.—Annealed ½ hr. at 700° C. × 100.

FIG. 9.—Annealed ½ hr. at 700° C. × 100.

TABLE II.—*Effect of Iron Additions on Diamond Pyramid Hardness and Grain-Size of Rolled and Annealed Brass.*

Condition.	No. F7.		No. F8.		No. F9.		No. F10.		No. F11.		No. F12.	
	0·01% Iron.		0·07% Iron.		0·11% Iron.		0·15% Iron.		0·24% Iron.		0·40% Iron.	
	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.
Hard-rolled .	179	...	174	...	180	...	177	...	184	...	197	...
Annealed at 220° C. .	185	...	182	...	187	...	183	...	189	...	210	...
,, ,, 300° C. .	160	...	164	...	172	...	179	...	174	...	184	...
,, ,, 350° C. .	116	...	122	...	122	...	127	...	133	...	142	...
,, ,, 400° C. .	97	0·015	100	0·015	104	0·015	106	0·01	115	0·01	132	0·005/0·01
,, ,, 440° C. .	85	0·02	92	0·02	99	0·015	103	0·015	110	0·01	131	0·005/0·01
,, ,, 500° C. .	75	0·03	83	0·02/0·03	96	0·02/0·03	100	0·02	107	0·01	130	0·005/0·01
,, ,, 540° C. .	68	0·04	73	0·03	82	0·03	97	0·02/0·03	107	0·015	126	0·005/0·01
,, ,, 610° C. .	62	0·05	62	0·04	64	0·04	75	0·04	95	0·015	120	0·005/0·01
,, ,, 650° C. .	57	0·07	58	0·07	60	0·06	60	0·06	74	0·02/0·03	110	0·005/0·01
,, ,, 700° C. .	53	0·12	55	0·11	56	0·11	52	0·10	57	0·10	82	0·02/0·03
,, ,, 750° C. .	51	0·17	51	0·17	53	0·17	50	0·16	50	0·15	73	0·05
,, ,, 800° C. .	47	...	50	...	50	...	47	...	47	...	69	...

Table III.—*Effect of Phosphorus Additions on Diamond Pyramid Hardness and Grain-Size of Rolled and Annealed Brass.*

Condition.	No. P1.		No. P3.		No. P4.		No. P6.	
			0·008% Phosphorus.		0·04% Phosphorus.		0·135% Phosphorus.	
	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.
Hard-rolled	169	...	173	...	178	...	182	...
Annealed at:								
200° C. .	174	...	178	...	183	...	189	...
305° C. .	160	...	172	...	178	...	186	...
375° C. .	101	...	105	...	115	...	154	...
420° C. .	91	0·02	98	0·01	108	0·005/0·01	125	0·005
495° C. .	77	0·03	87	0·015	93	0·01	109	0·01
560° C. .	65	0·04	82	0·02	86	0·015	92	0·015
620° C. .	60	0·06	75	0·03	83	0·02	76	0·04
670° C. .	54	0·09	68	0·04/0·05	73	0·02/0·03	61	0·05/0·06
720° C. .	51	0·14	63	0·06	71	0·03	60	0·08
770° C. .	48	0·21	61	0·07	70	0·03/0·04	59	0·10

Table IV.—*Effect of Manganese Additions on Diamond Pyramid Hardness and Grain-Size of Rolled and Annealed Brass.*

Condition.	No. M8.		No. M9.		No. M10.		No. M11.		No. M12.	
			1·05% Manganese.		4·95% Manganese.		9·00% Manganese.		13·85% Manganese.	
	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.
Hard-rolled .	179	...	177	...	187	...	190	...	212	...
Annealed at:										
200° C. .	185	...	183	...	190	...	200	...	215	...
310° C. .	166	...	181	...	187	...	195	...	209	...
380° C. .	92	...	107	...	168	...	179	...	195	...
430° C. .	79	0·02	90	0·02	131	0·01	140	0·005/0·01	133	0·005/0·01
490° C. .	74	0·03	82	0·03	109	0·01	119	0·01	127	0·01
530° C. .	70	0·03	76	0·03	109	0·01	115	0·01	127	0·01
580° C. .	64	0·04	74	0·04	107	0·01	114	0·01	127	0·01
650° C. .	57	0·07	63	0·06	83	0·02	100	0·02	114	0·02
690° C. .	54	0·10	60	0·09	71	0·04/0·05	91	0·03	100	0·02/0·03
750° C. .	50	0·17	52	0·13	63	0·08	77	0·05	86	0·03/0·04
800° C. .	48	...	51	...	60	...	75	...	83	...

Table V.—*Effect of Aluminium and Nickel Additions on Diamond Pyramid Hardness and Grain-Size of Rolled and Annealed Brass.*

Condition.	No. M8.		No. A1.		No. A2.		No. A3.		No. A4.		No. A5.	
			2·45% Aluminium.		1·63% Aluminium, 0·55% Nickel.		2·34% Aluminium, 1·1% Nickel.		1·62% Aluminium, 2·15% Nickel.		1·71% Aluminium, 5·17% Nickel.	
	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.
Hard-rolled . .	179	...	187	...	183	...	202	...	205	...	212	...
Annealed at 200° C. .	185	...	200	...	197	...	218	...	221	...	227	...
,, ,, 310° C. .	166	...	197	...	200	...	221	...	232	...	237	...
,, ,, 380° C. .	92	...	108	...	128	...	212	...	230	...	237	...
,, ,, 430° C. .	79	0·02	100	0·015/0·02	104	0·005	195	0·005	198	0·005	206	0·005
,, ,, 490° C. .	74	0·03	91	0·02	104	0·01	145	0·005	164	0·005	174	0·005
,, ,, 530° C. .	70	0·03	88	0·02/0·03	98	0·01	137	0·01	155	0·005	158	0·005
,, ,, 580° C. .	64	0·04	81	0·03	85	0·02	133	0·01	146	0·01	151	0·005
,, ,, 650° C. .	57	0·07	66	0·04/0·05	68	0·03	85	0·02	131	0·01	135	0·005/0·01
,, ,, 690° C. .	54	0·10	64	0·06	65	0·04/0·05	69	0·04	94	0·02	131	0·01
,, ,, 750° C. .	50	0·17	59	0·12	58	0·10	61	0·09	64	0·07	120	0·01/0·015
,, ,, 800° C. .	48	...	53	...	55	...	57	...	58	...	96	...

TABLE VII.—*Tensile Properties and Hardness Values of Rolled Brasses Containing Various Additions, after Annealing at Different Temperatures.*

Condition.	No. F7.			No. F11.			No. P4.			No. M11.			No. A1.			No. A4.		
	Straight α-Brass.			Containing Addition of 0·24% Iron.			Containing Addition of 0·04% Phosphorus.			Containing Addition of 9·00% Manganese.			Containing Addition of 2·45% Aluminium.			Containing Addition of 1·62% Aluminium and 2·15% Nickel.		
	Diamond Pyramid Hardness No.	Tensile Strength, Tons/in².	Elongation, % on 2 in.	Diamond Pyramid Hardness No.	Tensile Strength, Tons/in².	Elongation, % on 2 in.	Diamond Pyramid Hardness No.	Tensile Strength, Tons/in².	Elongation, % on 2 in.	Diamond Pyramid Hardness No.	Tensile Strength, Tons/in².	Elongation, % on 2 in.	Diamond Pyramid Hardness No.	Tensile Strength, Tons/in².	Elongation, % on 2 in.	Diamond Pyramid Hardness No.	Tensile Strength, Tons/in².	Elongation, % on 2 in.
Hard-rolled .	179	37·2	11	184	40·2	9	178	41·0	9	190	42·0	5	187	42·0	6	205	47·2	7
Annealed at :																		
200° C. .	185	38·2	8	190	42·2	7	183	42·6	5	200	44·0	5	203	42·8	4	228	52·4	1
310° C. .	160	31·2	27	164	35·6	20	172	40·0	10	195	43·2	7	200	41·8	9	235	54·0	1
400° C. .	97	24·5	50	116	28·2	43	114	27·6	43	172	36·2	16	110	29·2	48	227	47·6	7
450° C. .	84	23·2	57	110	28·0	43	103	27·0	49	134	30·4	30	100	27·7	50	183	38·2	24
500° C. .	78	22·8	60	107	28·0	43	96	26·4	49	120	30·2	35	94	27·2	55	160	35·3	33
550° C. .	71	21·8	65	106	27·8	45	91	25·4	50	115	29·7	36	88	26·4	61	151	34·8	34
600° C. .	63	21·0	67	100	26·6	47	84	25·2	55	108	28·4	36	78	24·8	67	141	32·9	38
650° C. .	58	20·4	71	74	23·8	55	79	24·4	58	100	27·6	37	68	24·0	74	127	31·7	38
700° C. .	55	20·0	74	58	21·7	66	73	23·2	58	91	26·2	38	62	23·6	71	94	28·8	47
750° C. .	49	19·4	78	50	20·6	70	70	22·6	59	80	24·2	43	58	22·8	71	64	24·4	68
800° C. .	48	19·2	78	47	19·6	72	68	22·2	62	76	23·0	46	55	22·4	78	59	23·6	69

TABLE VI.—*Effect of Aluminium and Silicon Additions on Diamond Pyramid Hardness and Grain-Size of Rolled and Annealed Brass.*

Condition.	No. M8.		No. A1.		No. A6.		No. A7.	
			2·45% Aluminium.		2·38% Aluminium, 0·55% Silicon.		2·38% Aluminium, 1·18% Silicon.	
	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.	Diamond Pyramid Hardness No.	Grain-Size, mm.
Hard-rolled	179	...	187	...	195	...	212	...
Annealed at:								
200° C. .	185	...	200	...	215	...	237	...
310° C. .	166	...	197	...	209	...	240	...
380° C. .	92	...	108	...	134	...	145	...
430° C. .	79	0·02	100	0·015/0·02	114	0·01	133	0·01
490° C. .	74	0·03	91	0·02	109	0·01	126	0·01
530° C. .	70	0·03	88	0·02/0·03	99	0·015	119	0·015
580° C. .	64	0·04	81	0·03	88	0·02	108	0·02
650° C. .	57	0·07	66	0·04/0·05	77	0·03/0·04	88	0·04/0·05
690° C. .	54	0·10	64	0·06	68	0·05	82	0·04/0·05
750° C. .	50	0·17	59	0·12	61	0·08	72	0·07
800° C. .	48	...	53	...	67	...	80	...

DISCUSSION.

MR. L. J. BRICE,* M.Sc. (Member): I should like to ask a question of the authors in connection with the annealing of these cold-worked brasses, as it is a point in which I am rather interested. Have the authors at any time carried out a similar series of tests on straight 70 : 30 brass of varying degrees of initial hardness? I ask because I am hoping that in a subsequent written communication I may be able to give indications that with extremely hard straight brasses there may be something in the nature of a discontinuity in the softening curve similar to that obtained by the authors with brasses containing certain additions.

DR. C. H. DESCH,† F.R.S. (Vice-President): I think, as regards the explanation of these facts, that it is not quite as complicated as might at first appear. The elements concerned increase the intrinsic hardness of the brass; that is to say, by entering into solid solution in the brass they produce a distortion of the lattice which manifests itself as increased hardness. When it comes to the relief of hardening after cold-work, by the application of heat, that softening is a re-arrangement of the distorted lattice to form the undistorted normal lattice of the annealed metal. Anything which produces the excessive distortion at the ordinary temperature will, as it seems to me,

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* Research Department, Woolwich.

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

also hinder that rearrangement at the higher temperature. The mobility of the atoms within the lattice will be reduced, and therefore the softening at a given temperature will be less than that of the initial α-brasses. I think that if we were to take the actual lattice structure of these alloys, look at the size of the atoms and the position they occupy on the lattice, and ascertain how much distortion is produced by introducing the foreign atoms, which are of quite different sizes, we would find that the whole matter would reduce itself to one of simple geometry. It is curious how in so many of these metallurgical problems if we look at the actual size of the atoms we find that merely geometrical considerations will explain most of these phenomena without resorting to any specific influence of particular elements.

I only put that forward as a suggestion, but it seems to me that the curves which are shown here follow the kind of course which might be expected if that were the explanation of the increased hardening.

Mr. MILLER (*in reply*): With regard to Mr. Brice's question regarding the effect of the amount of cold-work on the material prior to annealing, in our experiments we standardized this at 50 per cent. reduction in thickness, and have not considered the effect of different amounts of cold-work on the softening curves. This effect, however, is fairly well known, and it has been shown that the temperature at which softening commences decreases with increasing amounts of cold-work. Bassett and Davis * have given annealing curves for cartridge brass subjected to different amounts of reduction, varying from 20 to 59·1 per cent. before final annealing. These curves show the effect of increasing the amount of cold-work in lowering the temperature on initial softening, but in no instance is there any evidence indicating that the normal trend of the curve subsequent to recrystallization is effected. While we have no definite reply to make to Dr. Desch's remarks regarding the causes giving rise to the effect to which we have directed attention, I might mention that we have found that some of the copper–nickel–zinc alloys show this phenomenon, although the straight copper–nickel and straight copper–zinc alloys do not.

Dr. COOK (*in reply*): I should like to amplify what Mr. Miller has said *à propos* of an experiment which we have carried out, and which I think has some bearing on the interesting suggestion which Dr. Desch has put forward. We found that the softening curve of an alloy containing 90 per cent. of copper and 10 per cent. of nickel was quite normal, and a similar result was found with an alloy containing 90 per cent. of copper and 10 per cent. of zinc. With, however, an alloy containing 90 per cent. of copper, 5 per cent. of nickel, and 5 per cent. of zinc, we obtained a softening curve which showed an abnormal deflection, similar to those found on other alloys referred to in the paper. The fact that we obtained the effect in a system which is a combination of two simple systems which do not show the peculiarity, indicates that the retardation in the annealing process is not dependent on the addition of an element involving distortion of the lattice structure.

CORRESPONDENCE.

THE AUTHORS: To supplement our reply to the interesting suggestion which Dr. Desch made, we would quote further experimental results which we have obtained. Softening curves for 90 : 10 copper–zinc, 90 : 10 copper–tin, and 95 : 5 : 5 copper–zinc–tin alloys, are shown in Fig. A. For both the binary alloys the softening curves are quite normal, but for the ternary alloy of the same copper content there is evidence of the retarding effect subsequent

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* *Trans. Amer. Inst. Min. Met. Eng.*, 1919, 60, 428.

to recrystallization. This affords further evidence that the effect is not necessarily due to the presence of an element giving rise to distortion of the lattice structure.

Dr.-Phil. M. **Hansen** * (Member): I was particularly interested in that portion of the paper dealing with the influence of iron. For some time an investigation of the constitution of the ternary system copper–zinc–iron up to an iron content of 2 per cent. has been in progress at the Kaiser-Wilhelm-Institut für Metallforschung, Berlin-Dahlem, Germany, the results of which will be published early in 1933. Investigation has shown that α-brass is capable of taking up iron into solid solution in considerably larger quantities at high temperatures than at lower temperatures, as is the case with copper.† In view of this fact, age-hardening experiments were carried out. Results, as shown in Fig. B for an alloy with 71·17 per cent. copper, 0·71 per cent. iron, and the rest zinc, clearly indicate, in opposition to the authors' observations, that α-brass containing iron exhibits marked ageing effects. Similar results were obtained with 70 : 30 brass containing 0·20 and 0·53 per cent. iron. There is no doubt, therefore, that the retardation of softening in 70 : 30 brass containing iron subsequent to the commencement of recrystallization is due to precipitation hardening. As may be seen from the curves, the increase in hardness for an annealing period of 30 minutes is greatest with ageing

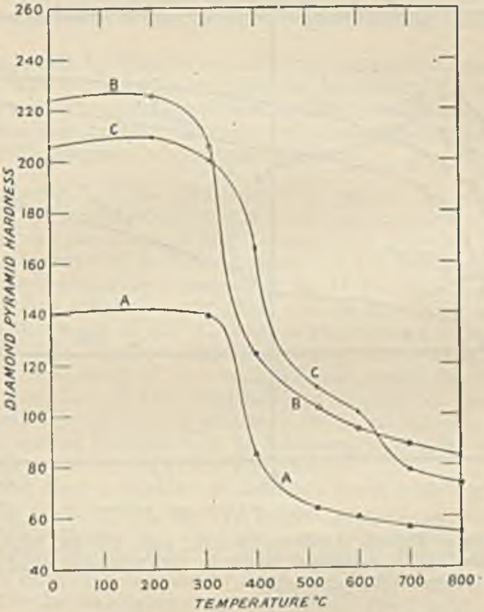

Fig. A.—Annealing Curves of: A. 90 : 10 copper–zinc; B. 90 : 10 copper–tin; C. 90 : 5 : 5 copper–zinc–tin Annealed 30 minutes at Different Temperatures.

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† D. Hanson and Grace W. Ford, *J. Inst. Metals*, 1924, **32**, 335–361; G. Tammann and W. Oelsen, *Z. anorg. Chem.*, 1930, **186**, 257–288.

temperatures of 450°–600° C. This is in accordance with the results of Dr. Cook and Mr. Miller.

Dr. F. Johnson * (Member): I have read the paper with much interest and appreciation. I should be glad if the authors would describe the method which they employed for introducing iron into their alloys and if they would state whether they experienced any difficulty in obtaining ingots in which the iron was uniformly distributed. I have investigated † the influence of iron on properties of copper–zinc alloys, and found that the influence on grain-size and softening temperature was unmistakable, but the data now presented by the authors give, to use their own words, quantitative indications of the extent of these effects which must undoubtedly be of great interest in the commercial annealing of brass.

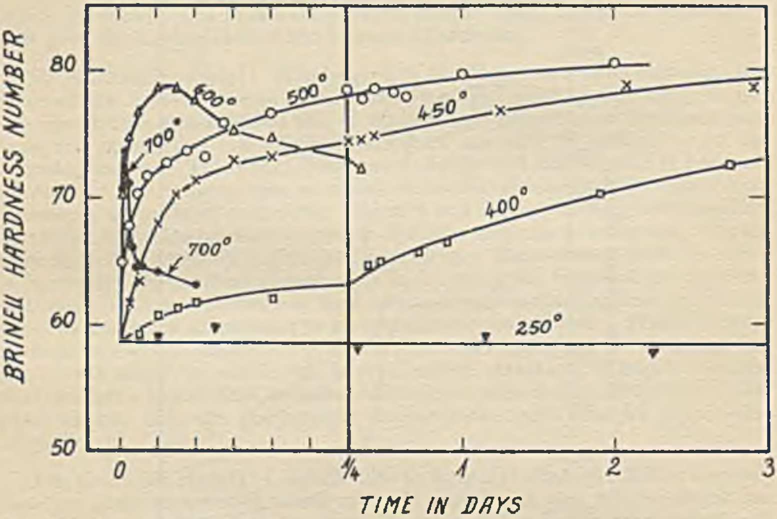

Fig. B.—Change in Brinell Hardness (5 mm. ball, 250 kg. load, 30 seconds) of α-Brass with 71·17% copper, 0·71% iron, rest zinc, quenched at 800° C., after Ageing at Different Temperatures.

Nevertheless, it would not be quite correct to state that no previous data on the subject have been published. Some work was done by O. Smalley,‡ who examined the influence of 0·5 and 1·0 per cent. of iron on the tensile, hardness, impact, and alternating impact test results as well as on the malleability of 70 : 30 brass, the cupping and drawing properties being also determined by the actual manufacture of ferrules and fuse primers. No annealing tests were made on material annealed below 650° C., the amount of reduction by cold-rolling being comparable to that effected by the authors, but much thicker material, which had been subjected to less *total* reduction, was used. Nevertheless, the retardation in softening shown by the authors over the range of temperature 650°–800° C. agrees fairly well with that shown by Smalley, whose conclusion was as follows: "Iron appreciably raises the annealing

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† *J. Inst. Metals*, 1918, **19**, 133; *Met. Ind.* (*Lond.*), 1921, **18**, 125–128.

‡ *Met. Ind.* (*Lond.*), 1920, **17**, 421–428.

temperature of brass, the correct temperature for 70 : 30 brass in the presence of 0·50 per cent. iron being 775° C. and in the presence of 1·00 per cent. iron, 825° C., if the period of heating is 30 minutes."

Photomicrographs were also published showing the influence of iron on grain-size. The authors state, on p. 250, that after cold-working and complete annealing, 70 : 30 brass containing 0·49 per cent. of iron appeared microscopically to be a homogeneous solid solution.

Smalley examined "small casts" containing 0·10–0·50 per cent. of iron, and found that iron-rich particles were just discernible at 0·35 per cent. iron, and that "the solubility of the iron-rich constituent is not enhanced by mechanical work or heat-treatment, its presence thus affording a rough guide to the iron content." There appears, therefore, to be a point of divergence here from the experience of the authors, whose opinion thereon I should welcome.

One discovery made by Smalley was of great commercial interest, *viz.* that such articles as ferrules and fuse primers can be successfully manufactured from "70 : 30" brass containing 1 per cent. of iron, by adjusting the annealing temperature to the iron content. Another claim was that, for the manufacture "of springs and the like, iron is beneficial in brasses."

Mr. K. G. LEWIS,* M.Sc. (Member). : I venture to suggest to the authors that the deflection commencing from the so-called softening temperature and through the range of 400° C. may very probably be due to the disappearance or absorption in varying degrees of the β-phase. It is known that straight copper–zinc alloys containing 64–71 per cent. of copper show some β-crystals when just solid, and these can be effectively absorbed only by annealing in the range of 400° C. when a structure of homogeneous α is obtained. This would apply to the majority of the brasses used in this work, although the amount of any such β-phase would be small. Again, there is the modification of the constitutional diagram of the copper–zinc series by the addition of various elements to be considered—the limiting solubility of the α-solid solution may be increased to a value above that of approximately 63 per cent. zinc at low temperature.

Guillet † found that a number of elements when added to copper–zinc alloys materially altered the apparent copper content (as determined by microscopical examination), and used the term "equivalent coefficient" to illustrate this effect in the case of each element. Thus, the equivalent coefficient has a definite minimum of copper in the α-solid solution and a different value for the maximum copper content in the β-solution. In practice, one value alone for each of the added elements can be used in the case of this series of alloys. Guillet has shown that silicon and aluminium appreciably lower the real copper content (as determined by analysis), and that manganese and iron lower the content only slightly. Nickel, on the other hand, gives an apparently greater copper content. Guillet's actual equivalent coefficient values were Si, 10; Al, 6; Fe, 0·9; Mn, 0·5; Ni, — 1·3.

Microscopically, the β-phase present would probably not be discernible, particularly at the magnification used (× 100), as the authors have given very ample evidence of the small grain-size obtained in the case of an addition of 0·49 per cent. of iron.

Although the copper contents of the brasses containing aluminium and silicon are in the neighbourhood of 77 per cent., I think that the same reasoning still applies in this instance, owing to the appreciable quantities of these elements (at any rate, of the former) which were used and also to their high equivalent coefficients.

* King's College, Cambridge.

† *Rev. Mét.*, 1905, 2, 111; 1906, 3, 143, 258, and 262.

None of the above remarks apply to those brasses containing phosphorus, since, according to Guillet, a separate constituent is formed.

The AUTHORS (*in reply*): We are very interested in the results which Dr. Hansen has quoted, and to learn that in the course of his investigations into the constitution of the ternary system copper–zinc–iron he has found α-brasses containing iron to exhibit ageing effects. We are not surprised to learn of these findings, for the ageing tests which we carried out on these and some of the other series were of only a very preliminary nature, and although we did not find any evidences of ageing as a result of these experiments, we had not concluded that the alloys did not therefore possess ageing characteristics, and in the paper we commented specifically on this possibility. We quite agree that the results that Dr. Hansen has put forward indicate that these alloys actually do possess ageing characteristics, and his results and ours on the iron series agree in indicating that the effect is most marked in the temperature range of about 400°–600° C.

In reply to the first query of Dr. Johnson's interesting communication, the iron was added in the form of ferro-zinc, which we made from electrolytic spelter and pure iron. This alloy contained 4 per cent. of iron, and a regular distribution of the iron in the brass was thereby obtained, for several analyses of different brasses in the iron series on samples from different portions of the ingot yielded very concordant results. We were not unaware of Smalley's work, but this was not carried out on material as thin as that which we used, and, furthermore, the annealing was not carried out over such a comprehensive temperature range. As Dr. Johnson has pointed out, Smalley did not make any annealing tests below 650° C., and did not observe the deflection in the annealing curve, to direct attention to which was one of the principal objects of our paper.

We have not made any systematic or serious attempt to establish the limit of solubility of iron in α-brass, and we are quite ready to admit that it may be less than 0·49 per cent. In fact, electrical conductivity measurements we have made indicate that the solubility is less than 0·2 per cent. at normal temperatures. Nevertheless, in an alloy containing this amount of iron we could not with certainty, by microscopic methods, distinguish the presence of free iron or an iron-bearing constituent.

There seems to be no evidence to indicate that the deflections in the softening curve were due, as Mr. Lewis suggests, to the presence of the β-constituent. The effect of β is shown on the softening curve for alloy No. A7 (Fig. 10) where annealing at temperatures in excess of 750° C. causes the curve to assume an upward direction. This alloy contains additions of such nature and amounts as to give rise to the presence of the β-phase. Even though straight copper–zinc alloys containing 64–71 per cent. of copper may contain small quantities of the β-phase when just solid, it becomes reabsorbed on subsequent annealing. The materials on which the softening curves were determined consisted of strip rolled from ingots, and in the fabrication of the strip the material was subjected to a series of alternate rolling and annealing operations, which would result in the complete absorption of any small amounts of β which might have been present originally from lack of equilibrium conditions in the cast materials. In most instances the additions were not of sufficient amount to increase the equivalent zinc content to such a degree as to result in the presence of β in the alloy. Although the photomicrographs included in the paper to illustrate the effect of iron on grain-size are at 100 diameters magnification, all the samples were examined microscopically at much higher magnifications, and except in the instance referred to, no β was seen. A magnification of 100 diameters was used only for convenience in covering the range of crystal structures illustrated in the photomicrographs.

THE CONSTITUTION OF THE LEAD-TIN ALLOYS.*

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

Synopsis.

An investigation of the constitution of the lead–tin alloys is described. The micrographic method, two thermal methods, and a modified electrical conductivity method have been used in the determination of the solubility of tin in lead, which is shown to be 19·5 per cent. by weight, at the temperature of the eutectic. This value is considerably higher than any other previously obtained. It is also shown that at ordinary temperatures lead probably cannot hold more than 2 per cent. of tin in solid solution. The cause of the evolution of heat in certain of the alloys at a temperature just below that of the eutectic is discussed. No definite conclusion has been reached, but two explanations are put forward, and it is also shown that the allotropic theory is probably untenable.

The alloys of lead and tin have been examined by many workers, and the results fall into three main classes typified by the work of Rosenhain and Tucker,[1] Jeffery,[2] and Honda and Abé.[3] Rosenhain and Tucker and Jeffery agree that the solubility of tin in lead at the eutectic temperature is about 16 per cent. by weight, and Honda and Abé place the limit at 18 per cent., but at lower temperatures they all differ widely. At 100° C. Rosenhain and Tucker find a solubility of about 12 per cent., Honda and Abé about 8 per cent., Jeffery about 4 per cent. The chief difference in opinion concerns the existence or non-existence of a transformation point in the intermediate alloys near 150° C. Rosenhain and Tucker believe that this is a real transformation, and are of the opinion that it is a change in the lead-rich solid solution from a β to an α modification, the latter possessing a smaller solubility for tin than the former. Their diagram is therefore slightly complicated. Jeffery, using the electrical resistance method, found that alloys cooled quickly between the liquidus and solidus showed this transformation even when cooled slowly from the solidus, but that alloys cooled very slowly throughout showed no change. He concluded that the transformations were due to metastability, and shows no line on his diagram, which is of the simplest type. Honda and Abé, using differential thermal analysis,

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† King's College, Cambridge.

attributed the change to a rapid decrease of the solubility of the tin-rich phase in the lead-rich solid solution with a fall in temperature. Their diagram is therefore similar to Jeffery's except that there is a marked and sudden inflection in the α-phase boundary near 160° C. and at about 18 per cent. of tin.

THERMAL ANALYSIS.

The alloys were made by melting together suitable weights of lead and tin in alundum crucibles under hydrogen, and bars 8 mm. in diameter were obtained by casting into a cold, heavy, iron mould. The weight of a bar was about 30 grm. Subsequent examination showed that these alloys were not uniform owing to inverse segregation. Attempts to cast more suitable bars failed. This non-uniformity would be expected to cause certain of the thermal arrests to be blurred and to cause the solidus to be placed at a temperature slightly too low and the α-phase boundary at a temperature slightly too high.

Lead from two sources was used: Kahlbaum lead and some very pure lead prepared by the Stas method by the late Colonel C. T. Heycock. The constitution of duplicate alloys made up from the different kinds of lead appeared to be identical after the same heat-treatment. The tin was " Chempur " and contained not more than 0·006 per cent. of impurities other than lead.

A differential method of thermal analysis similar to that described by Honda and Abé [3] was employed. Each specimen weighed 10 grm., and the neutral, a piece of pure lead, 12 grm.

The two pieces of metal, after squeezing to a suitable shape, were wrapped in thin asbestos paper and were then bound side by side, the whole being wrapped round with more asbestos paper.

Copper–Constantan couples of 24 s.w.g. were used, the short wire of the differential couple being of Constantan. Temperatures were measured on a millivoltmeter and also on a water-dropper, the mirror galvanometer of the water-dropper being in parallel with the millivoltmeter. The differential couple was connected with a second mirror galvanometer which also threw a spot of light on to the sheet of the water-dropper. In this way, direct and differential curves could be drawn on the same sheet of paper and their correlation was easy, as the two curves had the same time ordinate. The sensitivity of the direct couple was varied somewhat during the experiments; for the most part 1·5 mm. on the sheet represented 1° C. The sensitivity of the differential couple was high. A pair of typical curves is reproduced in Fig. 1. Except that they have been reduced to two-thirds for reproduction and that for convenience the differential curve (*b*) has been moved vertically over the direct curve (*a*), these, and all the others shown, are as they were on the original sheet. Curves (*a*) and (*b*) are cooling curves of 10 grm. of an alloy containing 20 per cent. of tin and the break is caused by a small quantity of eutectic present in that alloy. It is interesting to note that the peak of the differential curve corresponds with the completion of the transformation. This work has convinced the author that the temperature of a change is given by the first movement from the horizontal of the differential curve, and that, except in cases where extreme sensitivity is essential, the direct curve, which is always easier to interpret, is superior to all other types of curve.

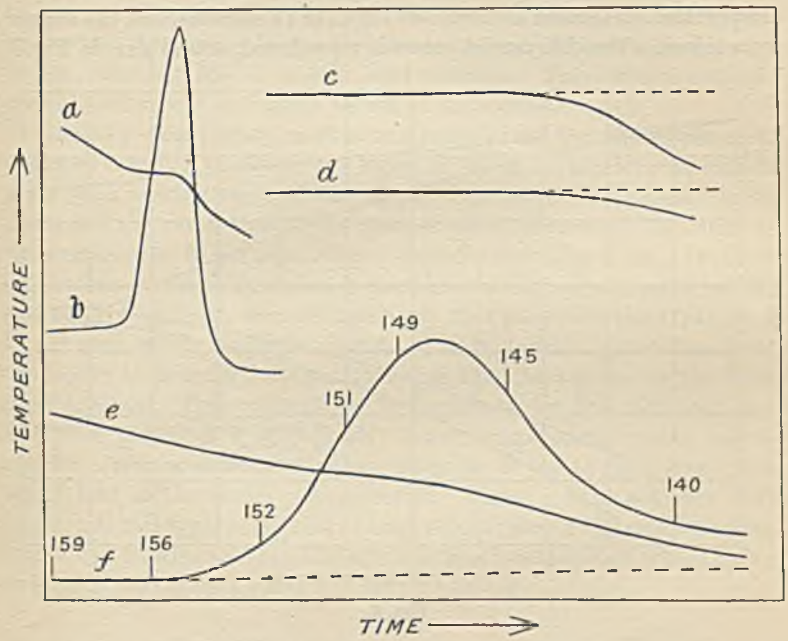

FIG. 1.—Typical Thermal Curves.

The couple used in measuring temperatures was calibrated on the steam, lead–tin eutectic (accepted as 183·3° C.), tin and lead points in the usual way. It was also calibrated under actual working conditions by taking differential heating curves of pure tin and of either a 20 or a 25 per cent. tin alloy using the eutectic point. In this way small corrections, of the order of 1° C., could be made to the original curve. It is suggested that measurements of temperature are correct to 1° C.

The Lead-Rich Solidus.

An electrically-heated tube furnace controlled by a thermo-electric thermostat was used throughout and the specimens were heated in hydrogen. The methods for finding the solidus of the lead-rich alloys are typified by the experiment with the 7 per cent. tin alloy which is given below. The specimen was introduced into the furnace running near 175° C. After 3 hrs., when the thermostat had settled down, it was set to raise the temperature to 179° C. After 16 hrs. at 179° C., the temperature was raised at a rate of 10° C. in 11 minutes, and the curves were taken. The differential curve is reproduced, actual size, in Fig. 1 (*c*). As soon as a definite break had been obtained, the heating was stopped. It is to be noted that each alloy was given a preliminary anneal at some temperature just below that of the eutectic, and the curve was then taken through the eutectic range. That an alloy was not in equilibrium was shown by the appearance of an arrest at the temperature of the eutectic.

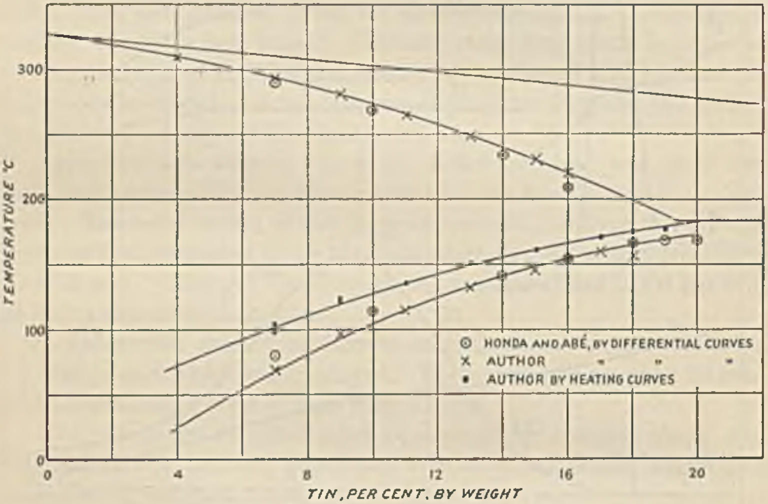

Fig. 2.

The results obtained are given in the Appendix and are plotted in Fig. 2, together with Honda and Abé's results. The two sets are in general agreement; the author's is about 4° C. higher, except that he finds the solidus of the 16 per cent. alloy to be at 221° C. as against 208° C.

The equilibrium diagram shows that in an alloy poor in tin the percentage of metal melted during a rise in temperature of 1° C. in the solidus–liquidus area is considerably greater than that in an alloy richer in tin. Breaks in the differential curves would therefore be sharper the lower the tin content. The points for the 15 and 16 per cent. alloys were indistinct, and no solidus points for richer alloys could be obtained by this method, although the curve indicates that the maximum solubility of tin in lead is about 20 per cent. The micrographic method also shows that the solubility is over 19 per cent. Indeed, a 10 grm. specimen of the 19 per cent. alloy was apparently obtained as a uniform solid solution as follows: the specimen was annealed at 190° C. for 16 hrs. and then cooled to 182° C. The presence of eutectic was shown by the cooling-curve. It was then heated to 185° C. and held there for 42 hrs., cooled to 180° C. in ½ hr., and reheated. There was no eutectic arrest, neither was any arrest shown at the solidus.

The 13 per cent. alloy melts over a range of 50° C.; the 20 per cent. might be expected to melt over a range of 100° C. Therefore the solidus point on a heating-curve of the 20 per cent. might be expected to be about half the size of that on the curve of the 13 per cent. The differential curve of the 13 per cent. alloy is reproduced in Fig. 1 (*d*). It shows an obvious arrest point and it is therefore unlikely that a point half its size would be missed, and still less likely that points for the 17, 18, and 19 per cent. alloys would be absent. The explanation put forward for the failure to pick up these points is that the alloys poorer in tin show super-heating. This explanation is confirmed by the fact that the solidus is placed at a considerably lower temperature by the micrographic analysis, although the heterogeneity of the thermal specimens would lead to the contrary expectation. There is then evidence that a lattice of this type, consisting of large solvent atoms and smaller solute atoms, can pass into a metastable state even when the phase which ought to be produced is the liquid.

THE LEAD-RICH α-PHASE BOUNDARY.

The method at first used for fixing this boundary was similar to that for fixing the solidus. The alloys were held for a time at a temperature somewhat above that of the eutectic. They were then cooled through the eutectic range in order to ascertain whether they were in equilibrium, as was shown by the absence of an arrest point. When the eutectic was absent, the cooling was continued and direct and differential curves were drawn. The rate of cooling was 10° C. in about 12 minutes. The results are given in the Appendix and are plotted, together with those of Honda and Abé, in Fig. 2. Although the author's temperatures are generally somewhat lower, there is again good agreement between the two sets. Rosenhain and Tucker, using the same method, apparently obtained similar results.

These differential cooling-curves show that there is a very considerable evolution of heat when the second phase appears, and that after a few minutes the heat evolved is not sufficient to maintain the difference in temperature between the specimen and the neutral. It is known that the separation of a second phase from a solid solution is seldom accompanied by a marked evolution of heat, and an examination of the lead–tin diagram indicates that if there is such a heat change in the 15 per cent. alloy, for example, the quantity of heat given out should be proportional to the fall in temperature, at least to about 100° C. The differential curve should therefore show a slow and small departure from the vertical until the heat produced by the change is just sufficient to maintain the difference in temperature. The curve should then become nearly vertical again over a considerable temperature range and should creep back slowly at temperatures below 100° C. The experimental curves differ markedly from this conception of the ideal curve. Therefore if the change which is taking place is a simple precipitation of the second phase, then there is super-cooling to such an extent as to render attempts to fix the phase boundary by direct thermal analysis a mere waste of time.

One-phase alloys were next annealed at a definite temperature. The temperature was then raised as quickly as possible and the presence or absence of an arrest-point at the eutectic temperature was observed. As an example of the method of working, consider the experiments with the alloy containing 19 per cent. of tin. A new specimen was annealed at 185° C. for 24 hrs. The temperature was then dropped to 180° C. in $\frac{1}{2}$ hr., a cooling curve being taken. There was no arrest at the eutectic temperature, and the alloy was therefore a uniform solid solution.

The temperature was then lowered to 177° C. and maintained there for 17 hrs. The heating-curve, taken up to 187° C., showed no arrest, therefore the α-phase boundary is below 177° C. The temperature was then lowered to 175° C. and maintained there for 22 hrs. The heating curve showed a large absorption of heat at the eutectic, hence the boundary must be above 175° C., and the size of the point places it very near 177° C. Such experiments are difficult to carry out successfully because of the narrow temperature limits between which some of the alloys are uniform solid solutions. During the work a thread recorder was used to show that there were no accidental temperature variations.

The method also suffers from three other disadvantages. First, there is no evidence that certain of the solid solutions were not super-cooled, despite the comparatively long annealing times. Longer times

FIG. 4.—19 per cent. Tin. Quenched from 182° C. × 40.

FIG. 5.—19 per cent. Tin. Quenched from 178° C. × 40.

FIG. 6.—19 per cent. Tin. Quenched from 191° C. × 100.

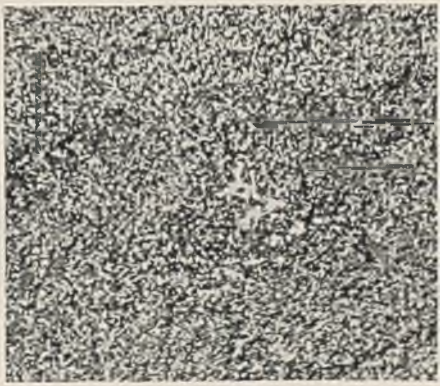

FIG. 7.—Same specimen as Fig. 5. Repolished after 14 days. × 100.

FIG. 8.—18 per cent. Tin. Quenched from 173° C. × 100.

FIG. 9.—Same specimen as Fig. 8. Repolished after 14 days. × 100.

would not remove this doubt. Supersaturated liquid solutions may remain metastable for years under certain conditions. Secondly, this work shows that tin will dissolve comparatively rapidly in solid lead. It is therefore possible that two-phase alloys may have become uniform on the way up from the phase boundary to the eutectic temperature. This applies particularly to the alloys poor in tin. Thirdly, results must be obtained by "creeping." "Bracketing" cannot be used, because when two phases have been produced much time is spent in obtaining a uniform solid solution again and in proving it to be uniform. The process is therefore slow; on an average, each point needed 5 days.

It is probable that the boundary given by this method, although much higher than that given by the differential cooling-curves, is still too low. The results are given in the Appendix and in Fig. 2.

THE LINE AT 150° C.

It is convenient to discuss this line here, because the evidence which has been obtained is purely thermal. There is no doubt at all that many of these alloys after annealing for a considerable time just above the eutectic show the eutectic arrest on cooling followed by a comparatively large evolution of heat near 150° C. Representative opinions about the cause of this line have already been summarized (p. 267).

It is generally agreed that the evolution of heat is greatest in an alloy containing approximately 18 per cent. of tin, that it decreases as the eutectic point is reached, and that it is absent in the tin-rich alloys. The pre-eutectic lead-rich solid solution is thus alone involved in this change.

Experiments with an alloy containing 90 per cent. of tin either yielded negative results or showed a very small heat evolution from near the temperature of the eutectic. This evolution appeared to fade out near 150° C., and its existence could be adequately explained by the fact that both lead and tin separate from the solid solutions as the temperature falls.

Honda and Abé [3] publish cooling-curves of the lead-rich alloys which show the 150° C. point in a most marked way, but their heating-curves, taken immediately after the cooling-curves, show only a steady absorption of heat starting about 100° C. and ending at the eutectic. The author's curves are similar, but he finds this steady absorption to take place over a narrower range, from about 140° C. to 170° C. It is probable that the change is not reversible because the large evolution of heat on cooling is completed at a temperature above that at which the steady absorption of heat on heating starts. There are then three arguments against the allotropic theory :

(*a*) The change does not take place in that part of the lead-rich phase which is present in the eutectic.
(*b*) The change is not sharply and clearly reversible.
(*c*) There is no break in the α-phase boundary.

Fact (*c*) was first pointed out by Jeffery,[2] and the author has failed to find a break either by micrographic analysis or by his modified thermal method. At the same time, he wishes it to be realized that this work is difficult and that a break may yet be discovered.

There remains the explanation of Honda and Abé that the change is due to the rapid decrease of the solubility of tin in lead with a fall in temperature. This explanation cannot be correct if the author's work is correct, because he finds that the boundary does not show the abrupt inflection given by Honda and Abé.

As the evidence leads to the conclusion that the change takes place only in the lead-rich solid solution, an investigation of the behaviour of the 18 per cent. alloy, which could be obtained as a uniform solid solution, and the 25 per cent. alloy, which would always contain a quantity of the second phase, was undertaken. This work shows that the temperature at which the change occurs and its size are dependent on the previous history of the specimen. The experiments are summarized in Table I.

TABLE I

Heat-Treatment.	Evolution of Heat Starts, ° C.	Evolution of Heat Ends, ° C.	Size. Arbitrary Units.
18 *Per cent. Tin.*			
(1) New specimen. Annealed at 180° C. for 90 hrs.	156	148	115
(2) After (1). Annealed at 184° C. for 18 hrs. Annealed at 172° C. for 18 hrs..	168	indefinite	20
(3) Then annealed at 171° C. for 90 minutes	no point	...	...
(4) Then heated to 188° C. ; above eutectic for 25 minutes	159	152	70
25 *Per cent. Tin.*			
(1) New specimen. Annealed at 190° C. for 18 hrs.	168	165	55
(2) Then annealed at 190° C. for 3 hrs. and at 179° C. for 43 hrs. . . .	160	155	50
(3) Then annealed at 179° C. for 18 hrs. .	161	155	25
(4) Taken to 181° C. after (3) and curve taken immediately . . .	162	152	5
(5) Then annealed at 188° C. for 15 minutes	168	162	35

In every case, except the first experiment with the 18 per cent. tin alloy, the specimens probably contained both phases.

The direct and differential curves obtained in the first experiment with the 18 per cent. alloy are given in Fig. 1 (*e*) and (*f*). The numbers along the differential curve (*f*) denote temperatures in degrees Centigrade.

The author is of the opinion that the line near 150° C. would not be found if it were possible to work with an alloy in equilibrium, and that its presence may be due to either or both of two causes. Other methods indicate that it is difficult to bring about the breakdown of the solid solution at the correct temperature. The difference between the eutectic temperature and the temperature of this line may correspond with the supersaturated range of a liquid solution and the line itself to the labile boundary. If this view is correct, it follows that direct cooling-curves do not give the position of the true boundary, but only that of this labile boundary. On the other hand, the evolution of heat occurs even in the presence of considerable quantities of the second phase. The second explanation put forward tentatively is that under the conditions of these experiments the tin is deposited from the solid solution at the correct temperatures, but that this tin is not the stable, white allotrope, but some other form. The heat noticed is the heat of transformation, possibly even the latent heat of solidification, of the tin. On the tin-rich side of the eutectic the lead-rich phase is in an intimate mixture with the white tin, and the possibility of an unstable form of tin persisting over a range of temperature is therefore less.

MICROGRAPHIC ANALYSIS.

The alloys were made in alundum crucibles under hydrogen. They were cast on a polished steel block standing in a mixture of ice and salt, and as soon as the plates were solid they were pushed into the freezing-mixture. It was noticed that the metal, even after considerable periods in the cold bath, when removed and dried, gave out so much heat that the plates were almost too hot to hold firmly in the hand. These specimens appeared to be homogeneous.

As chief stress is placed on the micrographic results, a chemical analysis of certain of these plates was made. That weight of an alloy which contained about 0·2 grm. of tin was taken and the specimen was rolled out and dissolved in 12 c.c. of concentrated nitric acid diluted with 6 c.c. of water. When the action was over, 50 c.c. of boiling water were added and the assay was left on a hot plate for 2 hrs. The tin dioxide was then filtered, washed with hot, 1 per cent. nitric acid, dried, and ignited. To check the assays, blanks were made up by wrapping a small, weighed piece of tin in lead foil. The metals were melted in a silica crucible by playing a small hydrogen flame on them and the whole of each tiny ingot was then analyzed. Blanks containing 10, 15, and 19 per cent. of tin gave 10·01, 15·04, and 18·97 per cent., respectively. The 11, 13, 16, 18, and 19 per cent. alloys were found to contain 11·08, 13·07, 15·94, 17·97, and 19·00 per cent. of tin respectively.

To prepare the alloys for micrographic examination, the specimens were taken down first on a coarse and then on a fine file moistened with alcohol. Next they were ground on fine emery papers lubricated with a considerable quantity of fine oil. After cleaning in ether, they were polished on a cloth disc using a fine suspension of chromium oxide in methylated spirits as the polishing agent. They were etched electrolytically in a saturated solution of lead nitrate diluted with four times its volume of water, using a cathode of platinum foil and a platinum spiral as anode. Current was supplied from a 2-v. accumulator, and there was a 40-ohm coil in the circuit. The best results were obtained when the alloys were kept out of water as much as possible. The essentials of this technique were originally suggested by Rosenhain and Tucker.[1]

A short period of annealing at a temperature just above that of the eutectic was all that was required to produce uniform solid solutions. Even the 19 per cent. alloy became uniform in less than 18 hrs. Then, without removing the specimens from the furnace, they were annealed at suitable temperatures. When the phase boundary was being determined the annealing periods were about 18 or 42 hrs., for the solidus 2 or 18 hrs. The later resistivity experiments indicate that these times were too short, but, in view of the fact that specimens annealed at a definite temperature for 18 or 42 hrs. behaved in exactly the same way, the ideal times are obviously prohibitively long. The work was accelerated somewhat and made more accurate by the use of a triple furnace. This consisted of a long, fireclay tube, 2 in. in diameter, electrically heated, and so wound that a temperature gradient existed along its length. The temperature of its inner surface was thermo-electrically controlled. The ends were closed by rubber bungs which were bored to carry loosely three glass tubes of about ½ in. internal diameter. The specimens were heated in hydrogen in these inner tubes, each of which could be moved horizontally to a hotter or colder part of the furnace. Hence three specimens could be annealed at different, but definite, temperatures at the same time. The necessary three thermocouples were easy to control.

The results are given in the Appendix and plotted in Fig. 3, and certain of the photographs taken are reproduced in Figs. 4–9 (Plate XLVII). In these and all the other photographs, the tin-rich phase is white, although sometimes if the specimens were not properly cleaned the liquid phase etched black. Figs. 4–6 (Plate XLVII) show the 19 per cent. alloy quenched from various temperatures. It will be noticed that all these photographs show black smudges. These smudges could not be removed by polishing and are probably due to the fact that the solid solution is not retained by quenching. The marks probably indicate the more stable patches.

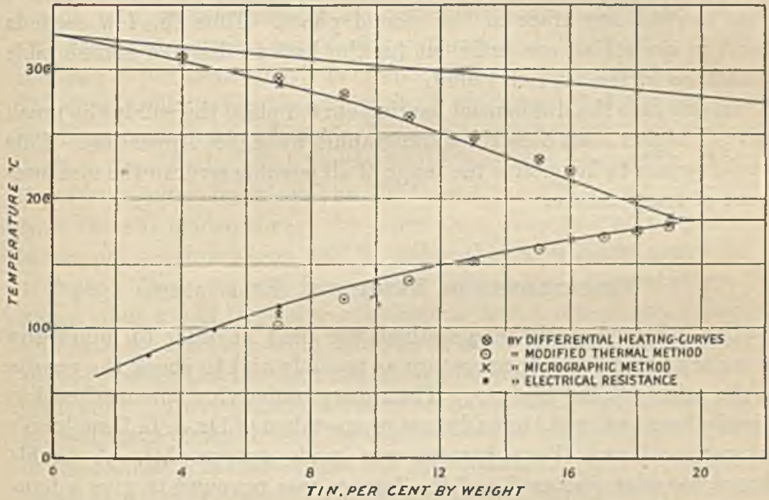

Fig. 3.

A remarkable property of these alloys is that grain-growth proceeds rapidly at ordinary temperatures. Fig. 7 (Plate XLVII) shows the specimen of Fig. 5, but repolished after 14 days at room temperature. It is evident that very considerable changes have taken place.

Typical structures seen when fixing the α-phase boundary are shown in Figs. 8 and 9 (Plate XLVII). The tin appears first at the crystal boundaries of a cooling specimen and then comes out of solution within the mother crystal. There is preferred orientation, but this orientation is noticeable only when the specimen has been annealed just below the boundary. If the alloy be annealed only 10° C. too low, or if it be kept at room temperature for a few days, this structure either does not appear or is completely obscured. The presence of free tin in alloys containing less than 8 per cent. of that metal is difficult to detect, and the practical limit of microscopy appears to be 7 per cent. of tin and near 120° C. Except at the lower temperatures the agreement between these points and those obtained by the modified thermal method is reasonably good. The latter are always the lower.

The solidus as fixed by micrographic analysis may still be a little high, at least for those alloys containing little tin, not only because of the apparent difficulty of making liquid appear at the correct temperature, but also because lead can dissolve tin very quickly indeed. For example, three specimens containing 4 per cent. of tin were quenched on a rising temperature at 305° C., 307° C., and 309° C. The last had collapsed in the furnace and the second had obviously been pasty; none showed any trace of the second phase. Thus the few seconds spent in quenching are sufficient for the lead to dissolve considerable quantities of the tin-rich liquid.

In one case the differential heating-curves place the solidus as much as 7° C. higher than does the micrographic work (see Appendix). This would appear to be outside the range of all possible error in the measurement of temperature.

MEASUREMENT OF ELECTRICAL RESISTANCE.

The difference resistance method was used in order to follow the boundary to as low a temperature as possible and to check the results of the micrographic analysis. The theory underlying this method has already been outlined,[4] but advantage was taken of Dr. J. L. Haughton's suggestions [5] and the apparatus was made autographic. A double thread recorder was used and the furnace was rewound to give a temperature difference of only 1° C. over the working length. Squirted alloy wires of diameter 0·75 mm. and length approximately 80 cm. were wound on a frame made of silica tubes. The ends lay side by side and were either soldered to stout copper leads or were bound to them by thin copper wire. The wires were then annealed to make them uniform solid solutions. The other arms of the Wheatstone's bridge were two Manganin wires of approximately the same resistance as that of the alloy wires. The length of one of the Manganin wires could be varied at will. When the connections were made, the resistances were adjusted so that there was practically no deflection of the thread recorder needle, and then the Manganin wires and all possible connections were sunk in paraffin wax. The thread recorder scale was 10 cm. and represented 1 m.v. The fall in potential across one side of the bridge was about 50 m.v. The sensitivity so obtained was amply sufficient and the arrangement was such that small changes in the voltage of the accumulator were of no importance. The second thread recorder was used for the measurement of temperature.

The clear results obtained for the copper–silver alloys could not be obtained here, probably because of the difficulty of preventing the alloys from becoming metastable. Transformations took place at much too low temperatures and accurate extrapolations were impossible.

In the present work two wires differing in composition by about 2 per cent. were chosen. After the final adjustments to the apparatus had been made, these wires were annealed for 24 hrs. At the end of that time their relative resistances were always constant. Then the temperature of the furnace was allowed to fall at a rate of some 3° C. per hr. until an inflection in the curve had been obtained and the relative resistances were again nearly constant. A time–e.m.f. curve for the pair 5 per cent. and 3 per cent. of tin is reproduced in Fig. 10. The time ordinate has been very much condensed, but the e.m.f. scale has been expanded five times. The numbers represent temperatures in degrees Centigrade. This curve would lead one to suppose that the 5 per cent. alloy transforms at 42° C. and the 3 per cent. near 26° C. Now there is evidence that the 5 per cent. alloy in stable equilibrium is two-phase below about 100° C., hence the curve shows nearly 60° C. of supercooling. It is to be expected that at low temperatures a two-phase alloy would be nearer equilibrium than a one-phase. Hence in this case the lead-rich solid solution of the 5 per cent. alloy at 30° C. should contain less tin than the metastable lead-rich phase in the 3 per cent. alloy. Its resistance therefore should be the lower, but ultimately the resistance of the latter alloy should decrease at a faster rate than that of the former. It follows that the curve should at first over-shoot the value at which it settles. This over-shooting was never found, and it is doubtful whether the lower point on the curves does really represent the transformation of the second alloy. On the other hand, these lower values agree well with the equilibrium diagram, and heating curves tended to show that the second alloy, too, always contained free tin.

When the resistance of the cold alloys had become constant (Fig. 10), the temperature was slowly raised. There was no change in the relative resistance up to 74° C., and the α-phase boundary of the 3 per cent. alloy therefore appears to lie near 74° C. When the temperature had reached 93° C., it was again lowered temporarily. There was a small rise in the potential difference, showing that the resistance of the 5 per cent. alloy had started to fall at once. This indicates that this wire was nearly in equilibrium as the temperature rose, even though the fall in resistance was not so great as had been expected, and also shows that it is much more difficult to reach equilibrium on a falling temperature. When the temperature reached 93° C. once again, the potential difference was almost exactly the same as it had been 32 hrs. earlier. As the temperature rose to 99° C. the potential difference continued to decrease, and the curve shows that the α-phase boundary lies near 99° C. It is to be noted that the potential difference returned to its original value after the 10 days.

The pairs 10–7, 7–5, 5–3, and 3–1 per cent. of tin were examined. All except the last gave curves similar to that shown in Fig. 10, and the results agreed well amongst themselves. This electrical method shows that the 10 per cent. alloy is a uniform solid solution above 145° C.; the micrographic and the modified thermal methods give 137° C. and 129° C., respectively. The highest figure is thought to be most accurate, but it is probable that the three methods would give almost identical results for alloys containing about 19 per cent. of tin.

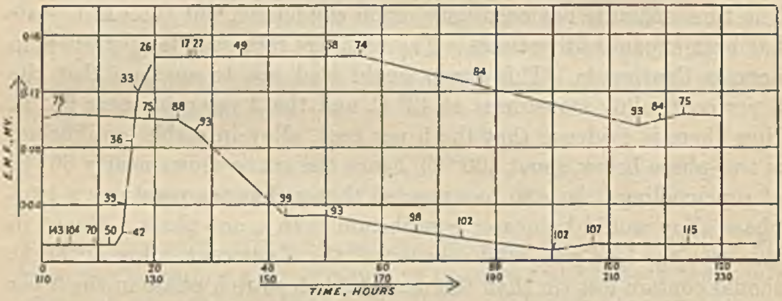

Fig. 10.—Potential Difference–Time Curve for Pair 5 and 3 per cent. Tin.

The point near 74° C. for the 3 per cent. alloy found by the curve shown in Fig. 10 is shown in the Appendix and is plotted in Fig. 3. This point must be accepted tentatively, because the 3 per cent. alloy, as a member of the 3–1 pair, apparently could not be broken down either by slow cooling, by keeping for long periods in ice and in iced brine, or by passing current from an induction coil through the cold wire.

THE TIN-RICH ALLOYS.

The solidus of the tin-rich alloys was fixed by the micrographic method. Alloys containing 1·0, 1·5, and 2 per cent. of lead begin to melt at 215° C., 207° C., and 198° C., respectively. These points lie on a straight line which passes through the melting point of tin and which meets the eutectic line at 2·9 per cent. of lead. On the other hand, an alloy containing 2·5 per cent. of lead still contained traces of liquid after it had been annealed at 185° C. for 5 days. No serious error will be introduced if the solubility of lead in tin be taken as 2·6 per cent. by weight.

SUMMARY.

The lead–tin alloys, particularly those rich in lead, have been examined by various methods, and an equilibrium diagram (Fig. 11) is given. Compositions are expressed in percentages by weight and also in atomic percentages (broken line). The data used for the construction of this diagram are given in this paper, except that the tin-rich phase boundary is after Jeffery,[2] the eutectic is placed at 61·86 per cent. by weight of tin,[6] and the liquidus is taken from some of the author's unpublished work. This new diagram differs very considerably from the older diagrams.

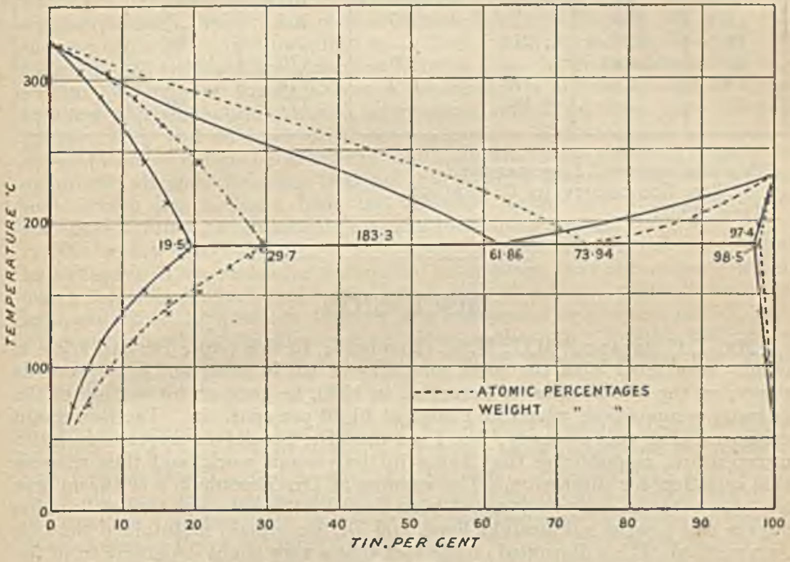

FIG. 11.

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[1] Rosenhain and Tucker, *Phil. Trans. Roy. Soc.*, 1908, [A], **209**, 89.
[2] Jeffery, *Trans. Faraday Soc.*, 1928, **24**, 209.
[3] Honda and Abé, *Sci. Rep. Tohoku Imp. Univ.*, 1930, [i], **19**, 315.
[4] Stockdale, *J. Inst. Metals*, 1931, **45**, 132.
[5] Haughton, *J. Inst. Metals*, 1931, **45**, 140.
[6] Stockdale, *J. Inst. Metals*, 1930, **43**, 193.

APPENDIX

Alloy.	Solidus, ° C.		Phase Boundary, ° C.			
Tin, Weight per Cent.	By Heating Curves.	Micro-graphic.	By Cooling Curves.	Method of Heating.	Micro-graphic.	Resistance.
3	...	...	...	...	...	74(?)
4	310	305	...	...	...	...
5	...	...	...	...	...	99
7	294	288	69	97–105	>110	117
9	281	...	97	121–124	...	...
10	...	268	...	...	137	145
11	264	...	115	136	...	...
13	248	242	132	151	152	...
15	230	...	145	161	...	...
16	221	214	...	...	168	...
17	absent	...	160	170	...	...
18	,,	196	156	174	176	...
19	,,	186	...	177	180	...

The Goldsmiths' Laboratory,
The University of Cambridge.
April, 1932.

DISCUSSION.

Mr. J. Cartland,[*] M.C., M.Sc. (Member): In this paper Dr. Stockdale is chiefly concerned with the solid solubility of tin in lead, but in a previous paper, on the composition of eutectics, in 1930, he gave an estimation of the eutectic composition, which he placed at 61·86 per cent. tin. Dr. Rosenhain criticized that very severely, but I see that Dr. Stockdale, apparently quite unrepentant, re-publishes that figure in the present work, and thus reopens this question for discussion. The essence of Dr. Rosenhain's criticism was that the eutectic composition had been fixed by the extrapolation of liquidus curves which were not straight lines, and Dr. Rosenhain maintained that his own method, which depended on the fact that a very slight departure from the eutectic composition made a very marked difference in the microstructure, fixed this point more reliably; and on that he placed the eutectic at 63·0 per cent. tin.

I would suggest that, in suitable circumstances, there is a third method of obtaining the eutectic composition—namely, that of draining from a mass the most fusible constituent and analyzing it. That method was first mentioned before this Institute in 1921 in the discussion on Haughton's paper on the system tin–copper. Haughton, by thermal methods, had placed the tin–copper eutectic at 1 per cent. copper, but Rooney explained that he had managed to drain out of a material containing 9 per cent. copper a material which analyzed only 0·75 per cent. copper. He asked Haughton for an explanation, possibly being too polite to state that in his opinion that was the true eutectic, but I think that is what he meant. Draining the most fusible constituent away and analyzing it is a method which is applicable only on a large scale, and it is therefore an example of the rather rare case of a large-

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scale process which can yield scientific information which the same process, done on a laboratory scale, fails to give.

We regularly employ a process of multiple draining combined with fractional crystallization, into the exact technique of which I need not enter here, and by which we obtain from lead–tin–antimony alloys a material which, I believe, consists of 100 per cent. eutectic. My evidence that this contains 100 per cent. eutectic is that the product, within very narrow limits, is uniform, and is independent within rather wide limits of the material with which we commence. I have recently examined 52 analyses of 2-ton batches representing 104 tons. Unfortunately the light that this might throw on the vexed question of the composition of the tin–lead eutectic is masked to some extent by the presence of antimony, but nevertheless research carried out by the British Non-Ferrous Metals Research Association, starting on a basis of a tin–lead eutectic of 63 per cent., shows that none of these antimonial alloys, which are 100 per cent. eutectic, can contain less than 56·4 per cent. tin. We regularly obtain, however, a product which I believe contains 100 per cent. eutectic and which contains rather more than 1 per cent. less tin than that. I took those 52 analyses, and using the formula given in the book issued by the British Non-Ferrous Metals Research Association I converted each of those analyses to their non-antimonial equivalents and 27 of them gave a result between 60·9 and 61·5 per cent. tin. Therefore, although this question is masked to some extent by antimony, I do claim that these results of large-scale operations are some evidence that the true eutectic is lower than the 63·0 per cent. which has hitherto been the accepted figure, and that the results therefore support Dr. Stockdale's conclusions in his paper.

The exact determination of this eutectic is of some small commercial importance; if we make the reasonable assumption that the value of a tinman's solder is proportional to the percentage of eutectic which it contains, independent of the question whether it is antimonial or non-antimonial, then on present markets the discrepancy between these two leading authorities would make a difference to the world's annual tinman's solder bill of the order of £40,000.

Dr. W. ROSENHAIN,* F.Inst.Met., F.R.S. (Past-President): As it seems to amuse some people to tread on my tail, I do not see why I should not respond, and I think that I can deal with Mr. Cartland's remarks very summarily. After all, large-scale operations are very important from a commercial point of view, but when one seeks to base actual scientific determinations on them it is necessary to prove the purity of the materials. Dr. Stockdale, rightly and wisely, has taken an immense amount of trouble in eliminating the last traces of impurity, and then Mr. Cartland says that he can support the author's conclusions by calculations on a very approximate formula from a material containing 1 per cent. of antimony and x per cent. of other things. I do not think we need consider the matter further.

I am much more seriously interested in Dr. Stockdale's views about the arrest point in the lead-rich alloys of the lead–tin system. I am not sure that I can claim to be the first discoverer of that arrest point, but I think that Mr. Tucker and I were the first to investigate it systematically, and it was very difficult indeed to arrive at an explanation of the result, and ours was put forward only tentatively at that time, and I do not attach any undue weight to it to-day.

One of the difficulties about it is the fact that so far as our observations were concerned (and they were made with a considerable amount of care, and with apparatus and methods which at that time were a great deal more

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* London.

sensitive than those anyone else had used) the arrest point ceased at the eutectic concentration and that the alloys containing primary tin did not show it.

Various workers have ascribed this arrest to an allotropic transformation in tin which is supposed to occur at about that temperature, forgetting that in that case surely we should expect to find the arrest most marked at the tin end of the series. To a certain extent that is also an argument against the view that this arrest is due to anything like allotropy in the lead, because if the lead undergoes allotropic transformation one would expect the eutectic lead to undergo that transformation as much as the primary lead, and apparently it does not. At any rate, the explanations put forward by others—by the Italian workers—did not impress me in the least. I could not understand how anything in the nature of instability or under-cooling of any kind could lead to the development of a line of arrest points strictly horizontal on the diagram occurring at a definite temperature for all concentrations of tin above a certain value, and then below that value—near the lead end—falling steeply down to temperatures in some cases below room temperature.

I think that the problem has yet to be solved, and I quite appreciate Dr. Stockdale's rather tentative attitude towards it. I believe that we must rather reserve our judgment until we know still more about these things. There are quite a number of these rather mysterious transformations in our alloy systems. We are gradually beginning to understand some of them, and perhaps we can also learn in the future something about these particular ones. I do not know whether anyone has yet attacked this particular problem by means of X-ray analysis. Perhaps Dr. Stockdale could tell me. I believe that he has not used the method, although he has used many others with great care.

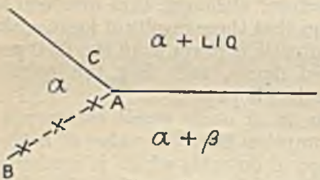

Fig. A.

As for the actual eutectic concentration, that also is apparently an open question. I think that the extrapolation of thermal data is unjustifiable to that extent. I do not claim infallibility for the other method, however, and possibly we shall find at some future time what the eutectic concentration is, if there is one. What I mean is this—that the change of melting point over a short range of composition may be so small that there is really no defining the point very accurately. I do not believe, in actual fact, that there is any theoretical reason for doubting the possibility of such a state of affairs, and Roberts-Austen actually drew a diagram with a tangential liquidus.

Dr. **Marie L. V. Gayler** * (Member): There are one or two questions that I should like to ask. I do not understand the reason why the author carries out certain heat-treatments. He deals (p. 271) with an alloy containing 19 per cent. tin, anneals it for 16 hrs. at 190° C. and then cools to 182° C. His eutectic temperature is 183·3° C. The composition of the alloy, 19 per cent., lies very near to the horizontal part of the solidus. If thermal curves are taken of a series of alloys as shown in Fig. A, it will be found that the temperatures of the eutectic arrest points generally tend to fall as shown by AB. Under equilibrium conditions the last eutectic arrest should be at A. The author has taken an alloy which, according to his diagram, is close to A. To start heating that alloy for 16 hrs. at a temperature *above* the eutectic temperature seems to me unwise, because the chances are that more eutectic may appear in the alloy.

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

There is another case in which he has done the same sort of thing, but in order to determine the phase boundary. It is stated on p. 272 that a specimen was annealed at 185° C. for 24 hrs. That again is presumably above the eutectic temperature, and again a 19 per cent. alloy is used, and consequently there may be liquid in the alloy. The temperature is dropped to 180° C. in 0·5 hr., a cooling curve being taken. There was no arrest at the eutectic temperature; the alloy is said, therefore, to be a uniform solid solution. Dr. Stockdale may be perfectly right, but his rate of taking that cooling curve is so slow that he may have masked that evolution of heat by his own conditions. I do not therefore think that he is absolutely justified in reaching that conclusion.

Again he lowers the temperature to 177° C. and maintains it there for 17 hrs.; he takes the heating curve up to 187° C. and finds no arrest, and deduces that the α-phase boundary lies below that temperature; he then decreases the temperature to 175° C. and maintains it for 22 hrs., which is 2° C. below the original temperature. Dr. Stockdale then says, "The heating curve showed a large absorption of heat at the eutectic, hence the boundary must be above 175° C." I do not follow that. If this alloy is in solid solution, when temperature is raised he ought not to get a *large* arrest at the eutectic temperature, because he has already said that that alloy is homogeneous at the eutectic temperature. The large arrest should occur where the temperature of solidus is reached at the point C in Fig. A.

I think, therefore, that the method used is right in principle, but that the author's deductions are not quite justified, because he has annealed at temperatures which might give him erroneous results.

Dr. STOCKDALE (*briefly replying to Dr. Gayler*): I would point out that I had at first only a vague idea of the solubility of tin in lead. The first quickly-taken heating and cooling curves fixed the approximate positions of the solidus and of the alpha-phase boundary. Then the modified thermal method gave the position of the boundary more accurately, but it is stated in the paper quite clearly that this method gives results which are probably too low. Now, knowing the general position of the various fields, the much more accurate micrographic and electrical resistance methods were used to work up finally to what is considered a comparatively accurate result.

CORRESPONDENCE.

THE AUTHOR (*in further reply to the discussion at the meeting*): I am interested to find that Mr. Cartland's evidence obtained by examining the drainings from large masses of freezing alloy adds confirmation to the view that the lead–tin eutectic contains less than 63 per cent. of tin, but as an academic I have to discard this evidence. I share Dr. Rosenhain's views on the subject of impurities in metals, and think that it is as yet impossible to predict the effect of the presence of even a very small quantity of a single impurity on the position of a ternary point of this kind. I welcome Mr. Cartland's contribution in that it reminds the research worker that pure research is often of direct use to practical men.

I am sorry that the question of the eutectic concentration has been reopened. If it had occurred to me that this was going to be the subject of a mild controversy I would have published my experimental results in greater detail. I can only say now that the published curve of the 63 per cent. tin alloy * shows a definite pre-eutectic point and the shape of this

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* *J. Inst. Metals*, 1930, 43, 201.

curve is definite evidence that the pre-eutectic metal is tin. A curve of the 61·5 per cent. alloy (unpublished) also shows a pre-eutectic point and indicates that the pre-eutectic metal is now lead. The extrapolation is then between 63 and 61·5 per cent. The mean result was obtained by extrapolating two different lines in two different ways, the individual results being 61·65, 61·75, 62·0, and 62·0.

I had hoped that Dr. Rosenhain would have been able to explain the cause of the lower arrest line from my results. A curious fact about this line is that it does normally occur some 25° C. below the temperature at which the primary lead solid solution might be expected to excrete tin, and this constancy might well be used as an argument against any explanation involving instability. Usually, however, a set of cooling curves is taken under more or less the same conditions throughout, and I have shown that wide variations in the conditions do cause a change in the temperature and size of the arrest in any one alloy. The analogy of the problem to that of the metastable state in liquid solutions inclines me to the view that here, too, we may be dealing with substances which are not in equilibrium. I had suggested that this question is suitable for attack by the X-ray method, but I am informed that there are technical difficulties, which I do not fully understand, which might make its solution by this method impracticable.

I think that Dr. Gayler's difficulties will largely disappear if she realizes (*a*) that at the time of these preliminary experiments I had only a vague idea of the solubility of tin in lead, and (*b*) that in my opinion the reaction $\alpha + \text{liquid} \longrightarrow \alpha$ is much faster than $\alpha + \beta \longrightarrow \alpha$, and that therefore for the object in view it was *safer* to anneal slightly above than slightly below the temperature of the eutectic. I would repeat that these experiments were used only to determine the approximate position of the phase fields. That they gave results in close agreement with those given by other methods is incidental.

Dr. Gayler seems to have missed the fact that if an alloy, which under ideal conditions will exist for a few degrees as a uniform solid solution (just to the left of A, Fig. A), is annealed either in the α + liq. field or $\alpha + \beta$ field, and then is cooled or heated respectively, that alloy will show an arrest at the eutectic temperature provided that the temperature changes are not slow enough to allow the alloy to be always in equilibrium.

I agree that the arrest points tend to fall as shown by AB in Fig. A, but only either when the alloys contain impurities or when the pyrometer is not truly sensitive. This was actually used as a test for the materials and apparatus, and no difference between the eutectic temperatures in 20 and 25 per cent. tin alloys was found, although the former could contain only traces of the eutectic.

MECHANICAL PROPERTIES OF NICKEL WIRES.*

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(COMMUNICATION FROM THE STAFF OF THE RESEARCH LABORATORIES OF THE GENERAL ELECTRIC COMPANY, LIMITED, WEMBLEY, ENGLAND.)

SYNOPSIS.

The paper presents data on certain mechanical properties of fine nickel wires. The materials used include commercial nickel, refined nickel prepared by melting in hydrogen, and the same material with small additions of the elements commonly present in commercial nickel. Measurements have been made to determine the following:

(1) The effect of wire diameter on the tensile strength and elongation of commercial nickel after annealing at various temperatures.

(2) The effect of temperature of annealing on the tensile strength and elongation of all the materials mentioned above in the form of wire 0·0425 mm. in diameter.

(3) The short-time tensile strength of the same wires at temperatures up to 1000° C.

(4) The breaking strength of commercial nickel wire 0·0425 mm. in diameter under prolonged loading at temperatures up to 1000° C.

INTRODUCTION.

IN connection with certain applications of fine nickel wires in the electrical industry it was desirable to know something of their mechanical properties both at normal and elevated temperatures. Experience showed that different consignments of commercial nickel wire varied considerably in both strength and ductility even when the material contained more than 99·5 per cent. of nickel. No data were found to be available regarding the mechanical properties of nickel wires as fine as 0·04 mm. in diameter. Sykes ‡ has published curves showing the effect of temperature on the tensile strength and percentage elongation of wire 0·63 mm. in diameter, both cold-drawn and annealed at 800° C. The nickel used contained 0·15 per cent. iron as the chief impurity. The effect of impurities on the mechanical properties of rolled nickel has been investigated by various workers and summarized by the U.S. Bureau of

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* Manuscript received April 30, 1932. Presented at the Annual Autumn Meeting, London, September 14, 1932.

† Research Laboratories of the General Electric Company, Limited, Wembley.

‡ *Trans. Amer. Inst. Min. Met. Eng.*, 1920, 64, 780.

Standards.[*] Other papers on the properties of nickel which should be referred to are those by Browne and Thompson,[†] and by Jordan and Swanger.[‡] None of these, however, relates to fine-drawn wire. The authors have, therefore, carried out tests on fine wires made from commercial nickel and from laboratory melts containing small percentages of other elements. Mechanical properties at various temperatures up to 1000° C. have been determined for wires of different diameters and after annealing at various temperatures.

MATERIALS.

A representative sample of commercial nickel was obtained in the form of wire 1·5 mm. in diameter. The impurities were identified spectroscopically and determined by chemical analysis, as recorded in Table I.

A quantity of " Inco electro nickel " was made available through the good offices of the Research and Development Department of Messrs. Mond Nickel Company, Ltd., and this was further refined by re-deposition in a chloride bath. This was carried out mainly to remove the last traces of sulphur. If this element is present in excess of 0·01 per cent., it renders the nickel unworkable unless additions of manganese or magnesium are made. The refined nickel was stripped from the cathode and heated in pure hydrogen for 1 hr. at 1000° C. to reduce any oxide. It was finally melted in magnesia crucibles in an atmosphere of pure hydrogen in a high-frequency furnace, treated with nitrogen, and cast into 0·5 in. diameter chill moulds. Full details of this method have been given in a previous paper.[§] Ingots prepared in this way, without the addition of a deoxidizer, can readily be rolled and drawn into wire. The analysis of the finished wire prepared in this way is given in Table I and represents a fairly high standard of purity.

A further check on the purity of this nickel was made by determining the temperature coefficient of electrical resistance. This is very sensitive to certain impurities. The value obtained between 0° C. and 100° C. was 0·00667 ohm per ° C. per ohm, compared with 0·0067 found by Jordan and Swanger[||] for electrolytic nickel containing 99·94 per cent. nickel.

The same nickel was used for preparing ingots to which deliberate additions of the common impurities had been made. The proportion of the added element only was determined by analysis for these wires

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[*] *U.S. Bur. Stand. Circ.*, No. 100, 1924.

[†] *Trans. Amer. Inst. Min. Met. Eng.*, 1920, 64, 387.

[‡] *U.S. Bur. Stand. J. Research*, 1930, 5, 1291.

[§] Smithells, Williams, and Grimwood, *J. Inst. Metals*, 1931, 46, 443.

[||] *Loc. cit.*

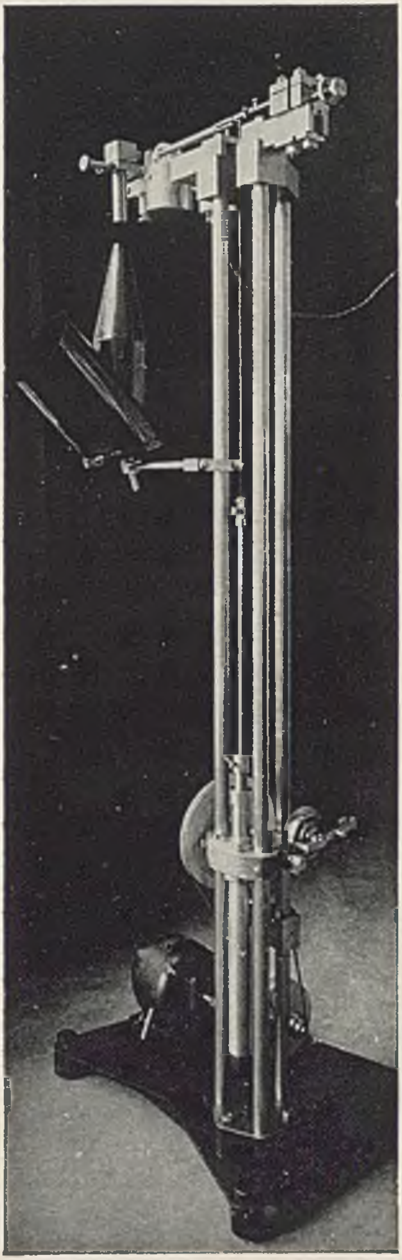

FIG. 1.—Wire Testing Machine.

FIG. 3.—Left: Fine-grained Wire showing general elongation.
Right: Coarse-grained Wire showing local elongation. × 20.

[To face p. 288

Fig. 4.—Etched Section of Wire shown in Fig. 3 (left). × 200.

Fig. 5.—Etched Section of Wire shown in Fig. 3 (right). × 200.

Fig. 6.—Etched Section of Tensile Specimen showing necking in a single crystal. × 200.

FIG. 8.—Refined Nickel.

FIG. 9.—Nickel + 0·07 per cent. Magnesium.

FIG. 10.—Nickel + 2·33 per cent. Iron.

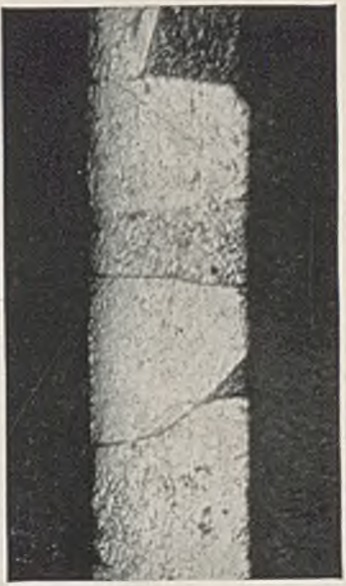

FIG. 11.—Nickel + 0·34 per cent. Manganese.

Nickel wires 0·0425 mm. in diameter annealed for 5 minutes at 1000° C. in hydrogen. Etched with nitric acid + acetic acid. × 500.

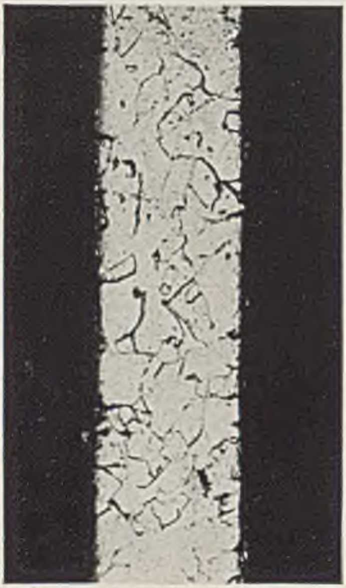

FIG. 12.—Nickel + Iron annealed at 620° C. × 500.

FIG. 13.—Nickel + Iron annealed at 720° C. × 500.

FIG. 14.—Refined Nickel annealed at 720° C. × 500.

and is given in Table I, the other impurities being assumed to be the same as for the refined nickel. Although 0·5 per cent. of magnesium was added, less than 0·1 per cent. remained in the melt owing to volatilization. In the case of manganese about 0·4 per cent. was added, and to the other melt about 2·0 per cent. of iron. These are approximately the amounts found by analysis.

The cast bars were cold-rolled, with intermediate annealing in hydrogen at 900° C., down to 6 mm. diameter, swaged cold to 1·0 mm. diameter, and drawn cold through diamond dies. The last anneal was given at 0·15 mm. diameter, after which the wires were drawn cold to the finished size. The same die was used for finishing all the wires, to avoid differences in diameter. All the tests, with the exception of one series, were made on wires 0·0425 mm. in diameter.

TABLE I.

Material.	Nickel + Cobalt (by difference), %.	Cobalt, %.	Manganese, %.	Magnesium, %.	Iron, %.	Silicon, %.	Aluminium, %.	Carbon, %.	Sulphur, %.	Calcium, %.
Commercial nickel .	99·39	0·45	0·21	0·09	0·22	0·24	...	0·036	0·033	...
Refined nickel . .	99·91	0·29	trace	0·006	0·004	0·016	0·024	0·022	0·003	0·013
Nickel + manganese.			0·34							
Nickel + magnesium				0·07						
Nickel + iron. .					2·33					

MECHANICAL PROPERTIES.

Tensile Tests at Room Temperature.

The tensile strength and percentage elongation were determined at ordinary temperatures on a special wire testing machine—Fig. 1 (Plate XLVIII)—which has been in use at the Laboratories for some years. It differs from the usual type of tensile machine in that the load is applied by straining at a constant rate. It consists essentially of a thin steel beam about 6 in. long, provided at one end with a small radius threaded rod round which the test wire is secured. The beam is fitted with an aluminium extension, which carries an oil-damper, and, at the extreme end, a small glass slide engraved with a very minute scale. The scale is projected at high magnification on an enclosed screen conveniently situated in front of the machine. A clamp similar to that on the beam is carried on a steel rod, which is pulled downwards at a constant rate by an electrically driven screw. The speed can be varied, but for the present experiments a fixed rate of extension of 0·4 cm. per minute was used. The extension is automatically registered by a cyclometer attachment. As the load increases the projected image of the scale attached to the end of the beam moves across a line marked on the screen, and the load is read off directly. This scale is calibrated by attaching known weights to the clamping screw on the beam, in place of the test wire. The standard length of test-piece employed was 4 cm., and each of the given values represents the mean of four tests.

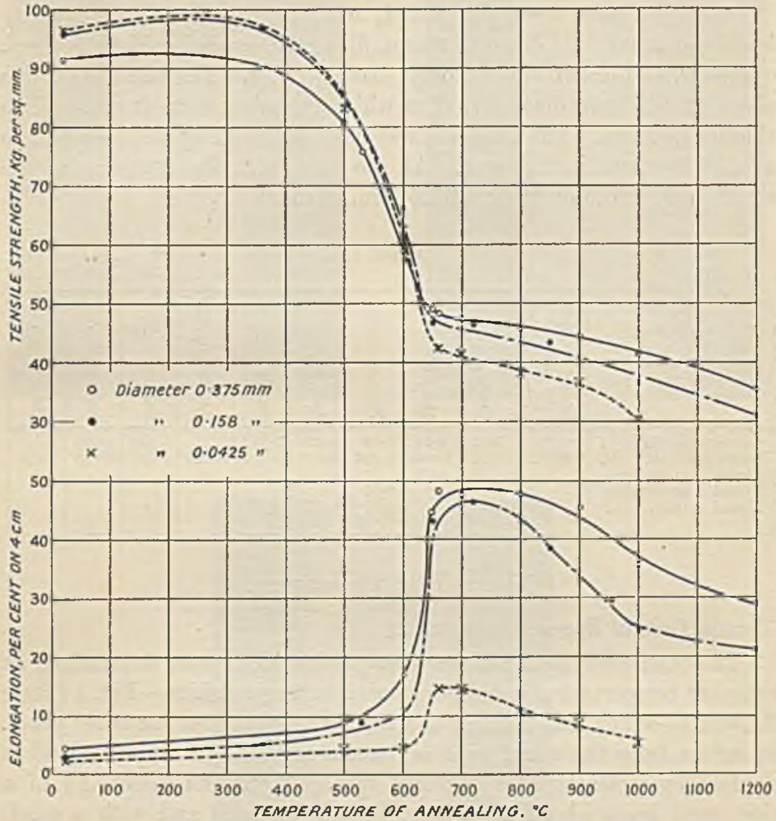

Fig. 2.—Tensile Strength and Elongation of Commercial Nickel Wires after Annealing at Various Temperatures.
Wires reduced 75 per cent. by cold drawing before annealing.

Fig. 2 shows the effect of the temperature of annealing on the tensile strength of commercial nickel wire of three different diameters (0·375, 0·158, and 0·0425 mm.), all of which had been reduced 75 per cent. in diameter since the previous anneal. The corresponding per cent.

elongation is also given. The wires were wound on spools and annealed for 5 minutes in hydrogen in a tube furnace.

From the shape of the curves it will be seen that the recrystallization temperature is about 640° C. for all the wires. It is noticeable that wires annealed below 640° C., which are presumably similar in structure, show an increase in tensile strength with decreasing diameter.

When the wires are recrystallized the effect is reversed. This is due to the fact that there is a wide difference in the number of crystals in the cross-section of the wires of different diameter. This number varies from about 20 in the case of wire 0·375 mm. in diameter to 2 or 3 for wire 0·0425 mm. in diameter, when annealed at 800° C.

The same effect is observed in the percentage elongation of annealed wires of different diameters, the curves for which are also given in Fig. 2.

The elongation varies only slightly with diameter for wires annealed below 600° C., but above this temperature there is a much smaller increase in the percentage elongation of the finest wire than of those of larger diameter. There is also a steady fall in elongation with increase in annealing temperature. This is due to the growth of large crystals, which frequently occupy the whole cross-section of the wire. If one of these crystals happens to be oriented so that the (111) planes lie in the position most favourable to slip, the extension is wholly confined to this crystal. When there is a sufficient number of crystals in the length of the test-piece for at least one crystal to be in this position, the percentage elongation appears low. Fig. 3 (Plate XLVIII) shows fine- and coarse-grained wires in which general and local elongation respectively have been produced. The structure of these wires is shown in Figs. 4 and 5 (Plate XLIX). Fig. 6 (Plate XLIX) shows a section through a single (twinned) crystal in which necking has occurred.

The actual values of tensile strength and percentage elongation for the wires 0·375 and 0·158 mm. in diameter annealed at 650° C. are the same as those usually found in commercial nickel—namely, about 49 kg./mm.^{2} for the ultimate strength and 48 per cent. elongation on 2 in.[*] The values are much lower, however, for the wire 0·0425 mm. in diameter, and for all the wires when higher annealing temperatures are used.

Fig. 7 shows the effect of annealing temperature on the tensile strength and elongation of nickel wires with various added elements, all the wires being 0·0425 mm. in diameter. These wires had all been reduced 70 per cent. by cold-drawing since the previous anneal. The curves for commercial nickel are included for reference. There are several points of interest. All additions increase the tensile strength of

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[*] Merica, *Trans. Amer. Soc. Steel Treat.*, 1929, **15**, 1054.

the cold-drawn wire, the effect of the very small addition of magnesium being quite marked. Whilst pure nickel softens with low-temperature annealing, the other wires show a slight increase in tensile strength when annealed below 400° C. The most noticeable effect of the addition of

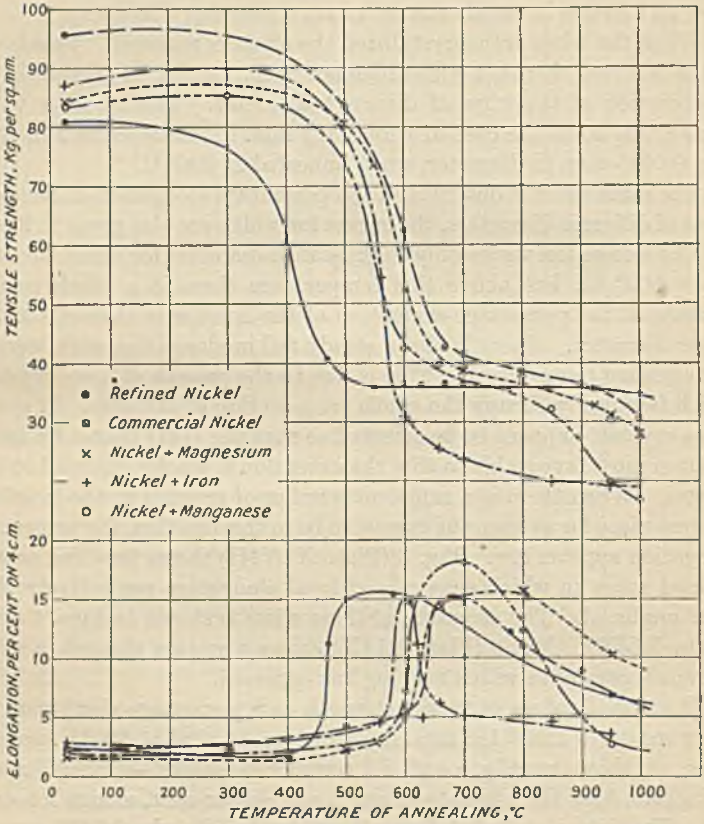

Fig. 7.—Effect of Minor Constituents on Tensile Strength and Elongation of Nickel Wire 0·0425 mm. in Diameter after Annealing at Various Temperatures.

other elements is on the recrystallization temperature, the values deduced from the curve being given in Table II.

A batch of Mond nickel specially selected for its purity, and which after melting in hydrogen could be worked without the addition of magnesium or manganese, also gave a value of 480° C. for the annealing temperature of pure nickel.

The fact that less than 0·1 per cent. of magnesium raises the annealing temperature 160° C. is remarkable. Similar effects have, however, been observed with other metals, for example, the effect of iron on silver * and antimony on copper.† The hardening effect of the added elements is still apparent in recrystallized wires, provided the annealing temperature is not too high. Added elements lead to the development of large crystals in wires annealed above 800° C., with consequent fall in tensile strength and percentage elongation as previously explained.

TABLE II.

Material.	Recrystallization Temperature, ° C.
Refined nickel	480
Nickel + iron	580
Nickel + manganese . . .	620
Nickel + magnesium . . .	640
Commercial nickel	640

The effect is slight with magnesium and with commercial nickel, but is particularly noticeable in the case of manganese.

Figs. 8, 9, 10, and 11 (Plate L) show the structure of the various wires after annealing at 1000° C. The very large crystals in the wire containing manganese will be noticed. The results obtained with the wire containing iron are also interesting. The very rapid fall in both tensile strength and elongation after annealing above 650° C. corresponds with a rapid increase in grain size at this temperature, as seen from Figs. 12 and 13 (Plate LI), which should be compared with Fig. 14 (Plate LI).

Short-Time Tensile Tests at High Temperatures.

The apparatus used for short-time tensile tests at temperatures up to 1000° C. is shown in Fig. 15, the principle being the same as in the machine already described.

It employs a mirror and scale, and to obtain a large angle of deflection the beam must be short. The beam is tapered to minimize zero shift. Since only part of the wire under test is at the required temperature it is not possible to determine elongation. The beam has to be very thin, as the strength of these wires at the highest temperature used is only of the order of 6–7 grm. The apparatus is designed to give a constant speed of extension of 3·6 cm. per minute. A hydrogen atmosphere was maintained in the furnace to protect the wires from oxidation.

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* Widmann, *Z. Physik*, 1927, 45, 200.

† Archbutt and Prytherch, *J. Inst. Metals*, 1931, 45, 265.

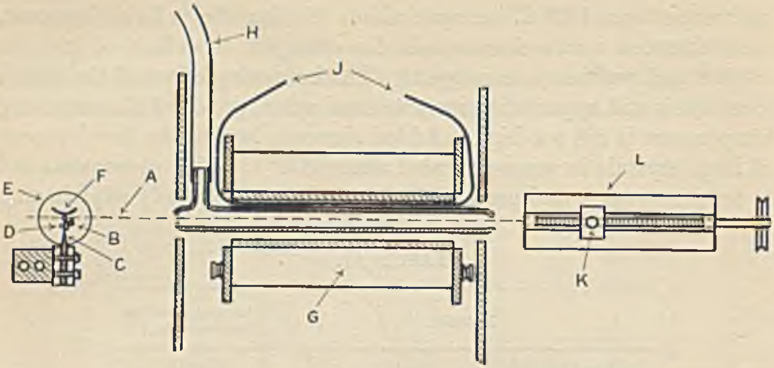

FIG. 15.—Tensile Testing Machine for Short-time Tests at High Temperatures.

A. Wire under test.	G. Electric furnace.
B. Clamp.	H. Hydrogen inlet.
C. Beam.	J. Thermocouple.
D. Oil damper.	K. Clamp.
E. Dash pot.	L. Straining mechanism.
F. Mirror.	

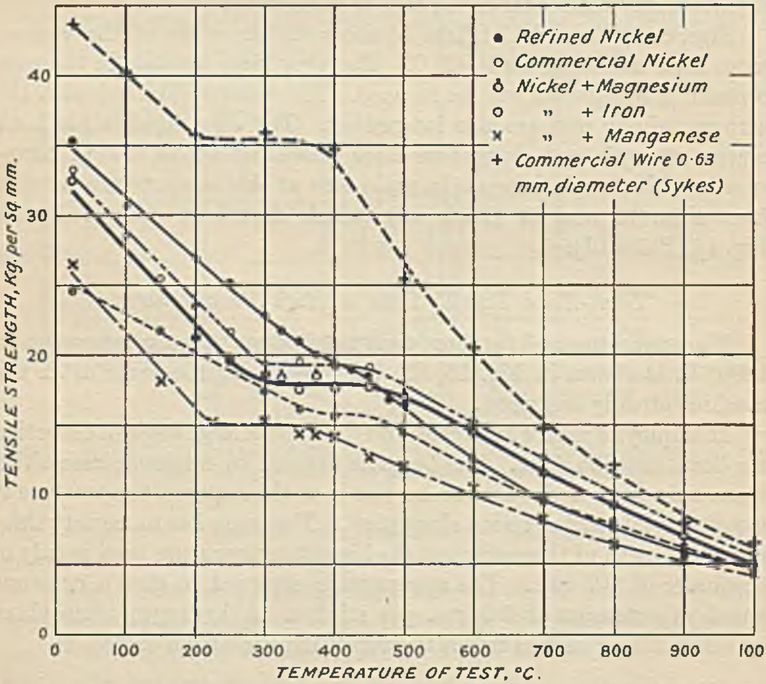

FIG. 16.—Effect of Minor Constituents on the Tensile Strength at Temperatures up to 1000° C. of Nickel Wires 0·0425 mm. in Diameter.

The wires used for these tests were first annealed by drawing continuously through a tube furnace at 925° C.

Tensile tests were made every 100° C. from room temperature to 1000° C. and at closer intervals over the range from 300° C. to 500° C. The results are plotted in Fig. 16. (Each point represents the average value from four tests.) Values obtained by Sykes * for wire containing 0·15 per cent. of iron and 0·5 per cent. of cobalt, 0·63 mm. in diameter and annealed at 800° C., are included for comparison.

All the wires have a well-defined arrest over the range 300°–450° C., except the refined nickel, in which it is very nearly absent. The cause of this discontinuity is not certain. Jeffries † considers that it is due to the spontaneous healing of slip-planes during deformation. There is also a magnetic change at approximately 360° C. (the actual temperature is much influenced by impurities), but it is not accompanied by any change in the lattice. The present curves show that both the period and temperature of the arrest are influenced by minor constituents, and might possibly be absent in absolutely pure nickel.

Slow Tensile Tests at High Temperatures (*Creep Tests*).

Tests were conducted on commercial nickel wire 0·0425 mm. in diameter to determine the time to fracture under small loads at high temperatures. This was done by suspending weights from single-strand filaments mounted somewhat like lamps in glass bulbs filled with argon. The filaments were maintained at temperatures ranging from 700° C. to 1000° C., as measured by a disappearing filament pyrometer, and the current–temperature curve was extrapolated to determine the current corresponding with 600° C. The temperatures recorded are brightness temperatures, and the true temperatures would be about 50° C. higher.

The arrangement of the wire and its weight before being sealed into the bulb is shown in Fig. 17.

To prevent the filament being damaged during sealing-in and pumping, a conical weight resting in a wire ring was used. The filament was welded with a slackness of 2–3 mm., and the bulb was inverted in a special rack and adjusted so that the weight swung clear of the ring while the test was carried out.

The current lead to the weight end of the filament consisted of a spiral of 0·06 mm. diameter nickel wire. This was at a dull red heat and had no retarding effect on the weight.

A suitable range of weights was found to be from 0·4 to 4·0 grm., and

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* Sykes, *Trans. Amer. Inst. Min. Met. Eng.*, 1920, **64**, 780.

† "Science of Metals," p. 188.

the time to fracture for filaments thus stressed was determined at 600° C., 700° C., 800° C., 900° C., and 1000° C. The load-time curves are given in Fig. 18, the average of three tests being taken for each of the plotted values.

It should be noted that the time scale has had to be altered for each diagram so that the points could be plotted. The curves are of the type usually found in tests of this kind, of which examples for various materials are given by Tapsell.* The measurements described in this section were made solely to determine what load could safely be applied to these fine wires without causing failure during a period of about 1000 hrs. The results obtained, however, indicate that the method might be adapted to give useful data on creep over much longer periods, and for various materials at temperatures nearly up to their melting points. The advantage of the method lies in its economy compared to the costly apparatus required for creep tests on large test-pieces.

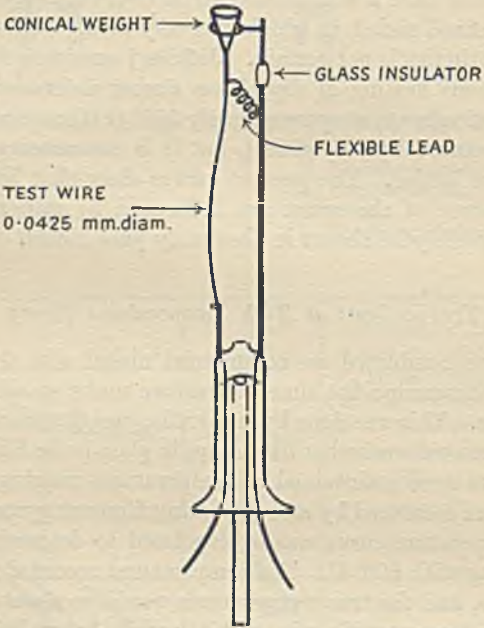

Fig. 17.—Method of Mounting Wire before Sealing into Glass Bulb for Creep Tests.

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* Tapsell, "Creep of Metals," p. 119. London: 1931.

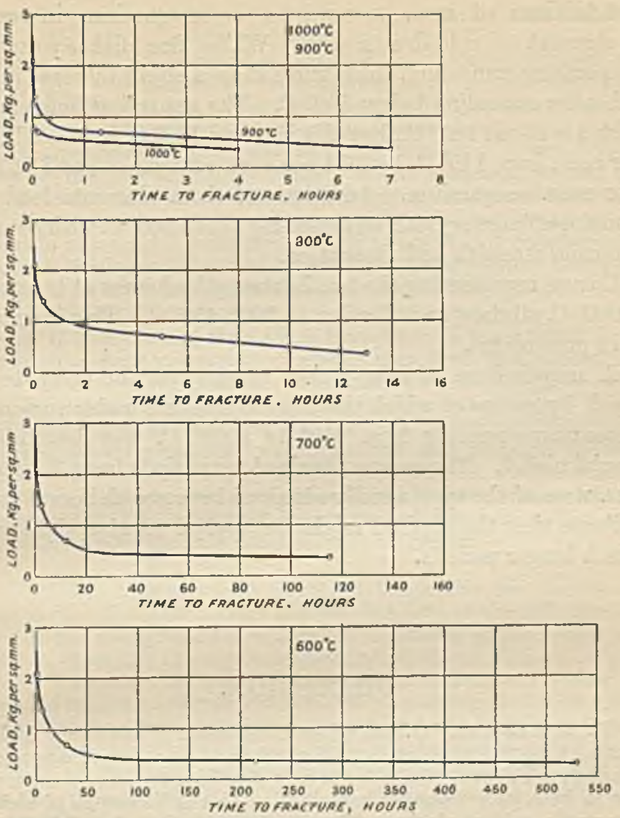

Fig. 18.—Slow Tensile Tests (Creep Tests) for Commercial Nickel Wire 0·0425 mm. in Diameter at Elevated Temperatures.

(*Note.*—The time scale is different for each temperature.)

Summary.

The main conclusions reached from the data presented in this paper are as follows:

(1) The annealing temperature of commercial nickel wire which has been reduced 75 per cent. by cold-drawing is independent of wire diameter. For the material used this temperature is 640° C. as judged by changes in tensile strength and elongation. For wires annealed below 600° C. the tensile strength is higher the finer the wire, but this is reversed when the wires are annealed above 640° C. This, and similar effects, are attributed to the relative dimensions of the wire and the crystals, which latter may occupy the full cross-section of the wire.

(2) Additions of iron, manganese, or magnesium increase the tensile strength of cold-drawn wire. Whilst fine nickel softens with low temperature annealing, these wires show a slight increase in tensile strength after annealing below 400° C. The annealing temperature of pure nickel is about 480° C., but this is raised 100° C. by the addition of 2·33 per cent. iron, 140° C. by 0·34 per cent. manganese, and 160° C. by 0·07 per cent. magnesium. Additions of these elements lead to the development of large crystals on annealing above 800° C. with consequent fall in tensile strength and elongation.

(3) Curves representing the tensile strength of wires at temperatures up to 1000° C. all show an inflection at 300°–450° C. This is practically absent in pure nickel.

(4) A simple form of long-period tensile test, or creep test, was developed, by means of which the time to fracture under various loads at temperatures ranging from 600° to 1000° C. was determined for commercial nickel. The curves obtained for periods from 30 seconds to 1000 hrs. were of the type usually obtained by more elaborate methods, and indicate that the method might be applied to give data on creep over much longer periods.

DISCUSSION.

Mr. W. R. Barclay,* O.B.E. (Vice-President): I have very little to say except that I do feel that, on behalf of those of us who are engaged in the nickel industry, I should offer a few words of tribute to the authors for what I consider to be a very valuable contribution to the literature of nickel, particularly on the subject of wire. There are many practical problems on which this paper offers suggestive ideas without definitely touching on them. The question of the purity of nickel wire is, in particular, vitally important, inasmuch as purity is absolutely essential for many purposes connected with the electro-magnetic properties of the material. On the other hand, in actual manufacture there are difficulties in the technique of manufacture of nickel wire, which have involved the necessity for making additions of elements such as magnesium and manganese, and this has definitely decreased the standard of purity of nickel wire as compared with, for instance, copper and other similar commercial products. It is, however, of interest to remark that, during the last two years, there has been a definite step in the direction of getting higher standards of purity in commercial nickel wire. We are now able, having a more thorough understanding of the subject, to cut down very materially the additions of other elements such as manganese and magnesium, and obtain a much higher standard of purity. It is, for example, no uncommon thing now to obtain in commercial materials a standard of purity of 99·6 per cent.

Dr. Maurice Cook,† M.Sc. (Member): There is one point in this paper

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

† Senior Research Metallurgist, I.C.I. Metals, Ltd., Birmingham.

that I find of special interest, for it seems to be possibly allied in nature to that dealt with in the paper by Mr. Miller and myself.*

The curves in Fig. 7, particularly that for nickel containing iron, relating tensile strength with annealing temperature, show a deflection from the normal smooth curve in the region subsequent to recrystallization, similar to that shown in annealing curves relating both tensile strength and hardness to annealing temperature for alloys discussed in our paper. It would seem that the causes giving rise to this retardation in the annealing process may be similar both in the case of the various nickels which the authors have examined and the different brasses which we have studied. The authors do not appear to have made any specific reference in their paper to this peculiarity on the tensile curves, but I should be very interested to know whether they have any comments to offer as to the causes which have given rise to it.

Professor R. S. Hutton,† D.Sc. (Vice-President): I think that it is obvious in discussing the degree of purity of metals that there is a liability to controversy on account of the different methods of analysis employed. I wonder whether the authors could give us the electrical conductivity of this nickel compared with others previously worked with? So far as I remember, the highest purity nickel previously examined was that prepared specially by the Physikalisch-Technische Reichsanstalt for electrical conductivity tests.‡ That was stated at the time to be very much purer than any commercial nickel; if this nickel of the G.E.C. Research Laboratories is purer than that, it might be interesting to have the fact definitely put on record.

Dr.-phil. W. J. P. Rohn ‖ (Member): I think that the authors deserve special thanks for giving such exact and detailed data on the influence of small impurities on the mechanical characteristics of a metal within a wide range of temperatures, especially as very little information on this subject has yet been obtainable. I suppose the purity of the nickel which was refined by the authors was of the same order as that tested some years ago in the Physikalisch-Technische Reichsanstalt and which contained only 0·02% of impurities. So far as I remember, the Physikalisch-Technische Reichsanstalt figure for the coefficient of electrical resistance was 0·0068, as compared with 0·00667 given by the present authors, so that it seems that the purity of both samples must be in very close agreement.

A point that may be of special interest to those interested in the behaviour of materials at elevated temperatures concerns the method described on p. 296 for making a special kind of creep test, and the results of this investigation given on p. 297. I think that all those interested in this kind of work will be very pleased with this new method, which I would regard as one by which it will be possible to obtain provisional results as quickly as possible, and at a very low cost. For that purpose, this method is very ingenious and helpful.

With regard to the results, figures are given for temperatures ranging from 600° to 900° C. The scales for time are not on the same scale. In spite of this, it appears that the creep limit is in all cases nearly the same; for instance, after a period of 10 hrs. this figure seems to be about 0·3 kg. for the whole range of temperatures. I would be very glad if a little additional information could be given about that figure, because one would expect the creep limit to fall to at least one-fifth or even more for an increase in temperature of 200° or 300° C.

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* This volume, p. 247.

† Professor of Metallurgy, The University, Cambridge.

‡ *Ann. Physik*, 1919, **59**, 147–169; *Z. Instrumentenkunde*, 1921, **41**, 162 and 170.

‖ Director, Heraeus Vacuumschmelze A.G., Hanau a. Main, Germany.

Dr. SMITHELLS (*in reply*): I thank Mr. Barclay for his remarks, which do not call for any immediate reply.

With regard to Dr. Cook's comment on the hump in the curve for the elongation of iron, I do not think that the curve for the nickel containing iron differs from the curves for nickel containing other elements. They all have the same type of hump, except that for the other alloys it is spread out further. In all cases the fall in elongation with increasing annealing temperature in these very fine wires appears to be due to development of crystals which go substantially across the wire and which confine the elongation to very short lengths in the wire. The whole wire does not extend uniformly, as it does in an ordinary test-piece, and therefore the percentage elongation falls, although locally the elongation increases.

Professor Hutton asked about the resistance, and Dr. Rohn has answered that for us. We did measure * the temperature coefficient of resistance and compared it with the figure published by the Bureau of Standards; it was shown that our nickel was not less pure than some nickel of very high purity which was used there.

With regard to Dr. Rohn's remarks on the creep-limit, the scale of these drawings is perhaps rather deceptive. The only two curves which have come anything like horizontal, and therefore really give the limiting creep stress, are those for 600° and 700° C. The upper curves, for the higher temperatures, are still falling rather rapidly and we did not continue them. It will be seen that these curves do not run anything like horizontally, and that the ends of the curves do not represent the limiting creep stress for the temperature at 800°, 900°, and 1000° C.

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* See p. 288 of the paper.

ON THE REMOVAL OF GASES FROM ALUMINIUM ALLOYS BY MIXTURES OF NITROGEN AND VOLATILE CHLORIDES.*

By J. D. GROGAN,† B.A., Member, and T. H. SCHOFIELD,† M.Sc., Member.

Synopsis.

Gas may be effectively removed from certain aluminium alloys by mixtures of nitrogen and certain volatile chlorides. Raw cylinder nitrogen may be employed. The quantity of chloride needed is small. Metal treated in this way possesses excellent mechanical properties.

Introduction.

This paper describes an investigation carried out under the direction of the Alloys Sub-Committee of the Aeronautical Research Committee for the Department of Scientific and Industrial Research, and constitutes a continuation of the systematic study of aluminium and its alloys, which has long been carried on in the Metallurgy Department of the National Physical Laboratory.

In a paper ‡ recently communicated to the Institute of Metals by Dr. Rosenhain and the present authors the influence of volatile chlorides on the gas content of aluminium alloys was described. When presenting the paper, Dr. Rosenhain stated that mixtures of nitrogen with the chlorides had been found to be effective in the removal of dissolved gases from the metal. This paper describes some experimental work performed in connection with that method.

Apparatus Employed.

The apparatus employed for passing the mixed vapours into the molten metal is substantially the same as that described in the previous paper. The chloride falls from a dropping funnel into a glass bulb into which the nitrogen is introduced through a side tube. The chloride and nitrogen pass through a nickel–chromium-iron pipe into an inverted

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* Manuscript received April 30, 1932. Presented at the Annual Autumn Meeting, London, September 13, 1932.

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

‡ *J. Inst. Metals*, 1930, **44**, 305–318.

Salamander crucible immersed in the molten metal. The rate of delivery of nitrogen was measured by a commercial flow-meter, the "Rotameter." The delivery of the chloride was evenly spread over the period of delivery of nitrogen.

The Salamander crucible, which is composed of clay and graphite, contains, when new, a considerable amount of water, both adsorbed and combined. To avoid the introduction of hydrogen into the metal from this source, it is necessary to preheat the crucible for some time at a red heat; it is also advisable to preheat used crucibles before use. If the melting furnace employs a fuel containing hydrogen in any form, it is necessary to shield the metal as far as possible from the products of combustion, to avoid the absorption of hydrogen from this source. This may be achieved by raising the crucible so that the rim is well above the gas outlet of the furnace. It is also convenient to heat the metal nearly to the pouring temperature before treatment, so that, during treatment the flame may be kept low.

MATERIALS EMPLOYED.

The chlorides used were those of titanium and carbon. The alloys employed were "Y"-alloy, silicon–aluminium alloy, and "2L5" alloy.

The nitrogen used was the commercial cylinder product. When necessary, it was purified by passage over heated copper gauze to remove oxygen and sometimes over calcium chloride to remove moisture.

ACTION OF PURIFIED NITROGEN AND TITANIUM TETRACHLORIDE.

In this series of experiments 4 lb. of metal were treated at 710 ± 10° C. and cast in an open sand mould 3 in. in diameter and 3 in. high at 700° C. The density of half the casting cut vertically down the centre was taken as a measure of the soundness of the material. Two groups of experiments were carried out. In one 15 litres of nitrogen were used at the rate of 1·5 litres per minute, while the quantity of titanium tetrachloride was varied; in the other 0·5 c.c. of titanium tetrachloride per lb. of metal was used, while the quantity of nitrogen was varied. In one series the metal was first treated with hydrogen to investigate the effects of the treatment on badly gassed metal. For comparison a series of tests was carried out with titanium tetrachloride alone.

The densities of half sections of the ingots cast after the various treatments are given in Tables I–III. The combined treatment appears to be slightly superior to the simple titanium tetrachloride treatment and requires considerably less of that reagent; 0·25 c.c. per lb. of metal proved sufficient even on small quantities of metal, while the simple treatment requires at least 2 c.c. per lb. On the other hand, little titanium is introduced into the metal by the combined treatment; consequently little or no grain refinement occurs. Previous treatment of the molten metal with hydrogen does not definitely influence the final results obtained. The additional gas introduced in this manner is removed rapidly during the early part of the treatment.

TABLE I.—*Influence of Titanium Tetrachloride Alone on the Density of 3 in. diam. Sand-Castings.*

Quantity of $TiCl_4$ c.c. per lb.	Alloy.			"2L5" Alloy.
	12% SiAl.			
0 0·5 2	2·626 2·645 2·639	2·636 2·643 2·642	2·563* 2·640* 2·647*	2·952 2·971 2·982

* Previously treated with hydrogen.

TABLE II.—*Influence of Varying Quantities of Titanium Tetrachloride Mixed with Nitrogen:* 15 *l. at* 1·5 *l. per minute.*

Quantity of $TiCl_4$ c.c. per lb.	Alloy.			"2L5" Alloy.
	12% SiAl.			
0 0·25 0·5	2·638 2·652 2·643	2·632 2·653 2·652	2·574* 2·651* 2·652*	2·945 3·009 2·997

* Previously treated with hydrogen.

TABLE III.—*Influence of Varying Quantities of Nitrogen Mixed with* 0·5 *c.c. of Titanium Tetrachloride per lb. of Metal.*

Total Volume of Nitrogen.	12% SiAl Alloy.	
0 3 6 9	2·588 2·598 2·646 2·650	2·576* 2·626* 2·633* 2·655*

* Previously treated with hydrogen.

To remove the gas satisfactorily from 4 lb. of metal it was found necessary to employ 9 litres of nitrogen when mixed with 0·5 c.c. of titanium tetrachloride per lb. of metal. These probably represent the maximum quantities required, and it is likely that, when larger quantities of metal are employed, relatively less nitrogen and titanium tetrachloride would be needed.

When comparison is made between the combined method and the simple titanium tetrachloride method it is necessary to realize that 9 litres of nitrogen measured at room temperature occupy approximately 30 litres at the temperature at which the treatment is carried out. The quantity of titanium tetrachloride employed in the simple method—namely, 8 c.c.—occupies approximately 6 litres. Consequently the combined treatment employs a very considerably larger volume of gas. The fumes produced are far less offensive owing to the dilution of the chlorides with nitrogen.

ACTION OF PURIFIED NITROGEN AND TITANIUM TETRACHLORIDE ON "Y"-ALLOY.

The combined treatment was applied at 760° ± 10° C. to a batch of "Y"-alloy which was subsequently cast at 750° C. into a slab 1·5 in. thick and rolled to sheet. 16 lb. of metal were treated with ½ c.c. of titanium tetrachloride and 4 litres of nitrogen per lb. of metal. The nitrogen was passed into the molten metal at the rate of 2 litres per minute. The slab was cut up into 3 pieces, the densities of which were as follows:

Top	2·788
Middle	2·797
Bottom	2·801

These figures show that the metal was sound.

The material rolled well and yielded sheet of satisfactory quality, inferior, however, to that treated with titanium tetrachloride alone. The difference is probably due to the fact that the combined process does not produce grain refinement to any marked extent.

ACTION OF CARBON TETRACHLORIDE ALONE AND MIXED WITH PURIFIED NITROGEN.

It was stated above that the volume of gas passed into the metal during the simple chloride treatments is much less than that employed in the combined chloride and nitrogen method. It appeared likely that the slight inferiority of the simple method would disappear if the quantity of gas employed were increased. A serious increase in the quantity of titanium tetrachloride employed would increase the titanium content to such an extent as to alter the specific gravity of the metal and lead to difficulties due to segregation. It was therefore decided to investigate the influence of relatively large quantities of carbon tetrachloride which does not introduce any significant quantity of carbon into the metal. The method already described in this paper was employed. The results obtained are given in Table IV. When 16 c.c. of carbon tetrachloride per lb. of metal was used, the metal had a slightly higher density than that treated by the combined method. The simple chloride treatment therefore appears to be as efficacious as the combined treatment. The metal treated with 16 c.c. of carbon tetrachloride was examined for carbon. None was detected except that the solution of the metal was slightly coloured by an infilterable substance thought to be colloidal carbon.

TABLE IV—*Influence of Carbon Tetrachloride Alone on the Density of* 12% *SiAl Alloy Previously Treated with Hydrogen.*

Quantity of CCl_4 c.c. per lb.	Density.
0	2·586
0·5	2·631
2	2·637
4	2·649
16	2·657

TABLE V.—*Influence of Varying Quantities of Carbon Tetrachloride Mixed with Nitrogen. Volume of Nitrogen* 15 *l. at* 1·5 *l. per Minute. Weight of Metal* 4 *lb. Previously Treated with Hydrogen.*

Quantity of CCl_4 c.c. per lb.	Density.
0·25	2·653
0·5	2·654

The effect of mixtures of carbon tetrachloride on silicon-aluminium alloy was examined by treating 4 lb. of metal with 15 litres of nitrogen at 1·5 litres a minute and 1 and 2 c.c. of carbon tetrachloride at 710° C. ± 10° C. The results obtained are given in Table V, and are very similar to those obtained by the use of nitrogen and titanium tetrachloride.

MECHANICAL PROPERTIES OF ALUMINIUM ALLOYS TREATED WITH MIXTURES OF NITROGEN AND VOLATILE CHLORIDES.

Some mechanical properties of cast "Y"-alloy and "2L5" alloy prepared from metal treated by the combined process were determined. For this purpose nitrogen purified in the manner previously described and also raw cylinder nitrogen were employed. One sample of raw nitrogen, on analysis, was found to contain 0·48 per cent. of oxygen and 0·000277 grm. of moisture per litre.

The following treatments were employed:

(1) Purified nitrogen with titanium tetrachloride.
(2) Raw nitrogen with titanium tetrachloride.
(3) Raw nitrogen with carbon tetrachloride.

In each case 13 lb. of metal were melted in a gas-fired injector furnace and heated to 760 ± 10° C.; this temperature was maintained during the treatment. The metal was first treated with hydrogen to ensure the presence of plenty of gas, and then with the mixture of nitrogen and chloride at the rate of 1·5 litres of nitrogen per minute. 2 litres of nitrogen and 0·5 c.c. of chloride were used for each lb. of metal. After treatment the temperature was adjusted to 750° C. and six 1-in. diameter chill bars were cast. Each treatment was carried out three times. In the first, six 1-in. diameter sand bars were cast immediately after the chill bars when the metal temperature was about 710° C. In series II and III the metal was allowed to cool to 680° C. before the sand bars were poured.

The density of each bar cropped to a length of 5 in. was determined. It was reported in the previous paper that sand castings made from metal treated with volatile chlorides alone exhibit a superficial porosity which extends to a depth of about $\frac{1}{16}$ in. into the metal. The same phenomenon appears after treatment with the nitrogen–chloride mixture. The density of each sand-cast bar was re-determined after the diameter had been reduced to $\frac{7}{8}$ in. by machining, and this latter figure was accepted as a measure of the soundness of the metal. The difference in density between the machined and unmachined bars (0·01 approximately) was independent of the particular treatment employed. The mean density of each batch and the maximum variation in the batch are given in Table VI.

Bars selected from each batch of "Y"-alloy were heat-treated in the usual manner, machined to test-pieces, and broken after the usual ageing period had elapsed. The "2L5" bars were tested in the "as cast" state. The results obtained are given in Table VII. Typical analyses of the material are given in Table VIII.

DISCUSSION OF RESULTS.

The results show that each of the three methods employed for the removal of gas yields metal of high density and good mechanical properties. Of the three, that which employs raw nitrogen and carbon

TABLE VI.—*Mean Density of Cast Bars.*

Series :—		I.			II.			III.		
Alloy.	Treatment.	1 in. Chill-Cast.	⅞ in. Sand-Cast.	Maximum Difference in Density of ⅞ in. Bars.	1 in. Chill-Cast.	⅞ in. Sand-Cast.	Maximum Difference in Density of ⅞ in. Bars.	1 in. Chill-Cast.	⅞ in. Sand-Cast.	Maximum Difference in Density of ⅞ in. Bars.
" Y "	Purified nitrogen and titanium tetrachloride.	2·800	2·784	0·005	2·803	2·787	0·005	2·807	2·802	0·005
" Y "	" Cylinder " nitrogen and titanium tetrachloride.	2·803	2·798	0·004	2·804	2·791	0·003	2·807	2·798	0·007
" Y "	" Cylinder " nitrogen and carbon tetrachloride.	2·807	2·798	0·004	2·808	2·796	0·005	2·812	2·806	0·005
" 2L5 "	" Cylinder " nitrogen and carbon tetrachloride.	3·011	3·000	0·006	3·006	2·954	0·006	3·020	3·009	0·006

TABLE VII.—*Mechanical Tests.*

Series :—		I.				II.				III.			
Alloy.	Treatment.	Chill-Cast Bars.		Sand-Cast Bars.		Chill-Cast Bars.		Sand-Cast Bars.		Chill-Cast Bars.		Sand-Cast Bars.	
		Ultimate Stress. Tons/in.².	Elongation. % on 2 in.	Ultimate Stress. Tons/in.².	Elongation. % on 2 in.	Ultimate Stress. Tons/in.².	Elongation. % on 2 in.	Ultimate Stress. Tons/in.².	Elongation. % on 2 in.	Ultimate Stress. Tons/in.².	Elongation. % on 2 in.	Ultimate Stress. Tons/in.².	Elongation. % on 2 in.
" Y "	Purified nitrogen and titanium tetrachloride.	18·4	1·5	15·9	1·0	20·2	2·5	15·0	1·0	19·9	2·0	17·5	1·0
		19·4	2·0	16·1	0·5	18·5	1·5	16·3	1·0	20·8	2·0	17·5	1·0
		20·0	2·0	16·0	0·5								
" Y "	" Cylinder " nitrogen and titanium tetrachloride.	17·8	1·0	17·0	0·5	20·9	3·0	16·9	1·5	21·3	3·0	17·2	1·0
		18·7	1·0	17·1	0·5	20·5	2·5	17·3	1·0	21·5	3·0	17·2	1·0
		19·0	1·5	17·0	1·0								
" Y "	" Cylinder " nitrogen and carbon tetrachloride.	20·1	1·5	15·8	0·5	19·7	2·0	16·6	1·0	22·0	3·5	17·7	1·0
		20·0	2·0	16·1	0·5	20·7	2·5	16·1	1·0	21·5	3·0	17·2	1·0
		20·0	2·0	15·5	0·5								
" 2L5 "	" Cylinder " nitrogen and carbon tetrachloride.	13·7	6·0	9·0	2·0								
		15·5	8·5	9·9	2·0	15·4	7·0	10·7	2·5	18·3	15·0	12·6	4·5
		15·7	9·5	9·4	3·5	17·1	12·0	10·1	2·0	17·9	13·0	12·4	3·5

Note.—Ultimate stress in British tons/in.². Interval between casting and testing " 2L5 " bars : in Series I, 29 days ; in Series II, 48 days ; in Series III, 34 days.

TABLE VIII.—*Analysis.*

	Cu.	Zn.	Ni.	Mg.	Fe.	Si.	Ti.
"Y"-alloy Series I (treated with "cylinder" nitrogen and carbon tetrachloride) . . .	4·08	...	2·01	1·50	0·39	0·22	0·03
"Y"-alloy Series III (treated with "cylinder" nitrogen and carbon tetrachloride)	4·05	...	1·99	1·56	0·34	0·29	0·02
"2L5" Alloy Series III (treated with "cylinder" nitrogen and carbon tetrachloride) . .	2·61	13·17	...	...	0·42	0·13	...

tetrachloride is definitely the cheapest and easiest to handle and causes far less fumes than the simple chloride process.

MECHANISM OF THE PROCESS.

It has been shown by Tullis * and also at the National Physical Laboratory,† that a number of volatile chlorides, when forced through molten aluminium, are active in the removal of dissolved gases from the metal. This paper shows that the same result is achieved when the chlorides are diluted with large quantities of purified or raw nitrogen. Tullis ‡ has employed chlorine gas and Koch § chlorine gas followed by nitrogen with satisfactory results. Hanson and Slater ‖ employed a mixture of nitrogen and chlorine. Sterner-Rainer ¶ employed a mixture of a volatile chloride and a fluoride. All these successful methods employ a halogen element or compound as a component of the material used to remove gas. On the other hand, a number of workers have failed to obtain generally successful results by the use of nitrogen alone.

It is known that there is present on any exposed surface of molten aluminium an oxide skin which is highly impervious to gases. In a system in which molten aluminium is exposed to a gas soluble in the molten metal, equilibrium will, in time, be reached between the gas dissolved in the metal and the surrounding gas : owing, however, to the resistance of the oxide skin, equilibrium will not be established rapidly. Bircumshaw ** has shown that aluminium maintained molten *in vacuo* for 109 hrs. still evolved appreciable quantities of hydrogen. To achieve

* British Patent Specification No. 272,326.
† *J. Inst. Metals*, 1930, **44**, 305–318.
‡ *J. Inst. Metals*, 1928, **40**, 55–62.
§ *Metallwirtschaft*, 1931, **10**, 69–72, 85–88.
‖ *J. Inst. Metals*, 1931, **46**, 187–215.
¶ *Z. Metallkunde*, 1931, **23**, 274–279.
** *Phil Mag.*, 1926, [vii], **1**, 510.

the rapid elimination of gas it is necessary to alter the character of the surface skin. This is thought to be effected in the methods cited above by the introduction into the metal of a halide capable of reacting with the oxide film on the surface of the metal and so reducing its resistance to the passage of the dissolved gas, which is then able to diffuse rapidly from the metal into the vapours bubbling through it. The nitrogen employed to dilute the halide serves to remove the gas thus set free from the scene of action.

SUMMARY.

Dissolved gases are readily removed from molten aluminium by passing through the metal a mixture of cylinder nitrogen, and the chlorides of titanium or carbon. It is not necessary to purify the nitrogen. The quantity of chloride required is quite small: 0·25 c.c. per lb. of metal has proved satisfactory even for small melts. Sand- and chill-cast "2L5" and "Y"-alloy treated by this method possess excellent mechanical properties.

ACKNOWLEDGMENTS.

The authors' thanks are due to the Aeronautical Research Committee and the Department of Scientific and Industrial Research for permission to publish this paper, to Dr. W. Rosenhain, F.Inst.Met., F.R.S., who suggested the employment of a mixture of nitrogen with a volatile chloride and also supervised the experimental work up to the time he left the National Physical Laboratory, and to Messrs. R. Pleasance and A. E. Bacon for valuable assistance in carrying out the experimental work.

DISCUSSION.

Dr. A. G. C. Gwyer * (Vice-President): As I have not had any experience with the nitrogen plus carbon tetrachloride treatment, I had not intended to discuss this paper, but I should like to say that it does seem to represent an improvement on most of the processes previously described, as it should be considerably cheaper to employ and also as there is a reduction in the quantity of fume. The only doubt which I have respecting this treatment is whether it will work really satisfactorily with large quantities of metal. The author has treated only very small quantities, and it is well known that there is no difficulty whatever in de-gassing very small melts. I consider, therefore, that what is required is either that the author should repeat the work on a much larger scale, or alternatively should give us some indication as to how far his methods have been introduced into, and followed in, industry.

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

Mr. H. W. G. HIGNETT,* B.Sc. (Member): I have attempted to use nearly all the processes which have been evolved for getting rid of gas in aluminium alloys, and most of them have been very dangerous to my life. Some of them have made our moulders move much more quickly than they do in normal circumstances.

This process, however, is a much more suitable one for use in a foundry, and we have actually had some very good results from it on a fairly large scale. We have used it on melts of up to about 300 lb., and the difficulties which we have found in connection with these large melts appear to be chiefly due to the difficulty of obtaining a sufficient area of contact of the mixture of vapour and nitrogen with the metal. When we get an apparatus suitable for dividing the gas stream into small bubbles we appear to obtain much better results. I have found—and it may be of interest from a practical point of view—that the oil-fired furnaces used for melting aluminium alloys are extremely bad. When we de-gas an alloy, which Mr. Grogan does, I think, at 710° C. (which temperature is, of course, useless for quite a large number of castings), and then heat in the furnace to a satisfactory pouring temperature of in some cases as much as 800° C., we find that the quantity of gas we put in is alarming. We also find that as the temperature at which we conduct the treatment increases, the difficulty of getting rid of the gas also increases. That introduces a problem with which Mr. Grogan has as yet, I believe, not dealt.

I would like to ask a question regarding the modified aluminium–silicon alloys. I have found that I can easily de-gas these alloys if I do not modify; but after modification—unless the de-gassification treatment has been extremely thorough (I mean by that that it must be more thorough than is necessary to obtain what appears to be a sound casting with the unmodified alloy) I appear to put gas back after modification. I cannot understand that, unless there is some alteration in the solubility of the hydrogen resulting from the modification.

Mr. E. L. RHEAD,† M.Sc.Tech. (Member): I have had some experience both with regard to the use of titanium in the manufacture of sound aluminium castings, and also the use of volatile chlorides in improving the casting properties of various alloys. In 1915, during the Great War, a problem arose with regard to the production of sound castings for the aluminium parts of Mill's bombs. Difficulty was encountered in connection with the difference in volume of the upper part and the lower parts, the casting becoming unsound immediately underneath the shoulder. We corrected that for the firm for which we were operating at the time by the introduction of titanium in small quantities in the solid form, and many thousands of those castings were subsequently made of a perfectly sound character.

The point in connection with volatile chlorides arose also on a war problem. Difficulty was encountered in connection with the re-melting of scrap cartridge case brass, of which at the time large quantities were being gathered and were intended to be re-used. The problem had been submitted variously before it came to me, without a successful result having been obtained in practice. I evolved a method for treating the cartridge brass during fusion with ammonium chloride vapour, with entirely successful results. When first submitted to the War Office it was said that difficulty would be encountered, and that it would be necessary to prepare a complete sample of the material sufficient in quantity to be sent through the mills, drawn and fired. The samples first submitted were not sufficiently large for that purpose.

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* Metallurgist, Aluminium Plant and Vessel Co., Ltd., London.

† Manchester.

Subsequently such an amount was prepared by this method and subjected to the tests, with complete satisfaction. The effect of the volatile chlorides in that case, therefore, although having nothing to do with aluminium, is on much the same lines as has evidently been obtained by means of the volatile chlorides on aluminium. I would like, however, to direct attention to one fact in connection with the figures given in the paper, namely, that the ultimate stress that is attained by the use of the carbon tetrachloride apparently does not reach the same standard as that which is obtained with titanium tetrachloride, and I wonder whether the effect of the titanium itself has not something to do with the advantage that is gained.

Dr. W. Rosenhain,* F.Inst.Met., F.R.S. (Past-President): I have no criticism to offer and I want to confine myself really to the main question raised by Dr. Gwyer, as to the applicability of this and other methods of de-gassing on a large scale. I think that there is only one economic and satisfactory method of de-gassing, and that is never to allow gas to enter the metal. That is not an easy problem. No one is more aware of that fact than I am. But if gas has to be removed, there are two or three possibilities. One of them is as follows—and it applies not only to aluminium alloys, but also to practically every metal, steel included. If the metal can be kept in quiet fusion at the lowest possible temperature in equilibrium with an atmosphere free from the particular gas which it is desired to remove, and if the surface can be so treated that equilibrium between the metal and the superincumbent atmosphere is fairly rapidly attained, then de-gassing must occur, and does occur in actual fact; this is a very simple and economic method. But there are two very great difficulties. One is to obtain an atmosphere free from the gas which is to be removed. If that gas happens to be hydrogen there must be no hydrocarbons, no hydrogen, and no moisture in the atmosphere of the furnace. That condition is difficult to obtain except in an electric furnace with, if necessary, a controlled atmosphere from the point of view of excluding moisture; but that again is also difficult.

The other condition—of so treating the surface of the metal that equilibrium is rapidly reached between the metal and the atmosphere above it—is also a difficult one, but that touches on the point mentioned by the authors—namely, that it is very frequently the surface film which prevents rapid diffusion of gas out of and into the metal. I believe that a study of fluxes would go a long way to elucidate that point and to enable us to obtain flux compositions that would serve that particular purpose. In the case of aluminium and its alloys we have a pellicle of rather tough, resistant material consisting partly of the ordinary oxide of aluminium and partly of other substances (possibly lower oxides), and that pellicle is apparently very resistant to the passage of gases in either direction. There is reason to think, however, that if, instead of that solid or semi-solid film, we have a liquid flux on the surface, then the passage of gas into and out of the metal is very much accelerated. In fact, Mr. Grogan's theory about the action of the chlorides in rendering that pellicle, even when it is extremely thin on the surface of a freshly formed bubble, more pervious to the gases, is very much on the lines of the idea which I am suggesting. Until, however, means can be found to overcome these very important obstacles to simple and economic de-gassing by diffusion alone—aided perhaps by agitation—I think that some such method as that which has now been developed by Mr. Grogan and his colleague is eminently promising. It can be used on a large scale. I can say that definitely, and I am glad to hear Mr. Hignett give us evidence of the same kind. As a rule, when attempts are made to use it on a large

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* London.

scale they are made very crudely. The gas is bubbled through the metal in great gulps. They are really not bubbles; they are "dollops" of gas that come rising up from the metal, throwing the metal about, and frequently the metal is at the same time exposed to a furnace atmosphere from which gas is being absorbed as quickly as it can be removed. That is probably the worst feature. If, instead of that, the metal were heated in conditions where the atmosphere is reasonably free from hydrogen and hydrogen compounds, and if the gas used were reasonably and economically employed in the form of finely divided bubbles carefully distributed throughout the whole mass, then success definitely would be achieved, and the quantity of gas required would be astonishingly less than would appear from the rather crude attempts which I have sometimes seen or of which I have heard.

I would suggest, however, that if these aluminium alloys are to be degassed in this way the operation should be carried out in a much more rational manner; we should learn something from our colleagues in the steel industry—namely, that instead of bubbling the gas through in a more or less makeshift fashion, we should use a vessel of the type of the Bessemer converter, heated if necessary, pour the charge into it in an atmosphere entirely free from products of combustion, and then blow the gas carrying these volatile chlorides through the tuyères or through a perforated bottom of a converter, so as to divide it thoroughly and to pass in a fine state of division through the whole bulk of the metal. Ultimately it may be necessary to use some such method; when we do so we shall be approaching a rational application of these processes.

Professor D. **Hanson**,* D.Sc. (Vice-President): Mr. Slater and I were probably the first to use nitrogen as the vehicle for conveying an active agent into aluminium for the purpose of removing gas; and it was with the object of breaking down the resistance at the film. We are very glad to see that the authors, quite independently, have used an exactly similar method.

My one criticism of the paper (I am not expressing any doubts as to the results) is that it is difficult to judge from the results given just what the amount of improvement is, because the figures given do not state exactly the degree of unsoundness in the aluminium at the outset. Some of the alloys were obviously very unsound, and an improvement of density by any form of gas treatment, however crude, would be bound to be obtained. Other samples of aluminium of which the densities are given were not so unsound, but it is not stated how unsound they were, and without some basis of comparison it is difficult to judge what the effectiveness of this particular method is. Some pictures of sections would have helped considerably to indicate the quantitative nature of the improvement. Gas removal processes of this nature may so improve a casting as to make it what would be called technically quite sound, but when the metal is examined microscopically it will be found that it still contains a considerable amount of gas. One per cent., or even more, of cavity in the form of minutely distributed pin-holes is by no means uncommon. If we are to know just what different investigators mean, we have, therefore, to have some standard—either a pictorial one or a more exact quantitative one than the authors have given.

The difficulty in applying these processes on a large scale is very real, but I agree with Dr. Rosenhain that it is largely a question of securing adequate sub-division of the stream of gas. If 9 or 15 litres of nitrogen are required to treat 4 lb. of metal, a very great deal of gas will be needed to treat 400 lb.; and, although it may be somewhat more economical to do it on a large scale, the volume of gas is still going to be very considerable. To sub-divide the

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* Professor of Metallurgy, The University, Birmingham.

stream into 100 or 200 parts (which would be necessary to imitate the conditions in the small melt) is industrially very difficult; and although "gulping" the gas through is not an ideal method, to sub-divide the gas to such an extent as to reproduce laboratory conditions is also extremely difficult. That, I think, is one of the reasons why treatment of even quite moderate quantities does not give anything like as promising results as do laboratory experiments on small quantities. To treat 4 lb. of metal, almost any gas removal treatment which has been suggested can be effective. Nitrogen alone, if it is bubbled through reasonably fast, will improve that metal and give what would be called quite sound metal. The difficulty is this extension to larger quantities.

Another point arises—namely, that if the stream of gas is subdivided to that extent it is very necessary for the nitrogen to be pure, because not only is the contact between the active elements and the metal more intimate, but also that between the metal and the moisture and oxygen which are contained to some extent in all nitrogen; the production of oxide films is a very serious trouble when oxygen-containing gas is used.

I am quite sure that Dr. Rosenhain was right when he said that the ideal method was to keep the gas out; we now know sufficient about the conditions under which gases get into aluminium to take reasonable steps to keep them out. The only real solution is to use good aluminium, and to store and melt it under the proper conditions.

Mr. GROGAN said that he would reply in writing.

CORRESPONDENCE.

THE AUTHORS (*in reply to the discussion at the meeting*): Mr. Hignett has to some extent answered Dr. Gwyer's question as to the efficacy of the method of treatment described in the paper when employed on a manufacturing scale. We have no knowledge of its application elsewhere. Mr. D. R. Tullis, however, has been employing a similar method for some years commercially.

The influence of the temperature of treatment on the efficiency of these methods of gas removal is at present a matter of dispute among workers on the subject. We have experienced difficulty in obtaining sound castings from metal treated at 800° C., but suspect that the unsoundness is due to contamination from the gas employed to heat the furnace, considerably more gas being required to maintain the metal at 800° C. than at 700° C. We also have experienced difficulty in obtaining sound castings from modified silicon–aluminium alloy, but suspect that the unsoundness is caused by hydrogen introduced by the sodium employed to produce modification.

We are very interested to hear that Mr. Rhead some years ago used titanium to improve the quality of aluminium, and ammonium chloride to improve remelted scrap brass. It is probable that the effect of titanium was to reduce the grain-size of the metal and so prevent the gas from forming large cavities. The evidence we have does not suggest that the presence of titanium in aluminium prevents the absorption of gas.

We thank Dr. Rosenhain for his exposition of the mechanics of gas removal, which, as he says, is very much on the lines of the hypothesis advanced by us, and for his exposition of the conditions necessary for the application of methods of gas removal on the commercial scale. We agree with the conclusion which both he and Professor Hanson express, that to ensure that no harmful gases enter the metal at any stage would afford an ideal solution to the problem of gas removal and might not be impossible of achievement. The problem of the treatment of high-quality recovered scrap, however, would still remain.

Professor Hanson raises a difficult problem by asking for a standard of measurement of the soundness of treated material. We consider that, at present, the best practical measure of gas in the metal is given by the difference in density of a chill casting of small diameter and a cropped sand-casting from which the surface skin has been machined. In gas-free material this figure should approach zero.

Professor Hanson has overlooked one very important factor in his calculation of the relative amount of gas needed to treat large quantities of metal—namely, the depth of the metal under treatment. It is difficult to treat adequately four pounds of metal, because the depth is so small that the gas employed for treatment is in contact with the metal for a very short time. When the depth is greater, the gas remains in contact with the metal for a considerably longer time, and each bubble of gas should remove a correspondingly larger quantity of dissolved gas.

Dr. H. W. **Brownsdon**,* M.Sc. (Member of Council): During the past few years several interesting papers have appeared dealing with the causes and prevention of unsoundness in castings of aluminium and its alloys. All these papers, including that under discussion, refer to gases in aluminium as being the cause of unsoundness and attribute the improved soundness obtained after various treatments to the removal of gases. On reading these papers I have been impressed by the fact that no direct evidence is put forward to prove that the improved soundness obtained is due to the removal of gases, all the conclusions being based on visual observations and density determinations. An increase in apparent soundness or density need not of necessity be due to a reduced gas content, but might be the result of the replacement of a gas of low solubility by one of higher solubility. What one would like to know in connection with all this work is the content and composition of the contained gases before and after treatment, and it is not until such data are available that we should speak of the removal of gases from aluminium and its alloys. Density determinations should be taken as evidence only of increased soundness and not of gas removal.

I have been tempted to make these remarks in view of my experiences with the relationship of density to gas contents in copper, where increase in density can be obtained accompanied by an increase in gas content by removing certain gases and replacing them by others.

Mr. R. S. **Dean**,† M.S., Met.E. (Member) and Mr. V. H. **Gottschalk** ‡ : The discovery of the effectiveness of removing dissolved gases from molten metals must be reckoned among the more important advances in refining technique. As in other phases of the gas-in-metals problem, practice far outruns theory. In other words, the paragraph in this paper on the mechanism of the process really begs the question, which is indeed about as much light as the present state of theory is able to throw on the subject.

Dr. D. **Stockdale**,§ M.A. (Member): The chloride method for the purification of metals has evidently come to stay. I suggest that a more

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§ King's College, Cambridge.

satisfactory way of introducing the purifying agent would be to bubble the nitrogen through a reservoir of the chloride kept at some suitable temperature by means of a crude form of thermostat.

Mr. D. R. Tullis * (Member): I have read this paper with interest. It is pleasing to note that the authors have confirmed not only many of the results I obtained some years ago, but also the high tensile strengths claimed by me and by my firm in commercial production.

The use of boron trichloride will give even better results; users of metals refined by this process frequently report tensile strengths up to 18 tons/in.^{2} from sand-cast bars in " 2L5 " and " 50A " alloys.

The paper by Dr. Rosenhain, referred to by the authors, was due to work carried out by him as a result of a visit to the laboratory of my firm in 1928. During his visit we discussed the application of volatile chlorides, particularly boron trichloride, as a means of causing grain-refinement and gas removal. I consider that the apparatus employed by the present authors for the purpose of gas removal is quite unsuitable, as it does not give a sufficiently intimate contact between the chloride vapours and the metal. I do not consider that the use of mixed vapours offers any advantages except that it makes the process more convenient. In fact, the use of nitrogen as a vehicle for introducing chlorine or its chlorides definitely results in loss of valuable time. The use of chlorine and nitrogen alone as a means of removing dissolved gases is not a commercial proposition. These remarks are confirmed in the paper by the fact that a very large volume of mixed gases is required to remove such a very small proportion of dissolved gases.

I carried out experiments in this direction as far back as 1925. In all the processes of gas removal recently described in various papers it is a significant fact that the active agent is chlorine. In these circumstances it is only natural to conclude that the use of pure chlorine and its volatile chlorides, when properly applied, gives the best results.

It may be of interest to know that my firm has used these processes on a commercial scale for the past 6 years. During the last few years very considerable tonnages of these de-gassed and grain-refined metals have been put into service in all branches of engineering.

The Authors (*in reply*): We thank Dr. Brownsdon for pointing out that density measurements do not indicate the quantity of gas which remains in solution in the solid metal. In the case of solid aluminium, however, in which it is generally agreed gases are not appreciably soluble, density may be taken as a measure of the gas content of the metal.

We also thank Messrs. Dean and Gottschalk for their communication, and hope that work which is now in progress at the National Physical Laboratory will help to close the gap between practice and theory, to which they direct attention.

The method which Dr. Stockdale suggests for the application of the volatile chloride will, we think, prove very useful.

It was interesting to hear from Mr. Tullis that such remarkably high tensile figures have been obtained by the use of his boron trichloride method of treatment. It is, of course, a matter of general knowledge that he has been employing this method on a commercial scale for some years.

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* Director, Cindal Metals, Ltd., Liverpool.

THE EFFECT OF PRESSURE ON THE LIBERATION OF GASES FROM METALS (WITH SPECIAL REFERENCE TO SILVER AND OXYGEN).*

By N. P. ALLEN, M.Met.,† Member.

Synopsis.

The liberation of oxygen from silver during solidification has been studied by means of cooling curves. It is found that the gas is evolved when the "internal pressure" of the dissolved gas becomes greater than the hydrostatic pressure of the liquid metal, and that by applying a sufficiently large pressure to the liquid metal, the formation of blowholes can be prevented. The equilibrium of the silver–oxygen system is discussed and the existence of a eutectic shown. A method of eliminating blowholes in cast metals is recommended. The "internal gas pressures" developed in metals when gaseous constituents capable of interaction are present, are discussed.

Introduction.

The study of gas porosity in metals is much hampered by the lack of precise knowledge as to the conditions necessary for the appearance of gas bubbles in a solidifying metal. The assumption that bubbles are formed as soon as the amount of gas dissolved in the metal exceeds the solubility of the gas in the metal breaks down when it is considered that the solubility of a gas in a metal depends on the partial pressure of that gas in the vapours surrounding the metal, and it is not known what partial pressure of the gas in question in the neighbourhood of a solidifying ingot is to be assumed. The object of the present paper is to propose a method of approaching the problem which has been suggested, to some extent, by the author's investigations for the British Non-Ferrous Metals Research Association, and to illustrate its application in certain cases.

The "Internal Pressure" of a Dissolved Gas.

In the majority of cases, the volume of gas dissolved by a metal at a certain temperature is given by

$$v = k \, . \, p^{\frac{1}{2}}$$

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† Lecturer in Metallurgy, The University, Birmingham.

where v is the volume of gas dissolved by a unit mass of metal, p is the partial pressure of the gas in contact with the metal, and k is a constant characteristic of the metal and varying with the temperature.

This relationship, having been found true for the di-atomic gases hydrogen and nitrogen, is interpreted to mean that the gases are present in the metal in the atomic state. Since gases with any number of atoms in the molecule may have to be dealt with, the equation may be put into the form

$$p = \left(\frac{v}{k}\right)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The value $\left(\frac{v}{k}\right)^n$ is a characteristic of the solution containing v c.c. of gas per unit mass of metal. It is the *only* pressure of the solute gas, and the *minimum* pressure of *any* gas mixture with which the solution can be in equilibrium. It is here referred to as the *internal pressure* of the dissolved gas. If several gases are dissolved in one metal, in concentrations v_1, v_2, v_3, &c., the constants in their respective solubility equations being k_1 and n_1, k_2 and n_2, k_3 and n_3, &c., the *total internal pressure* of dissolved gases will be

$$\Sigma p_x = \left(\frac{v_1}{k_1}\right)^{n_1} + \left(\frac{v_2}{k_2}\right)^{n_2} + \left(\frac{v_3}{k_3}\right)^{n_3} + \text{\&c.} \quad . \quad . \quad . \quad (2)$$

The Condition for Liberation of Gas Bubbles.

If a bubble forms at a given depth below the surface of a molten metal the pressure within the bubble is given by

$$p = P + \frac{2T}{r}$$

where P is the hydrostatic pressure of the molten metal in the neighbourhood of the bubble, T is the surface tension of the metal, and r the radius of the bubble.

The condition for the continued existence of a gas bubble is that the total internal gas pressure of the solution be not less than this pressure

$$\Sigma \left(\frac{v}{k}\right)^n \nless P + \frac{2T}{r}$$

The surface tension term in this expression presents difficulties. The bubble cannot begin at an infinitely minute size and gradually grow to the dimensions of the blowholes of the ingot, for then no amount of dissolved gas, however great, could cause its initiation. The bubble must begin its existence at a finite size, and the pressure required to overcome the surface tension resistances in a bubble of this size must constitute an initial resistance to bubble formation, over and above the hydrostatic pressure in the liquid metal. Denoting the resistance by θ, we may write as the condition for the formation of gas bubbles in the liquid,

$$\Sigma\left(\frac{v}{k}\right)^n \nless P + \theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The value of θ is likely to vary according to the presence or absence in liquid of " nuclei " on which the gas bubbles may separate. Examples of the values it can assume are given later.

Considerations of the same kind govern the appearance of gas blisters in solid metals, but to the values P and θ must be added a term representing the mechanical resistance of the metal to the growth of the blister. This is a function of the strength of the metal, and the depth of the gas blister below the free surface. Thus, for the formation of blisters

$$\Sigma\left(\frac{v}{k}\right)^n \nless P + \theta + f(s, d) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where s and d are respectively the strength of the metal and the depth of the blister below the surface of the metal.

Where liquid and solid metal are present together, as in a solidifying ingot, the condition for liberation of gas from the liquid will be the more easily attained, and gas bubbles will separate from the liquid phase.

Rise of Internal Gas Pressure as a Result of Solidification.

It is clear from equation (1) that if the solubility of a gas in a metal falls, the internal gas pressure of a solution containing a given amount of the gas rises. There is usually a sharp fall in the solubility of the gas on solidification, and this will be accompanied by a corresponding rise in the internal gas pressure. It is a condition of equilibrium that the internal gas pressure of any two phases in contact with each other be equal. If therefore

p_x is the common internal gas pressure of the liquid and solid phases when a fraction x of the metal has solidified,
k_l is the solubility constant of the gas in the liquid metal,
k_s is the solubility constant of the gas in the solid metal,
v is the volume of gas dissolved per unit of metal

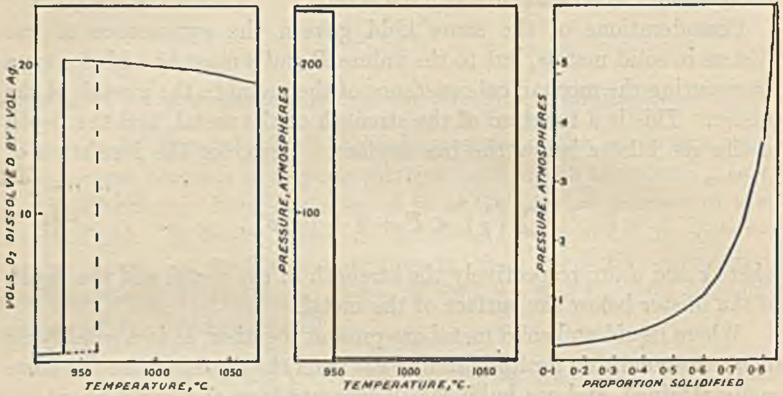
$$xk_s\sqrt[n]{p_x} + (1 - x)k_l\sqrt[n]{p_x} = v \quad . \quad . \quad . \quad . \quad (5)$$

The condition for the formation of gas bubbles during solidification is

$$\left\{\frac{v}{k_l - (k_e - k_s)x}\right\}^n \nless P + \theta \quad . \quad . \quad . \quad . \quad (6)$$

From this it is possible to calculate the proportion of metal which must solidify before gas bubbles can separate, under given initial conditions. The equation assumes that no gas escapes from the metal except in the form of bubbles.

Fig. 1 gives the solubility of oxygen in silver as determined by Sieverts and Hagenacker[1] together with the calculated changes in internal gas pressure of a melt saturated with air at 1030° C. during solidification, assuming that no gas escapes. Under atmospheric pressure, oxygen should not be liberated from the melt before 59 per cent. of the melt has solidified.



(*a*) Solubility of Oxygen in Silver at 1 atm. Pressure.

(*b*) Rise of Internal Gas Pressure as a Result of Solidification.

(c) Rise of Internal Gas Pressure during Solidification.

Fig. 1.

Experimental.

The presence of oxygen lowers the melting point of silver, and when silver melted in air solidifies, the evolution of oxygen takes place at a temperature somewhat lower than the freezing point of the alloy (Heycock and Neville[2]). A cooling curve taken on silver saturated with air shows two arrest points, one at 951° C. and the other at 930°–940° C. The second point accompanies the well-known "spitting" phenomena.

The present experiments in which the evolution of oxygen from silver was studied by means of observations on this arrest point were carried out on chemically pure silver supplied by Messrs. Johnson, Matthey & Co., by means of a standard platinum/platinum-rhodium thermocouple and potentiometer. The thermocouple was checked frequently against the freezing point of pure silver, melted under charcoal.

FIG. 5.
Ingots Cooled under Pressure : 30 lb./in.² and 49 lb./in.²

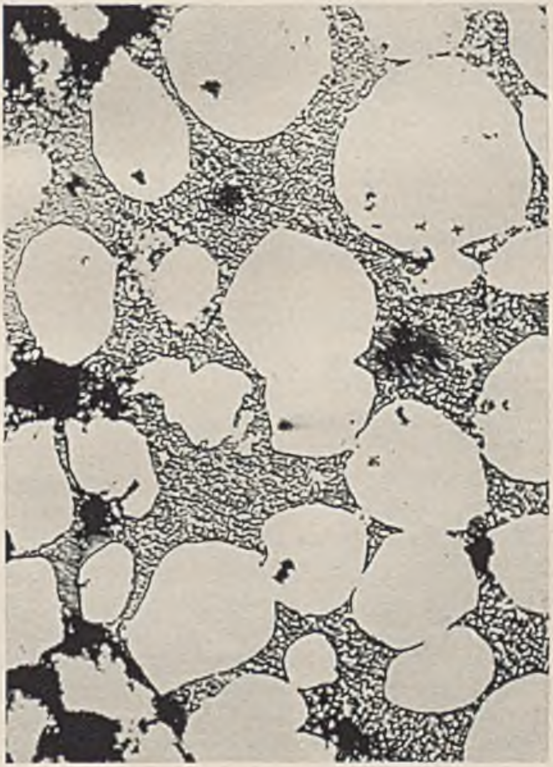


FIG. 9.
Silver–Silver Oxide Eutectic. × 150. Unetched.

[*To face p.* 320.

1.—*Correlation of the Second Arrest Point with the Evolution of Oxygen.*

About 40 grm. were melted in air, and held for at least 1 hr. at constant temperature. A cooling curve was then taken, and with the aid of a mirror, observations of the surface of the metal were made between the intervals of reading. Five experiments were made, with different saturation temperatures, and the results are recorded in Fig. 2, Curves 1–5. The arrows indicate the points at which evolution of gas was observed to begin and end. The corresponding temperatures are recorded in Table I. The evolution of oxygen took place over a range of temperature rather than at a definite temperature, and the second arrest point, which also was spread out over a temperature range, occupied the centre of this range.

TABLE I.—*Temperatures of the Second Arrest and of Oxygen Evolution.*

Saturation Temperature, ° C.	Beginning of Oxygen Evolution, ° C.	Peak of Second Arrest, ° C.	End of Oxygen Evolution, ° C.
968	934	930	925
976	937	932	...
1030	934	932	...
1072	940	935	931
1090	940	932	929

Note.—Solidification of the sample was not complete until the evolution of oxygen had ended.

2.—*Effect of the Oxygen Content of the Atmosphere.*

The silver used in the previous experiments was placed in a deep "pythagoras" crucible, 4 in. deep and 1 in. in diameter. The top of the crucible was closed with an alundum plug, through which passed the thermocouple sheath, and a silica tube by means of which gas could be passed over the surface of the melt. Mixtures of cylinder oxygen and nitrogen, dried with calcium chloride, were admitted to the crucible from an aspirator, and the oxygen content of the mixture was determined before and after each experiment, by absorbing the oxygen with copper in an ammoniacal solution. The metal was exposed to the gas for half an hour at 960° C. before taking the cooling curve. As the oxygen content of the gas was increased, the freezing point of the silver was continuously depressed, in such a manner that the depression of the freezing point was proportional to the square root of the oxygen content of the gas. This is shown in Table II. Since the amount of oxygen dissolved by the silver is, according to Sieverts and Hagenacker, proportional to the square root of the oxygen pressure, the depression of the freezing point was proportional to the concentration of oxygen in the molten metal. The temperature at which spitting occurred, on the

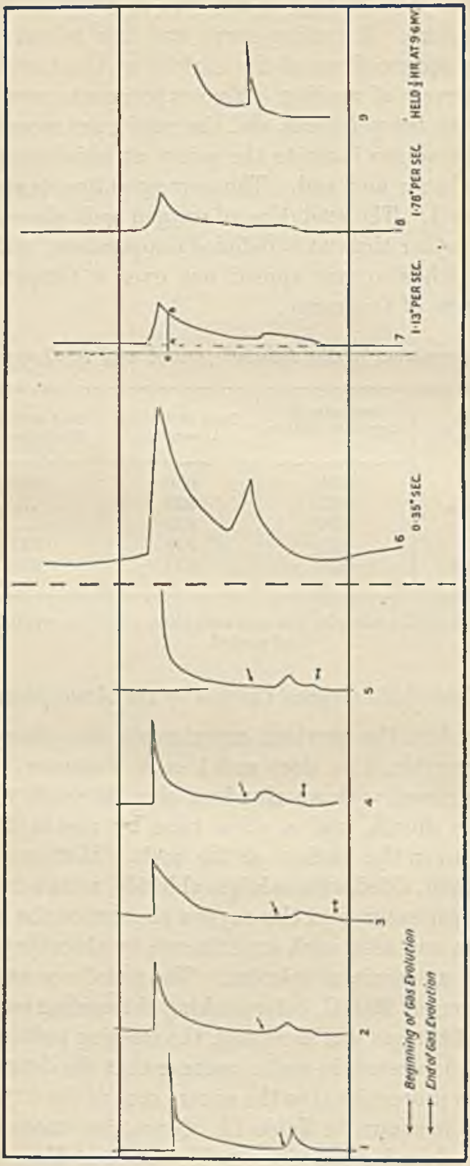


FIG. 2.

other hand, was not affected by the oxygen content of the gas, but the

TABLE II.—*Cooling Arrests of Silver containing Different Quantities of Oxygen.*

Oxygen Content of Atmosphere.%	Liquidus, ° C.	Second Point, ° C.	Depression of Liquidus, ° C.	$\left(\text{Oxygen Content}\right)^{\frac{1}{2}}$	$\frac{\text{Depression}}{\left(\text{Oxygen Content}\right)^{\frac{1}{2}}}$
0	961	...	...	...	...
7·8	958	929(?)*	3	2·8	1·1
20·6	951	932	10	4·55	2·2
64·0	942	931	19	8·0	2·4
97·4	938	930	23	9·86	2·3
97·4 gas bubbled through metal 1 hr.	938† 936 934 (undercooling)				

* Maximum of heat evolution. † Beginning of heat evolution.

intensity of the second point increased very rapidly with increasing oxygen content. At 7·8 per cent. of oxygen the second point was only very doubtfully shown on the cooling curve, but when practically pure oxygen was passed over the silver, the second point was much more pronounced than the first. The arrest temperatures are plotted in Fig. 3 against the square root of the oxygen content of the gas. The resulting diagram is very similar to that obtained in eutectiferous alloys.

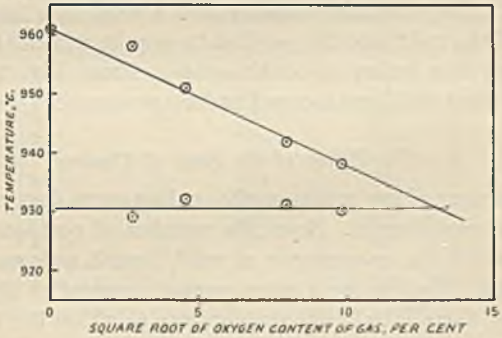


FIG. 3.

During solidification of the silver–oxygen alloy, crystals of silver comparatively poor in oxygen separate out first, whilst the oxygen concentrates in the residual liquid. This process continues, with falling temperature, until the oxygen content of the residual liquid reaches a certain figure, when oxygen begins to be given off. If oxygen could be given off sufficiently fast, the whole of the residual liquid would probably solidify at this temperature, and give up the majority of its oxygen. In these experiments, however, the oxygen apparently did not escape quickly enough, with the result that the crystallization of silver consequent upon the continued loss of heat caused a further concentration of oxygen in the residual liquid, and the temperature continued to fall, although more slowly than before, until solidification was complete.

It is important to know what relationship the temperature at which the gas is evolved bears to the freezing point of silver saturated with oxygen at atmospheric pressure. As it was possible that the two points observed on the cooling curve of silver melted in cylinder oxygen (97·4 per cent. of oxygen) might have been due to incomplete saturation of the melt, three experiments were carried out in which 100 grm. of metal were used, and cylinder oxygen was bubbled through the melt for 1 hr., at as low a temperature as was feasible, namely, at about 950° C. As a result, only one point was observed on the cooling curve, at the temperatures recorded in Table II. These temperatures agree well with the temperatures at which spitting was observed to begin in the first experiment (Table I). It is therefore possible to say that gas begins to escape when the oxygen content of the melt has reached the amount required to saturate it at an oxygen pressure equal to the total pressure above the melt—that is to say, when the internal gas pressure reaches 1 atm.

In these experiments most of the gas usually escaped at a lower temperature. The reason is probably that a solid skin formed first on the surface of the melt, and the gas had to acquire sufficient pressure to break through this before it could escape. From Fig. 3 it may be deduced that most of the gas escaped under a pressure of 1·7 atm.

3.—*The Effect of the Rate of Cooling.*

The appearance of two points on the cooling curve does not represent a condition of equilibrium. Since the number of components is two, the conditions for the co-existence of solid, liquid, and gaseous phases are univariant. That is, for a given partial pressure of oxygen in the gaseous phase, there is only one temperature at which the three phases can be present in equilibrium together.

It is therefore of interest to examine the effect of slow cooling on the solidification procedure. For this purpose, 100 grm. of silver were melted in a fireclay crucible in a poorly lagged electric furnace, and air was bubbled through the melt for not less than half an hour at 1000°–1030° C. The current through the furnace was then lowered, and the cooling curve taken. In this way, a wide range of cooling rates could be obtained. Great care was taken to see that the thermocouple was central in the metal.

A selection of the curves obtained is reproduced in Fig. 2, Curves 6–8, but their interpretation is not easy. Apparently the lower point decreases very much in intensity as the rate of cooling is increased, but the effect is not so large as it appears, and the method of measurement is important. A straight line has been drawn joining the smooth curves above and below the freezing range, and the displacement of this line from the ordinate has been used as a measure of the rate of loss of heat. Then for each point on the curve, the displacement from this line divided by the distance of the line from the ordinate, *i.e.* AB/OA in Fig. 2, is proportional to the latent heat liberated in the temperature interval represented by the point. The sum of the values AB/OA has been found for all points below the beginning of the second arrest, and divided by the sum of the same values for the whole freezing range. Assuming the heat of solution of oxygen to be negligible in comparison with the latent heat of silver, this ratio gives the fraction of silver still molten when the liberation of oxygen bubbles commenced. The accuracy is not high, on account of the difficulty of deciding where the second arrest begins.

The figures are given in Table III. Neither the liquidus temperature, nor that of the second arrest, is affected by the rate of cooling, and when every allowance is made for error it still appears that, if anything, the intensity of the second point increases as the rate of cooling becomes less. Thus the loss of oxygen by diffusion must be very slow.

TABLE III.—*The Effect of Rate of Cooling.*

Mean Rate of Cooling, ° C. per second.	First Arrest, ° C.	Second Arrest, ° C.	Proportion of Liquid at Second Arrest.
0·24	957	940	0·372
0·35	954	941	0·285
0·45	955	938	0·300
0·50	954	939	0·314
0·97	955	942	0·292
1·13	953	936	0·302
1·40	953	934	0·266
1·48	952	939	0·256
1·78	954	937	0·186
Held constant ½ hr. at 952° C.	...	938	...
Held constant ½ hr. at 945° C.	...	940	...

To confirm this conclusion the silver was saturated with air as before, cooled to a temperature between the two arrests, held at constant temperature for half an hour, and then cooled. This was done twice, and on both occasions the second arrest appeared with undiminished intensity (Fig. 2, Curve 9). It seems therefore that no important loss of oxygen takes place at temperatures above 940° C.

The proportion of silver which solidified before bubbles were formed was never less than 63 per cent., which agrees well with the theoretical figure of 59 per cent. The tendency of this proportion to increase when the cooling is rapid is not readily explained.

4.—*Effect of External Pressure.*

The effect of pressure on the evolution of the dissolved gas was studied with the aid of a furnace built inside an autoclave, the construction of which is shown in Fig. 4. The furnace leads and thermocouple wires were led in through rubber bungs held in position by means of steel caps, and kept from overheating by water cooling coils. The thermocouple was introduced through a bolt in the autoclave cover, which could be removed in order to saturate the metal with gas, and quickly replaced. By means of the cap *G*, it was also possible to remove the couple independently of its sheath. Pressure was applied through a tube (not shown) let into the cover and connected to a gas cylinder through a reducing valve. A gauge attached to this valve served to record the pressure.

Two series of experiments were carried out, both of which are summarized in Table IV.

In the first series the silver was exposed to air, with occasional stirring, for half an hour at 1000°–1020° C. The weight of metal was 100–

TABLE IV.—*Solidification under Pressure.*

Method of Saturation.	Pressure on Solidification, P, lb./in.^{2}.	First Arrest (θ_1), ° C.	Second Arrest (θ_2), ° C.	Arrest Time (θ_2), t seconds.	*Density of Ingot.	$961 - \theta_2 = (D)$.	$P^{\frac{1}{2}}$.	$\frac{D}{P^{\frac{1}{2}}}$.	$\frac{1 - 0{\cdot}058 P^{\frac{1}{2}}}{tP^{\frac{1}{2}}}$
Under charcoal	15	961	...	...	10·51	...	...	...	...
½ hr. in air at 1000°–1020° C. with occasional stirring.	15	953	928	20	†8·31	33	3·87	8·52	...
	30	950	901	4	10·01	60	5·48	10·4	...
	30	959	882	2½	10·15	79	5·48	14·4	...
	49	952	none above 880	...	10·31	...	...	...	...
	115	946(?)	,,	...	10·46	...	...	...	...
Cylinder; oxygen bubbled through for ½ hr. at 1000°–1020° C.	15	942	938	89	...	23	3·87	5·94	0·0022
	38	939	928	68	...	33	6·16	5·36	0·0015
	45	944	923	21	...	38	6·71	5·66	0·0043(?)
	59	944	921	53	...	40	7·79	5·14	0·0013
	62	...	916	...	...	45	7·87	5·71	...
	77	934	906	37	...	55	8·77	6·26	0·0015
	89	938	902	35	...	59	9·44	6·25	0·0014
	110	938	897	30	...	64	10·5	6·09	0·0012
	125	949	898	25	...	63	11·2	5·63	0·0013
	150	944	888	15	...	73	12·25	5·96	0·0016
	164	946	887	12	...	74	12·8	5·77	0·0017
	195	951	878	9	...	83	14·0	5·93	0·0015
							Mean	5·81	0·0015

* Apparent density in water at 13° C.

† Too high, since water penetrated the sample.

110 grm., and it was contained in a fireclay crucible. After the saturation period, the thermocouple plug (*H*, Fig. 4) was inserted, and the

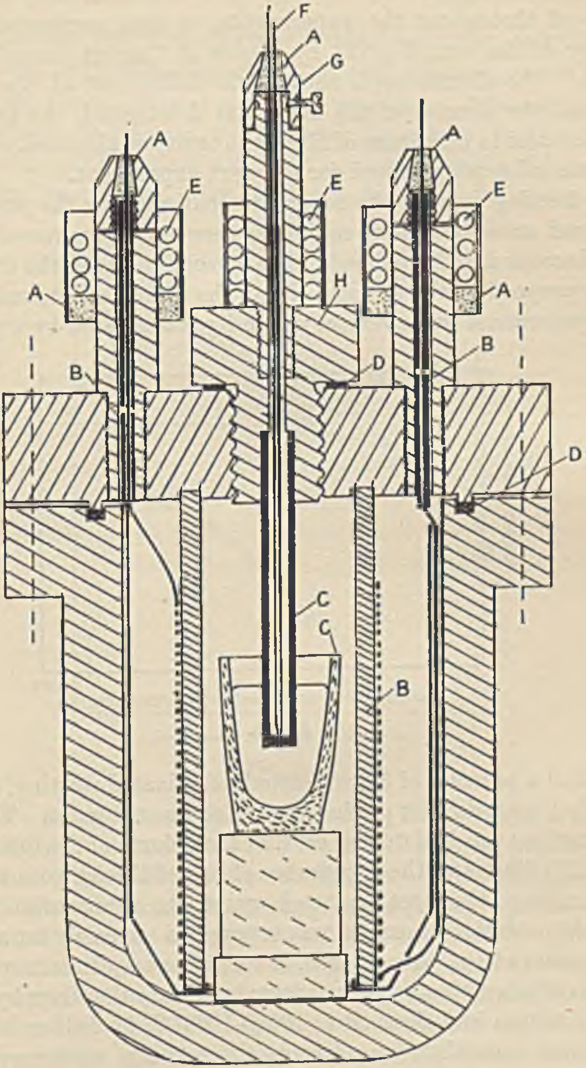


Fig. 4.

A. Rubber bungs.
B. Silica tube.
C. Fireclay.
D. Lead washers.
E. Water-cooled copper tubes.
F. Thermocouple.
G. Thermocouple cap.
H. Thermocouple plug.

couple was placed in position. Nitrogen was then admitted from a cylinder until the pressure reached the desired value, at which it was maintained throughout the cooling. The rate of cooling was 1·8° C. per second throughout the experiments, so that comparisons of the intensity of the second point by means of "arrest times" are permissible. The thermocouple sheath was drilled out of the resulting ingot, and the density of the ingot was determined, the ingot being boiled in water to make sure of filling the cavity so obtained. The same silver was subsequently used for the next experiment.

The freezing point of the silver was unaffected by the pressure, but the second arrest was very rapidly lowered and suppressed, and the ingots increased in soundness. The unsoundness of the ingots was roughly proportional to the intensity of the second arrest, and although a very pronounced improvement in density was secured by a pressure of 2 atm. and a pressure of 3 atm. entirely eliminated spitting, a pressure of nearly 8 atm. did not produce an entirely sound ingot. The volume of the cavities was still 0·5 per cent. of the volume of the ingot. Fig. 5 (Plate LII) illustrates the appearance of two of these ingots, and in Fig. 6 the density of the ingot is plotted against the solidification pressure.

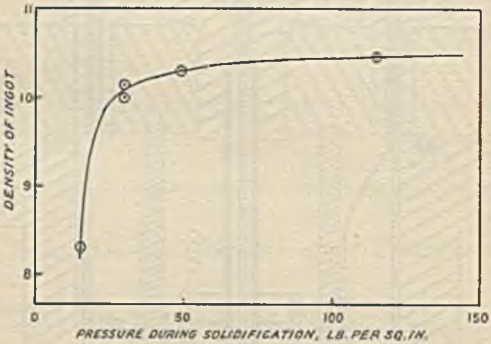


Fig. 6.

As the evolution of oxygen was suppressed too easily for a thorough investigation of the phenomenon, a second series of melts was undertaken, in which more oxygen was introduced into the silver by bubbling cylinder oxygen into the melt at 1000°–1020° C. for half an hour. The results were somewhat irregular, as the readings were very sensitive to the position of the couple in the melt, on account of the small mass of metal and the high rate of cooling. Nevertheless they show definitely that the temperature at which oxygen is evolved from the melt falls in proportion to the square root of the external pressure, and that the quantity of silver which is still liquid when the evolution takes place decreases with increasing pressure in roughly the same manner. The data are plotted as circles in Fig. 7.

5.—*The Lowering of the Melting Point of Silver by Oxygen under Pressure.*

On account of the difficulty of passing oxygen under pressure through the melt, the procedure was somewhat modified. A small button of silver, weighing about 6 grm., was placed in the crucible, and the thermocouple sheath was dispensed with. In its place a length of 1 mm. bore silica tubing was slipped over the hot junction of the thermocouple and bent in a flame to the shape of a hairpin. Using this form of covering very satisfactory cooling curves could be obtained, and the small mass of metal was readily saturated with gas. The silver was heated to 1000° C. and a brisk stream of oxygen was passed into the crucible for 15 minutes, to sweep out all nitrogen from the furnace. The couple was then placed in position, and the required pressure of oxygen admitted to the autoclave from a cylinder. The temperature was slowly lowered over about 15 minutes to about 30° C. above the anticipated freezing point of the metal, and held constant for a further 15 minutes. The cooling curve was then taken, at a rate of 0·35° C. per second. Table V records the results obtained, which are plotted as crosses in Fig. 7. The depression of the freezing point was proportional to the square root of the oxygen pressure, as is shown by the constancy of the figure

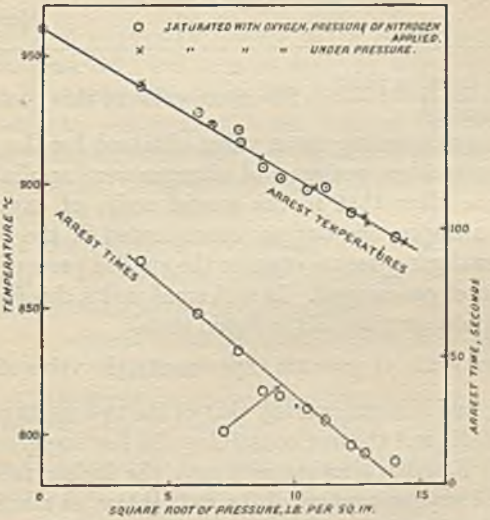


FIG. 7.

TABLE V.—*Depression of the Freezing Point of Silver by Oxygen under Pressure.*

Pressure, lb./in.^{2}.	Freezing Point, ° C.	Depression of Freezing Point, ° C.	(Pressure)$^{\frac{1}{2}}$.	$\frac{\text{Depression}}{(\text{Pressure})^{\frac{1}{2}}}$
15	939	22	3·87	5·69
45	923	38	6·70	5·66
75	910	51	8·66	5·89
115	898	63	10·72	5·86
165	884	77	12·84	5·99
163	886	75	12·78	5·86
205	876	85	14·31	5·94
				Mean 5·82

$\frac{\text{depression of freezing point}}{(\text{Pressure})^{\frac{1}{2}}}$. The mean value of this quotient was very close to the corresponding mean value obtained for the depression of the second arrest when pressures of nitrogen were applied (Table IV). It is therefore clear that in the second series of experiments with pressures of nitrogen, the oxygen concentrated in the residual liquid until an internal gas pressure equal to the applied pressure was reached, before bubbles of gas escaped. In such small melts, this pressure is equal to the hydrostatic pressure of the liquid metal.

In the first series of pressure experiments, the value of $\frac{D}{P^{\frac{1}{2}}}$ was very much higher, and it is noteworthy that of the two melts cooled under a pressure of 30 lb./in.^{2} the one containing the less oxygen (as indicated by its higher liquidus temperature) gave the higher value. It seems that when the oxygen content of the melt is low, so much silver has to solidify before the required internal gas pressure is reached that additional pressure is needed to enable the liquid to be squeezed out through the interstices between the dendrites.

6.—*Undercooling at the Second Arrest Point.*

Undercooling to the extent of several degrees not infrequently occurred at the second arrest point, and must have been due to supersaturation with regard to oxygen, since silver crystals were already present. This phenomenon affords a means of evaluating the surface tension resistance to gas separation (θ) from the difference between the temperature of initial separation and the maximum temperature reached during the heat evolution. Some of the values obtained are given in Table VI. The occurrence of undercooling was spasmodic, and the values obtained are irregular, which is not unusual where undercooling phenomena are concerned.

TABLE VI.—*Undercooling at the Second Arrest Point.*

Lowest Temperature before Gas Evolution, ° C.	Corresponding Pressure, lb./in.².	Maximum Temperature during Arrest.	Corresponding Pressure, lb./in.².	θ, Lb./in.².
900	108	906	99	9
925	71	933	61	10
930	65	932	62	3
945	42	948	36	6
870	229	875	211	18

DISCUSSION OF THE RESULTS.

1.—*The Constitution Diagram.*

The solubility of oxygen in molten silver has been measured by Sieverts and Hagenacker,[1] and in solid silver by Steacie and Johnson.[3] In both cases it is proportional to the square root of the pressure. These measurements, combined with the thermal data now obtained, enable a ternary diagram expressive of the complete behaviour of the melts to be constructed. This diagram is given in Fig. 8, for the region 0–6 atm. pressure and 800°–1000° C.

It consists of five regions, respectively

ABECFD	liquid silver–oxygen solution.
CFGKLH	solid silver–oxygen solution.
CFDG	liquid silver–oxygen solution, solid silver–oxygen solution
CRDMAOBN	liquid silver–oxygen solution, gaseous oxygen
CRGMHQPK	solid silver–oxygen solution, gaseous oxygen.

Consider the cooling of silver in equilibrium at 980° C. with an atmosphere containing 2 atm. partial pressure of oxygen with a total pressure of 6 atm. It is represented in composition, temperature, and internal gas pressure by the point *a*. If the conditions are such as to maintain equilibrium with the atmosphere throughout, it will in solidifying follow the course *abcd*. There will be no change in internal gas pressure, and the silver will solidify at one temperature, giving off oxygen in the proportion *bc*, and ending up with a small quantity *d* of oxygen in solution. Since, however, the internal gas pressure will never reach the external pressure, no gas bubbles will be formed and a sound ingot will result. Extremely slow cooling is necessary to achieve this result. This course of solidification is represented on the more familiar temperature–composition diagram by the projection of the curve *abcd* on the plane, *NEL*, that is to say, by $a^1b^1c^1d^1$.

Under ordinary conditions of cooling, the silver loses little or no oxygen until the internal gas pressure has reached the total external pressure. The course of solidification is then given by aeg^1GK (assuming the external pressure to be 6 atm.). At first the internal gas pressure, on account of the increasing solubility of oxygen in molten silver with decreasing temperature, falls to *e*. Crystals of silver of the composition *f* then begin to separate, and as a result of the concentration of oxygen in the residual liquid, the internal gas pressure and composition of the liquid move along the curve *eD* as the temperature falls. The composition of the solid deposited at the same time moves along *fG*, the relative quantity of solid increasing continuously. At the temperature of the line *DG*, the internal gas pressure becomes equal to the external pressure, and further loss of heat causes oxygen to be evolved at constant temperature until the whole of the silver is solid. The composition of the solid silver is represented by the point *G*, that is to say, more oxygen is retained than is the case when equilibrium conditions exist. The proportion of liquid which solidifies at *DG* is given by $\frac{Ga^1}{GD}$. It decreases in an approximately linear manner as the reciprocal

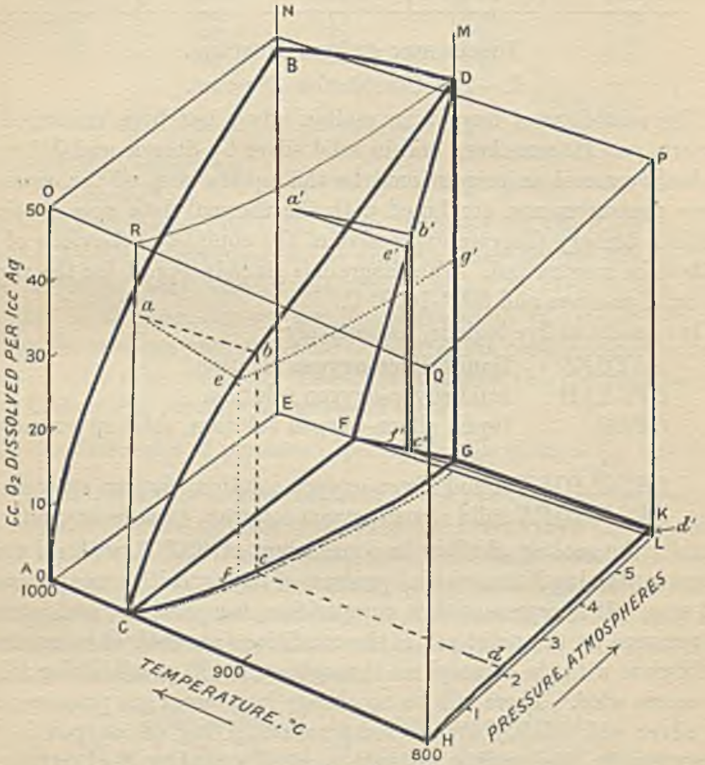


FIG. 8.

of the square root of the external pressure is decreased, when the initial oxygen content of the silver is maintained constant. That this is true within the limits of experimental error is shown by the last column of Table IV.

The melting point of silver is connected with the pressure of oxygen in equilibrium with it by the relationship

$$T = 961 - 5{\cdot}82P^{(\frac{1}{2})} \quad (P = \text{pressure in lb./in}^2.)$$

or, more conveniently,

$$T = 961 - 22{\cdot}31P^{(\frac{1}{2})} \quad (P = \text{pressure in atmospheres}).$$

The reaction concerned is

Silver saturated solution $\longrightarrow$
Silver saturated solid solution + oxygen (gas),

and the heat of reaction calculated from the equation is 10·0 kilojoules per gram atom of silver. This is fairly close to the latent heat of silver (11·7 kilojoules, International Critical Tables) and justifies the use of the intensity of the second arrest as a rough measure of the amount of molten metal present.

By extrapolation of the melting-point curve, the conditions under which molten silver can be in equilibrium with silver oxide can be found. According to Keyes and Hara[4] the dissociation pressure of silver oxide is connected with the absolute temperature by the equation

$$\log p = \frac{-2859}{T} + 6{\cdot}2853.$$

This intersects the melting-point curve at 507° C. and 414 atm., and a eutectic between silver and silver oxide may be expected near this temperature, provided the pressure is high enough. Fig. 9 (Plate LII) shows the structure obtained by heating silver and silver oxide together in a steel bomb to 600° C. The eutectic is clearly shown, and the result indicates that the difference in the behaviour of silver and copper towards oxygen is not one of kind, but of degree.

2.—*The Elimination of Blowholes by Means of Applied Pressure.*

If ingots can be cast under pressure in such a way that the hydrostatic pressure in the liquid metal is always greater than the greatest internal gas pressure that can be developed, sound metal free from blowholes should result. Although the pressures theoretically necessary for silver are high, for many metals, where the gas concerned has an appreciable solubility in the solid state, pressures of a few atmospheres only are required.

The method of applying the pressure is important, since the contraction on solidification of the metal can play a decisive part. Suppose, for example, we have a volume of metal in an ingot mould, to which pressure is applied by means of a piston as shown in Fig. 10. Suppose the pressure produced in the liquid metal to be P, and the volume V. After an interval of time, the piston will have descended somewhat, and the volume beneath it will be $V - v$. Meanwhile a mass m of metal will have solidified, and undergone its solidification contraction, x, so that the reduction of volume on this account will be mx. Now, if mx is greater than v, the effect on the liquid metal will be to reduce the pressure to an extent equal to $\frac{mx - v}{L} \cdot e$, where e is the volume elasticity of the liquid metal and L the volume of liquid remaining. If the rate of solidification is sufficiently high, it is clear that this phenomenon will reduce the pressure of the liquid until blowholes can form, in spite of the fact that the outer crust of the ingot may be continuously yielding under the pressure.

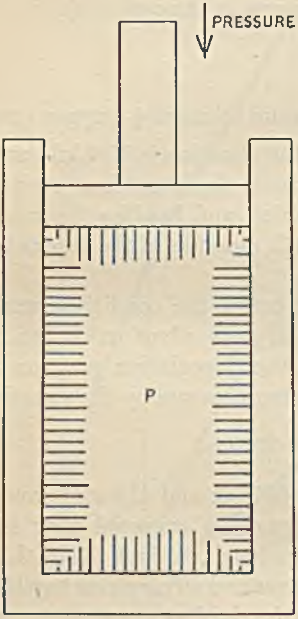


FIG. 10.

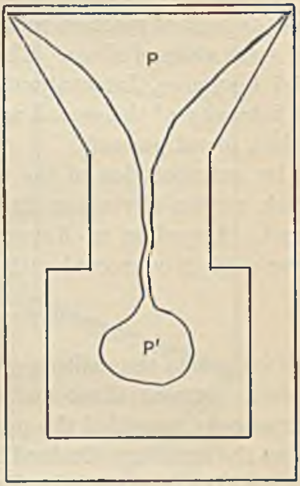


FIG. 11.

Another way in which the contraction can lead to a release of the pressure is illustrated in Fig. 11. In the course of solidification a point must be reached at which all the liquid metal necessary to feed the end of the casting must pass down an exceedingly narrow channel, and its flow will be hindered by its own viscosity. If P is the pressure in the feeder head, P^1 the pressure in the casting, and η the viscosity of the metal, the rate of flow will be given by

$$\text{Rate of flow} = \frac{P - P^1}{\eta R}$$

where R is a function of the length and diameter of the channel and tends to increase as the channel becomes narrower. Now, if $\frac{dm}{dt}$ is the rate of solidification of the casting, and x the solidification contraction, the rate of contraction in the casting will be $x\frac{dm}{dt}$, and so long as no cavities are formed

$$\frac{P - P^1}{\eta R} = x\frac{dm}{dt}$$

$$P^1 = P - \eta R x \frac{dm}{dt}$$

Thus, as the channel becomes narrower, the pressure in the casting falls until it is again low enough to allow gas to be liberated. These conditions are likely to occur in alloys having a long freezing range, in which long dendrites, with narrow liquid channels between them, are apt to form. Consequently it is essential for the successful use of pressure to allow for the proper feeding of every part of the casting. The ideal method of applying pressure to an ingot during solidification is suggested in Fig. 12. The ingot mould is contained in a chamber to which the necessary gas pressure can be applied. It is tapered towards the bottom, so as to allow of complete feeding, and a hot dozzle and hot brick serve to ensure that the surface is kept liquid and that the full pressure is maintained on every part of the liquid, until solidification is complete. Facilities for the quick opening and closing of the mould would, of course, be necessary.

CALCULATION OF INTERNAL GAS PRESSURE WHEN REACTIONS OCCUR.

We shall consider the case when oxides are present in the melt, and are liable to be reduced by reducing gases, simultaneously present. Taking as an example the reduction of cuprous oxide by hydrogen, we shall endeavour to arrive at a figure for the maximum internal gas pressure that can be developed during the solidification of tough pitch copper.

The internal gas pressure of a metallic solution has been defined as the minimum pressure of the gas mixture which can be in equilibrium with it.

In accordance with the principles of Nernst's Distribution Law, it is assumed that molecular oxygen is soluble in molten copper to some extent, and that it undergoes the reversible reaction

$$O_2 + 4Cu \rightleftharpoons 2Cu_2O.$$

Assuming that the molecular formula of the dissolved oxide is Cu_2O it follows, provided the concentration of oxide is so small that the concentration of copper can be considered as unity, that

$$[Cu_2O] = k_O p_O^{\frac{1}{2}}$$

where $[Cu_2O]$ = concentration of dissolved oxide.
p_O = partial pressure of oxygen above the metal.
k_O = constant, dependant upon temperature.

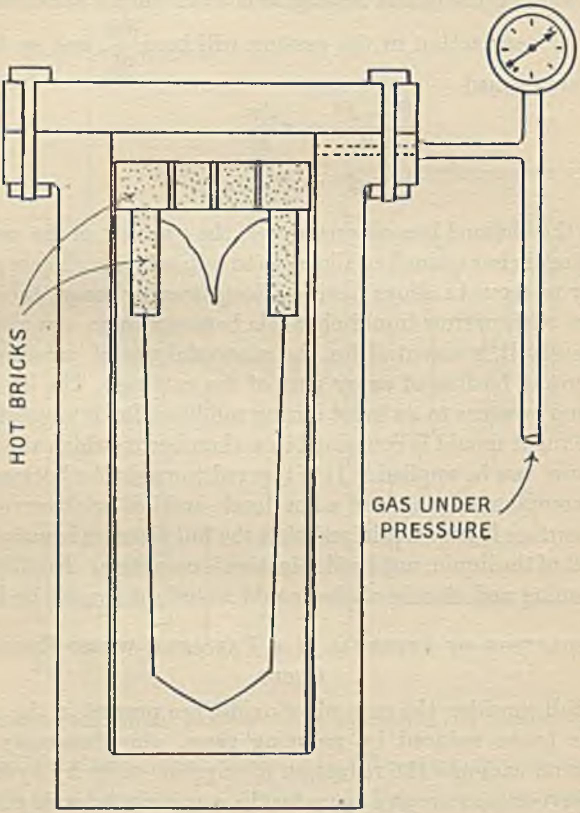


Fig. 12.

Thus copper containing dissolved oxide can be considered as having an internal gas pressure p_O of oxygen, such that

$$p_O = \left(\frac{[Cu_2O]}{k_O}\right)^2$$

This pressure is quite analogous to the dissociation pressure of a metallic oxide and will therefore be called the *oxygen dissociation pressure* of the metallic solution. Every metal or alloy containing dissolved oxide may be considered to have a similar oxygen dissociation pressure. It will as a rule be small and of the same order as the dissociation pressure of the lowest oxide of the metal. It will increase from zero, in the pure metal, with rising oxygen content of the metal, and it is a condition of equilibrium that the saturated oxide solution must have the same oxygen dissociation pressure as the oxide phase in contact with it.

Now, if the copper contains, besides a concentration $[Cu_2O]$ of oxide, a volume v_H of hydrogen per c.c., the hydrogen will have an internal gas pressure of p_H, where

$$p_H = \left(\frac{v_H}{k_H}\right)^2$$

k_H = solubility constant of hydrogen.

Thus any atmosphere in equilibrium with the melt must have a partial pressure p_O of oxygen, and p_H of hydrogen. But no atmosphere can contain these constituents unless it also contains a partial pressure p_{H_2O} of steam such that

$$\frac{p_H^2 p_O}{p_{H_2O}^2} = K$$

where K is the dissociation constant of steam at the temperature in question.

Thus the least pressure of the atmosphere which can be in equilibrium with the solution contains

$p_H = \left(\frac{v_H}{k_H}\right)^2$ partial pressure of hydrogen

$p_O = \left(\frac{[Cu_2O]}{k_O}\right)^2$,, ,, ,, oxygen

$p_{H_2O} = \frac{1}{\sqrt{K}}\left(\frac{v_H}{k_H}\right)^2 \cdot \left(\frac{[Cu_2O]}{k_O}\right)$,, ,, ,, steam

The sum of these is the total internal gas pressure of the melt.

In all base metals, the partial pressure of oxygen may be neglected. In the case of copper, unless the oxygen content of the melt is very small, that of hydrogen may also be neglected: it is rarely more than 2 per cent. of the whole.[5] Consequently the value $\frac{1}{\sqrt{K}}\left(\frac{v_H}{k_H}\right)^2 \cdot \left(\frac{[Cu_2O]}{k_O}\right)$ may be taken as the internal gas pressure.

Suppose now that we have a bath of copper under atmospheric pressure, and oxide and hydrogen are together present in such amounts that the internal gas pressure is above 1 atm. Reaction will take place, and a gas will be evolved, having the composition

$$\frac{100p_O}{p_O + p_H + p_{H_2O}}\ \%\ \text{of oxygen} \qquad \frac{100p_{H_2O}}{p_O + p_H + p_{H_2O}}\ \%\ \text{of steam}$$

$$\frac{100p_H}{p_O + p_H + p_{H_2O}}\ \%\ \text{of hydrogen.}$$

In this particular case it will be mostly steam. As a result, the internal gas pressure will fall, and the gas evolution will cease when the composition is such that the internal gas pressure is 1 atm. This does not represent a condition of equilibrium, since the ultimate physico-chemical equilibrium depends on the composition of the external atmosphere, but it represents the practical end of the reaction, where deep baths of metal are concerned, for any subsequent adjustment of the composition must take place by diffusion, without gas evolution, which is very slow. If we assume a certain oxygen content for the bath, the corresponding internal pressure of hydrogen, at a given temperature, can be calculated.

Let us assume a temperature of 1150° C., and an oxygen content of 0·03 per cent.* which corresponds with the conditions within a refinery furnace during lading.

The dissociation pressure of cuprous oxide at 1150° C. is, by interpolation from Stockdale's figures,[6] $2{\cdot}57 \times 10^{-5}$ atm. The solubility of cuprous oxide in molten copper at that temperature is equivalent to 0·84 per cent. of oxygen. Consequently the oxygen dissociation pressure of a melt containing 0·03 per cent. of oxygen is $\frac{0{\cdot}03^2}{0{\cdot}84^2} \times 2{\cdot}57 \times 10^{-5}$ atm. $= 3{\cdot}27 \times 10^{-8}$ atm.

The dissociation constant of steam at 1150° C. is given by

$$\log_{10} \frac{p_{H_2O}}{p_H p_O^{\frac{1}{2}}} = 6{\cdot}138 = \log \frac{1}{\sqrt{K}}$$

the pressure being in atmospheres. This value is calculated from Lewis and Randall's[7] free energy equation for water, and agrees very closely with the mean between Langmuir's experimental values and those of Nernst and von Wartenberg.

Now, the internal gas pressure being 1 atm. when the evolution of gas ceases we have:

$$\frac{1}{\sqrt{K}} p_H p_O^{\frac{1}{2}} = 1 \text{ atm.}$$

whence:

$$p_H = \frac{\sqrt{K}}{p_O^{\frac{1}{2}}} = \frac{1}{1{\cdot}37 \times 10^6 \sqrt{3{\cdot}27 \times 10^{-8}}}$$
$$= 0{\cdot}00403 \text{ atm.} = 3{\cdot}06 \text{ mm. Hg.}$$

We are now in a position to calculate the maximum internal gas pressure that can be developed during solidification, provided no hydrogen escapes during the process. This occurs at the moment when the last drop of eutectic liquid solidifies, the oxygen content of the liquid being then at its highest, and the internal gas pressure of hydrogen, by a

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* Normally 0·02–0·05 per cent. of oxygen is taken up by the metal during pouring.

process similar to that described for oxygen in silver, having also reached its maximum. The oxygen dissociation pressure of the eutectic liquid at its freezing point is the same as that of cuprous oxide at that temperature. By interpolation from Stockdale's figures p_O (1065° C.) $= 3{\cdot}8 \times 10^{-6}$ atm. The internal gas pressure of hydrogen at 1065° C. is calculated from Sieverts's figures by means of equation (5) putting $x = 1$. Copper dissolves 0·655 mg. of hydrogen per 100 grm. at 1150° C. and 0·39 mg. in the solid at 1065° C.

Hence
$$p_H \text{ (1065° C.)} = \left(\frac{0{\cdot}655}{0{\cdot}39}\right)^2 \times p_H \text{ (1150° C.)}$$
$$= \left(\frac{0{\cdot}655}{0{\cdot}39}\right)^2 \times 0{\cdot}00403 \text{ atm.}$$

The dissociation constant of steam at 1065° C. is $4{\cdot}17 \times 10^6$. Hence, maximum internal gas pressure at 1065° C.

$$= 4{\cdot}17 \times 10^6 \times \sqrt{3{\cdot}8 \times 10^{-6}} \times \left(\frac{0{\cdot}655}{0{\cdot}39}\right)^2 \times 0{\cdot}00403$$
$$= 92 \text{ atm.}$$
$$= 0{\cdot}60 \text{ ton/in.}^2$$

This is a pressure that can readily be applied by means of a gas. It is perhaps worth mentioning that the pressure necessary might be substantially reduced by adding an impurity which would alter the composition of the last liquid to solidify in such a way as to lower its oxygen dissociation pressure. Indeed, a deoxidant may be regarded as an addition which brings the maximum internal gas pressure below 1 atm. Pressure is employed industrially for producing sound castings of tough-pitch copper, but the pressures are several times this value.

CONCLUSIONS.

1. The melting point of silver is lowered by oxygen in proportion to the square root of the oxygen pressure, according to the equation

$$T = 961 - 22{\cdot}31 \,.\, P^{\frac{1}{2}}$$

(P = pressure in atmospheres, T = melting point in ° C.). This behaviour is consistent with the known solubility of oxygen, and the latent heat of silver.

2. When silver containing oxygen solidifies, comparatively pure silver separates first, and the oxygen concentrates in the residual liquid until its composition is such that the pressure of oxygen that would be in equilibrium with it is not less than the external pressure. Bubbles of oxygen are then given off.

3. Very little or no oxygen escapes from the metal before the bubbles are liberated.

4. Accordingly, the escape of oxygen can be retarded, and eventually prevented by the application of pressure during solidification.

5. The rate of cooling has no effect on the temperature at which the gas is evolved. It appears to have some effect on the quantity evolved, more gas being liberated at slower rates of cooling.

6. Supersaturation phenomena and the presence of previously solidified silver may provide resistances to the escape of oxygen, in addition to the external pressure.

7. When pressure is employed to prevent gas liberation within a casting, efficient feeding must be provided.

8. The pressure necessary to prevent gas liberation can be calculated, both when the evolution is due to solubility changes, and when reactions occur, by means of the conception of the " internal gas pressure " of the melt. The pressure is found to be about 0·5 ton/in.^{2} for tough-pitch copper.

9. A silver–silver oxide eutectic forms at a temperature between 500° and 600° C., if the pressure is sufficient to prevent the dissociation of the oxide.

ACKNOWLEDGMENTS.

The author wishes to express his gratitude to the Research Grants Committee of the University of Birmingham for the facilities enabling this work to be done, and to Professor D. Hanson, D.Sc., for his constant interest and help throughout the work.

BIRMINGHAM,
April 16, 1932.

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DISCUSSION.

MR. W. P. REES,* M.Sc. (Member): The subject of gases in metals is interesting from the theoretical point of view, and is extremely important from the practical point of view. The study is not very easy, and the author has, in a previous paper, already emphasized the complexities of the subject. The "spitting" of silver during solidification in the particular case with which Mr. Allen has largely dealt, has received a great deal of attention, and it has been assumed previously that the " spitting " was due to the dissociation of

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silver oxide; I think that the author's experiments are the first to prove fairly conclusively that that is actually the case, and that the "spitting" is due to the evolution of oxygen from silver oxide which dissociates at the temperature at which it is precipitated from the molten solution of the silver.

Mr. Allen is to be highly commended for the production of the photograph of the silver oxide eutectic reproduced in Fig. 9 (Plate LII). I should like more information as to how that eutectic was formed. If a mixture of silver oxide and silver be taken, and heated together to, say, 500° or 600° C. (the temperature at which the author has heated them together) under a pressure of oxygen, then it would be expected that the eutectic would be formed, because the dissociation pressure of silver oxide is an oxygen pressure; whereas if the same thing be done, but, using an oxygen pressure instead of a nitrogen pressure, the nitrogen pressure would not necessarily prevent the silver oxide from dissociating, and I do not think that that eutectic would be obtained. I should like to have the author's opinion about that, as well as a few more details as to how he did obtain that eutectic.

The question of the pressure preventing the formation of the eutectic brings me to that of the pressure preventing the escape of oxygen from molten silver. The author appears to have done this by solidifying under a pressure of nitrogen. If solidifying under a pressure of oxygen has prevented nitrogen from escaping (and from the density of the ingots it appears that it has done so), then the silver oxide eutectic ought to be found in that ingot. Such would scarcely be expected. If, on the other hand, it had been solidified under a pressure of oxygen (as was the case in other experiments), then it would be expected that the eutectic might be formed. The nitrogen pressure will not prevent the oxide from dissociating. Actually the very opposite appears to have happened to that which occurs in the well-known method of de-gassing aluminium. If aluminium be de-gassed by passing bubbles of nitrogen through it, hydrogen is displaced. The actual displacement of the hydrogen is determined by the partial pressure of the hydrogen in the nitrogen bubble. The mere fact that the gas is bubbling through the metal at atmospheric pressure does not affect the argument. If the nitrogen is bubbled through at a higher pressure, the elimination of the hydrogen would not be any quicker, because it depends on the partial pressure of the hydrogen in the nitrogen bubble, and the pressure of the nitrogen would not affect that partial pressure of the hydrogen.

This brings me to the conception of the internal pressure of the gas in a solution. There has been no attempt—quite rightly—to make any analogy with the osmotic pressure of a salt in solution. But I find it rather difficult to make out exactly what the author intends to convey by this internal pressure. He defines internal pressure as being the partial pressure of the gas—of that particular gas that is in solution—in the gaseous atmosphere which is in equilibrium with the solution. What happens if there is a fall in the solubility of the gas due, say, to a fall or rise in temperature? The pressure of the gaseous phase now becomes too low for the equilibrium conditions to be maintained, and therefore gas is evolved from the solution; and since the internal pressure of the gas, as defined by the author, is determined by the partial pressure of the gas in the gaseous phase, I think that the factor that determines whether the gas comes off or not is not the internal pressure of that gas in the solution, but the partial pressure of the gas in the gas phase. In other words, it simply follows Nernst's distribution law.

In using this conception of internal pressure I should like to have the author's opinion as to whether it conveys to him an idea of the pressure keeping the gas in solution, or a pressure tending to make the gas come out of solution. He states that as the solubility of the gas decreases the internal pressure increases, but, as I have just said, I do not think that that actually happens.

It is the partial pressure that is too low. Therefore the gas has to come out of solution. It would be easier if it could be considered more as the dissociation pressure of the gas solution system.

Mr. Allen (*in reply*): I feel that many of Mr. Rees' questions would be better answered in writing. The apparatus in which the silver–silver oxide eutectic was produced is illustrated in Fig. A. It was essentially a small steel bomb, closed by the screw *A*. A hollow plug of silver was placed at *B*, filled with pure silver oxide, and covered with a cap of silver (*C*). The screw was tightened in such a way as to force the silver cap partly into the cavity containing the silver oxide. The whole was then placed in a furnace at 600° C. for 1 hr., cooled, and cut across the line *DE*. The section was polished, and the eutectic structure found. There was a definite penetration of the silver oxide into the silver to a small depth; the silver oxide and the silver had alloyed quite well together. As the pressure was not released until the bomb was cold, the silver oxide was quite stable when the bomb was opened, and the photomicrograph could be taken in the ordinary way.

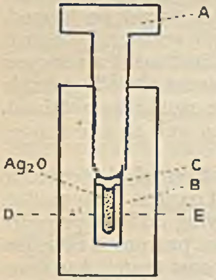

Fig. A.

It is always an awkward thing to introduce new terms. By the internal gas pressure I mean the value $\left(\frac{v}{k}\right)^n$, which is the pressure to be associated with the existence of *v* c.c. per unit mass of gas dissolved in a metal, in which its solubility constants are *n* and *k*. I conceive it as the pressure at which the gas strives to come out of solution. If, for example, a melt of silver contain 1 c.c. of dissolved oxygen per grm. of metal, there is one partial pressure of oxygen in the atmosphere above it, which is just sufficient to maintain the gas in solution, without any increase or decrease of its amount. That pressure I call the internal gas pressure of the solution of oxygen in silver.

CORRESPONDENCE.

The Author (*in further reply to the discussion at the meeting*): Mr. Rees appears to be confusing himself by overlooking the distinction between the conditions necessary for complete physico-chemical equilibrium, and those necessary for the formation of gas bubbles, which is the kernel of the matter. For complete equilibrium the internal gas pressure of the melt must equal the partial pressure of the solute gas in the external atmosphere. For bubble formation, the internal gas pressure must be greater than the hydrostatic pressure of the melt. These conditions are the same only when the atmosphere consists of the pure solute gas and the metal bath is shallow. Nitrogen has no influence on the former condition, but affects the latter. These experiments show that in the silver–oxygen system complete equilibrium is not readily obtained, and that the escape of oxygen from the melt is determined by the hydrostatic pressure, as affecting the process of bubble formation. Nitrogen pressure is no more than a convenient means of altering this pressure. One will not expect to find the silver–silver oxide eutectic in ingots rendered sound by the application of pressure, since oxygen has an appreciable solubility in solid silver. When a melt containing gas changes in temperature, its internal gas pressure alters. If it were initially in equilibrium with its atmosphere, it will no longer be in equilibrium with it unless the composition of the atmosphere changes appropriately at the same time. An exchange of solute between the gas and metal phases will begin, but no bubbles will form unless the change has raised the internal gas pressure of the melt above the external pressure.

Mr. W. P. Rees,* M.Sc. (Member): (*Continuing the remarks made at the meeting*). I should like to discuss further the effect of pressure in preventing the escape of oxygen from silver during solidification. Is the author sure that the ingots solidified under a pressure of nitrogen were sensibly free from blowholes because the pressure prevented the formation of bubbles; or was the rôle of the nitrogen to remove oxygen from the silver before it solidified? This point requires careful consideration, especially in view of the work of Smithells † and his co-workers on the remarkable rapidity with which nitrogen "de-gases" nickel–chromium alloys. As previously stated, the application of a nitrogen pressure would not be expected to *prevent* dissociation of Ag_2O, but it might retard the reaction. Such a retardation may have been observed by the author, but the action is entirely different from the effect of an oxygen pressure. The latter could prevent blowhole formation by preventing dissociation of the silver oxide. The production of sound ingots under a nitrogen pressure may have been caused by (1) a slowing down of the rate of dissociation of silver oxide, (2) removal of oxygen from the molten silver, (3) prevention of bubble formation by the nitrogen pressure. If the last occurs, then the pressure of an inert gas must be considered as one of the factors which tend to make the removal of gases from molten metals difficult. These factors, as pointed out by Bircumshaw, ‡ include the surface tension and hydrostatic pressure of the metal.

Another point on which I should appreciate further information is the effect of pressure on the freezing point of silver. On p. 328 the statement is made that the freezing point was unaffected by the pressure. On p. 329 it is stated that the depression of the freezing point was proportional to the square root of the pressure. I appreciate that the first statement refers to a nitrogen pressure, which would not be expected to depress the freezing point to any appreciable extent. On the other hand, it would be expected that an oxygen pressure would depress the freezing point in virtue of the increased oxygen content of the melt, but a second arrest would also be expected. In addition to the data in Table V, it would be interesting to know whether a second arrest was found. If no second arrest occurred on the cooling curves, it would appear that a solution of silver oxide in molten silver freezes at a constant temperature.

Mr. R. S. Dean,§ M.S., Met.E. (Member), and Mr. V. H. Gottschalk ||: The fact that sound metal free from blowholes can be obtained by using pressure is interesting and important, and the author's study of conditions for the application of this method is a valuable practical contribution to the vexed gas-in-metals problem. It has seemed to us, however, that the theoretical basis for the discussion of the relation of gases to metals at higher temperature needs thorough revision and purging from the traditional ideas which obscure rather than elucidate experimental facts.

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† C. J. Smithells, S. V. Williams, and E. J. Grimwood, *J. Inst. Metals*, 1931, 46, 443.

‡ L. L. Bircumshaw, *Phil. Mag.*, 1926, [vii], 1, 510–522.

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For example, this paper opens with the proposition that gases are present in the metal in the atomic state, which, if true at all, is almost certainly not the case with the system silver–oxygen, as has been shown repeatedly from 1904 * to 1932,† and as the author himself shows when he says—on p. 333: "The result indicates that the difference in the behaviour of silver and copper towards oxygen is not one of kind but of degree."

It is generally agreed that the solubility of oxygen in copper represents the formation and solution of cuprous oxide, and that conception is incompatible with the presence of atomic oxygen in the melt. What we wish to emphasize is the inadequacy of the present state of the theory underlying the phenomenon of the solution of gases in metals; there must be something wrong when, by starting with the assumption of the atomic state of the gas, you can deduce its antipode, the formation of a compound.

We attempted a statement of the problem and made some suggestions of possible solutions in a paper read last year before the American Institute of Mining and Metallurgical Engineers.‡

Dr. D. **Stockdale**,§ M.A. (Member): The conception of internal gas pressure, as put forward by the author, is of fundamental importance. I suggest that his definition is not strictly correct and would substitute the following: "The internal gas pressure is the *only* pressure of the solute gas with which the solution can be in true equilibrium and is also the *least* pressure of *any* gas mixture required to prevent the formation of gas bubbles within the solvent."

I presume that the factor 0·058 in the formula at the top of the last column of Table IV (p. 326) was obtained by graphical methods. It follows from the experimental results that

$$\frac{1}{P^{\frac{1}{2}}} - 0{\cdot}058 = 0{\cdot}0015\, t$$

Mr. R. Taylor ‖ points out that if $n = 2$, equation (5), p. 319, can be put in the form

$$\frac{1}{P^{\frac{1}{2}}} - \frac{k_s}{v} = \frac{(k_e - k_s)}{v} \cdot ct$$

where c is a constant connecting the time of solidification with the amount of solid solidifying.

This work shows that $\frac{k_s}{v} = 0{\cdot}058.$

According to Sieverts and Hagenacker,¶ the solubility of oxygen in solid silver at the freezing-point and 1 atmosphere is approximately 0·5, and it is probable that under the experimental conditions v was initially approximately 20.

Hence $$\frac{k_s}{v} = \frac{0{\cdot}5}{20\sqrt{15}} = 0{\cdot}0065.$$

The very considerable discrepancy between the calculated and determined values indicates that a large proportion of the total oxygen escapes from the metal before the temperature of the second arrest is reached.

The relationship between the arrest times and the square root of the pressure cannot be represented both by the formula $\frac{1 - 0{\cdot}058\, P^{\frac{1}{2}}}{tP^{\frac{1}{2}}} = 0{\cdot}0015$

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* Roozeboom, "Die Heterogenen Gleichgewichte," 1904, Vol. 2, p. 355.

† J. H. Simons, *J. Physical Chem.*, 1932, 36, 652–657.

‡ "The Solubility of Gases in Metals." *Amer. Inst. Min. Met. Eng. Preprint*, 1932, Feb., 1–16.

§ King's College, Cambridge.

‖ Downing College, Cambridge (Member). ¶ *Loc. cit.*

and by a straight line (lower curve, Fig. 7, p. 329). It appears that a curve which is concave upwards would represent the experimental results more correctly.

Mr. Allen's work is very important, and I hope that he will be able to carry it still further.

The Author (*in reply*): I very much appreciate the attention which the correspondents have given to this paper. Replying to Mr. Rees, I do not think the production of sound ingots by applied pressure can be explained as a degasification effect, since the experimental conditions were fundamentally different from those obtaining in degasification. If a system consisting of V c.c. of liquid metal phase and V' c.c. of gas phase contain v c.c. of a gas soluble in the metal, the gas is distributed between the phases in such a way that

$$V'p + Vk\sqrt[n]{p} = v$$

k, n, and p having their usual meanings. A degasification process consists of progressively increasing V', with the result that $Vk\sqrt[n]{p}$ (the gas content of the metal) falls. In my experiment an inert gas was forced into the system, but V and V' remained unchanged, so that the distribution of the solute gas between the phases was unaltered. No degasification was to be expected, and the rapidity of the effect does not enter into the question. A degasification effect, although it would explain the decrease of the *intensity* of the second point, would not account for the very marked fall of *temperature* which was observed. The question as to whether a second arrest point is found on the cooling curve of silver melted in oxygen is considered theoretically and experimentally on pp. 324 and 332. No second arrest was to be expected, and none was found. A solution of silver oxide in molten silver, if it solidifies under conditions of complete equilibrium and at constant pressure, freezes at a constant temperature, but the composition alters. If it freezes in such a way that the composition remains unchanged, it does so over a temperature range, but the pressure must be progressively raised in order to prevent loss of oxygen.

I am acquainted with and have much admired the stimulating paper by Messrs. Dean and Gottschalk on " The Solubility of Gases in Metals." They have done a service in again calling attention to the discrepancies between the results of various workers in this field, and their suggestions to account for the variations are so fascinating that one awaits with interest their experimental confirmation of the assumptions they have made. Nevertheless, in view of the known difficulty of experiment on gases in metals, the possibility of experimental error as an explanation should not be overlooked, and it would be rash to discard fundamental conceptions which have served well in many fields, before the fact of their inapplicability is established.

The difficulty concerning the state of combination of oxygen dissolved in silver arises out of a misunderstanding of my position, due, no doubt, to the paper having been somewhat severely compressed. It is not assumed that gases are present in metals in the atomic state (although, as has been said, this is a usual interpretation of the square root law), but only that the observed solubility of the gas obeys the law expressed in equation 1. Assumptions as to the state of combination of the gas are not required except to arrive at probable values of the coefficient " *n*," where this is not known. In the case of silver and oxygen, n is known to be 2, and no assumption is necessary. The equation would be equally true were the gas in the combined form, and, indeed, is used later in the paper for the case of cuprous oxide dissolved in copper.

I have been particularly careful to come to no conclusions as to the state of the oxygen in the melt, since, as has been pointed out by Donnan and Shaw, measurements of this kind will not distinguish between Ag_2O and atomic oxygen. Even the production of the silver–silver oxide eutectic does not prove that the oxygen is present in the melt as silver oxide, but only that a melt can be produced which on solidification decomposes into silver oxide and silver.

The probable state of affairs present both in silver and copper melts is illustrated in Fig. B.

If k = solubility constant of oxygen
K = equilibrium constant of reaction $2X + O \longrightarrow X_2O$
Regarding $[X]$ in metal phase as unity, we have

$$[O] = k\sqrt{p_0}$$
$$[X_2O] = K[O] = kK\sqrt{p_0}$$
$$\text{Total dissolved oxygen} = [O] + [X_2O]$$
$$= (k + kK)\sqrt{p_0}.$$

The square-root law is still obeyed, independently of the value of K. The "difference of degree" between silver and copper is probably that in copper melts K is so large that $[O]$ is negligible, whereas in silver melts $[O]$ has an appreciable value. According to Ellis, oxidized copper gives off oxygen gas if melted under sufficiently low pressures, as would be expected.

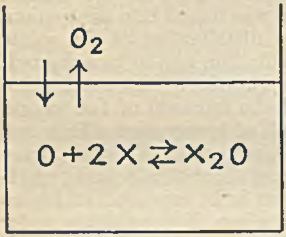

Fig. B.

Looked at from this point of view, the presence of a dissolved oxide appears no longer "incompatible with the presence of atomic oxygen in the melt," but the solution of atomic oxygen in the melt becomes the necessary accompaniment, rather than the antipode, of the formation of a compound. Moreover the viewpoint accounts admirably for the fact that the silver solutions behave in some ways as if they contained a dissolved gas, and in others as if a dissolved oxide were present. Traditional ideas seem to be peculiarly successful in explaining the characteristics of this interesting system.

I thank Dr. Stockdale for his encouraging remarks, but do not see my way to adopt his definition of the internal gas pressure, since the first part of his definition does not cover the case of reacting gases simultaneously present in the melt, and the second part tends to suggest that the presence of a gas mixture under pressure is *necessary* to prevent the formation of gas bubbles within the solvent, whereas a hydrostatic pressure produced by mechanical compression of the liquid would be equally satisfactory. I prefer my definition in the form given on p. 335.

The discrepancy between the experimental and calculated values of $\frac{k_s}{v}$ is important, and has two possible explanations. One is that given by Dr. Stockdale, the other is that the solidified silver retains more oxygen that it should under equilibrium conditions. I incline to the latter, for the reason that the experiments on the effect of rate of cooling showed that the intensity of the second arrest increases with decreasing rate of cooling, whereas, if the discrepancy had been due to the escape of oxygen before the second arrest, the reverse would have been anticipated. Moreover, if a large proportion of the total oxygen escaped from the melt above the temperature of the second point, there would be no reason to suppose that the theoretically anticipated law (which is derived on the assumption that the total quantity of gas in the metal remains constant) would be obeyed at all. We appear to have something akin to the "forced solid solution" of carbon in α-iron which is produced when a steel is quenched.

LIQUATION OR "INVERSE SEGREGATION" IN THE SILVER-COPPER ALLOYS.*

By J. H. WATSON,† M.C., B.Sc., A.R.S.M., MEMBER.

SYNOPSIS.

1. The behaviour of silver-copper alloys in regard to the segregation of their constituents during solidification, which is usually referred to as "liquation" or "inverse segregation," has been further investigated.

2. It has been established that the first formed primaries, whether of silver or of copper, are free to move under the influence of gravity, when the alloy is maintained for sufficient time at temperatures between the "liquidus" and the "solidus."

3. It has also been established that the primaries which have segregated under the influence of gravity are repelled from their position by the application of severe local chilling to their vicinity.

4. All the effects of "liquation" and "inverse segregation" observed in these alloys in ordinary practice can be explained by the formation of primaries at the chilling surfaces of moulds and between the temperatures corresponding with the "liquidus" and the "solidus," followed by their immediate migration towards the hotter portions of the mass.

INTRODUCTION.

THE behaviour of certain alloys in regard to the segregation of their constituents during solidification has been recognized from at least as early as the seventeenth century. With greater experience and more accurate methods of analysis, the problem has of recent years received considerable attention, and many hypotheses have been put forward to account for this behaviour. Most of these hypotheses have been set out and discussed by S. W. Smith ‡ and have been further reviewed by R. Genders,§ so that recapitulation here is unnecessary. None has, however, been generally accepted as wholly explaining the mechanism and cause of the phenomenon.

As early recognized by Roberts-Austen, there is considerable difficulty in invoking the aid of the equilibrium diagram to provide an explanation of the mechanism of liquation, which is always associated with two conditions: (1) the existence of a temperature-gradient in

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* Manuscript received April 11, 1932. Presented at the Annual Autumn Meeting, London, September 13, 1932.

† Assayer, Royal Mint, London.

‡ *Trans. Inst. Min. Met.*, 1926, 35, 248 *et seq.*

§ *J. Inst. Metals*, 1927, 37, 241.

the solidifying mass of metal, and (2) a temperature range, or " solidification interval," between the beginning and the end of solidification. It is generally agreed that under the influence of a temperature-gradient, such as occurs in casting an alloy in a chill mould, the composition of the resulting mass may no longer be uniform, but varies from the chilled surface to the interior in such a way that those portions which solidify first—that is, the outer portions—have the composition of an alloy with a lower freezing point than that of the inner portions which have solidified last.

All observations hitherto made with regard to " liquation " make it appear that this takes place laterally or normally to the chilling surface, and independently of gravity, which is, of course, the determining factor in the separation of *immiscible* molten material, such as the products of smelting operations—metal, speiss, matte, and slag.

Evidence was provided, however, by experiments carried out by Dr. S. W. Smith and by the author, under the direction of Sir Thomas Rose, that, although gravity effects are not usually observed in normal chill-castings, they are capable of exerting considerable influence on the distribution of the constituents in a slowly-cooled casting.

PROBLEM STUDIED.

It appeared from these experiments that it should be possible to explain liquation in alloys if it could be shown that the first formed primaries were free to move in the molten matrix, either under the influence of gravity, or as a result of repulsion from a chilling surface. The problem particularly studied in this paper is the explanation of the effect of chilling on the liquation of the constituents of silver–copper alloys.

In this connection, it is necessary to distinguish three types of silver–copper alloys : (1) hyper-eutectic alloys (containing more than 71·8 per cent. silver), in which enrichment of silver is towards the centre or last portions to solidify, (2) eutectic alloy (71·8 per cent. silver), which is uniform in this respect under ordinary casting conditions, and (3) hypo-eutectic alloys (containing less than 71·8 per cent. silver), in which enrichment of silver is towards the outside or first portion to solidify. The extent to which this segregation takes place is illustrated by the curves given in the Annual Report of the Royal Mint for 1930.

Attention has been directed, in the first place, to determining whether, under favourable conditions, the first formed primaries of copper in a hypo-eutectic alloy of silver and copper are free to move under the influence of gravity and apart altogether from any effect brought about by a chilling surface or a temperature gradient. These conditions are provided by the interval of temperature between the "liquidus" and the "solidus," and the alloys were therefore held or "soaked" at a convenient temperature between these two points for a period of time sufficient for them to attain a measure of equilibrium. By this means it has been found possible to accentuate the manifestation of liquation to such an extent as to render it possible to differentiate between the factors which promote the phenomenon.

A further advantage in this accentuation lay in the removal of the difficulty of demonstrating any change in the microstructure corresponding with marked differences in composition. The method here adopted introduced differences of composition of such magnitude that corresponding differences in the structure were often readily visible under the microscope, and sometimes even to the naked eye.

EXPERIMENTAL PROCEDURE.

The experimental procedure in general was as follows :—

The required amounts of electrolytic copper and fine silver were melted in a gas furnace, well stirred, and poured into a pre-heated cylindrical Salamander crucible and covered with charcoal, thus giving a cylinder of metal 7–8 cm. high × 3 cm. diameter. The crucible was placed in a platinum-wound electric furnace, the heating chamber of which consisted of a vertical silica tube closed at the top end by a refractory cover and at the bottom by a long plug of fire-brick, extending below the furnace. The crucible containing the molten metal rested on this plug, which could be withdrawn when it was required to lower the crucible for the purpose of chilling the bottom of the melt. The furnace was heated to about 100° C. above the temperature at which the metal was to be held, and the temperature was then slowly lowered to the required point and maintained there for about 5 hrs. This was effected by means of a Cambridge temperature-control relay.

To simulate and accentuate the form of segregation obtained in ordinary casting operations, a method of differentially chilling the partly molten mass was devised. In this partly molten state, the metal contains primaries segregated towards either the top or the bottom by gravity, and it is necessary to avoid disturbing them mechanically, as is done, of course, in pouring. To this end, in the case of the copper-rich alloys, a steel cylinder, providing a loose fit in the crucible, was racked down firmly on to the surface of the metal, after the removal of the charcoal, and was left there until the whole of the metal had solidified in the furnace.

In the case of the hyper-eutectic alloys, the crucible was supported with tongs, the bottom of the furnace removed, and the crucible rapidly lowered into a shallow dish of running water. This method, although effective in demonstrating the result of bottom chilling, was necessarily less drastic than the steel plunger method, owing to the thickness of the crucible through which heat had to be abstracted. Thinner crucibles of alundum were tried, but they introduced the risk of breakage, and also allowed the metal to seep through the walls. Melts which were not to be chilled were allowed to cool in the furnace. When cold, the ingots were removed from the crucible, sawn in half vertically, one half being polished for micro-examination, the other being sectioned horizontally at intervals of 1·5 mm. for assay, use being made of both the sections and of the sawings for this purpose.

HYPO-EUTECTIC ALLOYS.

50 : 50 *Silver–Copper Alloy.*

The initial and final freezing points of this alloy are 870° C. and 778° C. respectively, providing a working range of about 90° C.

A short cylindrical melt, 4·5 cm. in height, was held at 810° C., *i.e.* 60° C. below the liquidus and 30° C. above the solidus for 4 hrs. The extreme top then assayed 38·8 per cent. silver and the extreme bottom 57·3 per cent., an enrichment of copper at the top, as opposed to the bottom, of 18·5 per cent. due to gravity alone. The microstructure is distinctive, as shown by the photomicrographs (Figs. 1 and 2, Plate LIII). The top section consisted of large, rounded copper primaries in a matrix of eutectic, the maximum size of these primaries being about 0·15 mm. The bottom section consists of long, straight dendrites surrounded by eutectic. These structures are in accord with what would be expected from the composition. The above experiments were repeated with varying conditions as to the time and temperature of " soaking," and substantially the same results were obtained. The results of a typical experiment are shown graphically in Fig. 8.

It is thus seen from these experiments that in these alloys, having initial and final freezing points separated by a range of temperature, the copper primaries, being lighter than the molten matrix, will tend to segregate at the top of the mass, when it is held at a uniform temperature within this range.

Chilling.

A cylinder of metal 8 cm. in length was held at 810° C. for 3½ hrs. and then top-chilled as described above. The polished surface of the vertical section showed, to the naked eye, a boundary line extending from one corner at the top to a point on the opposite side about 0·5 cm. down as shown in Fig. 8*a*, and another similar but horizontal boundary about 2·5 cm. from the bottom. Above the upper boundary was a region of very small primaries which assayed 51 per cent. silver. Between the two boundaries was a region of large primaries, interspersed with some smaller ones in a matrix of eutectic. This area assayed 49 per cent. Below the lower boundary was a region of long, dendritic primaries, similar to those occurring near the bottom of the " soaked "

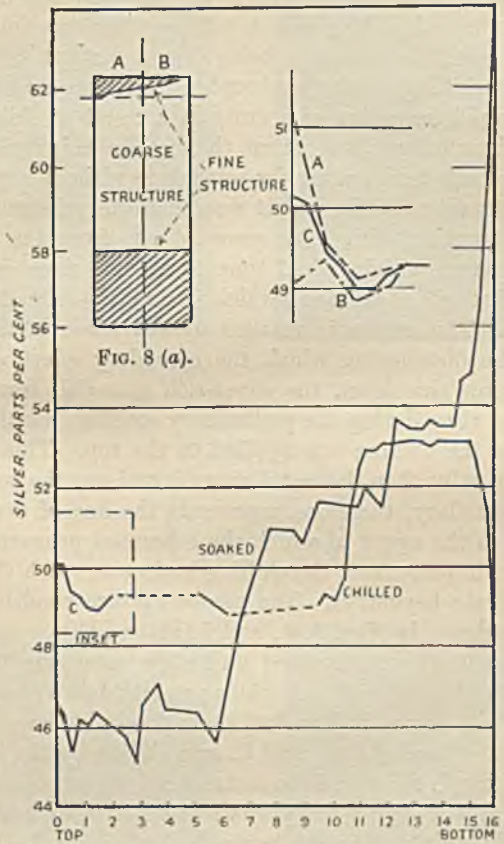

FIG. 8.—50% silver–copper alloy, melted and " soaked " for 8¼ hrs. at 900°–785° C. Same alloy, " soaked " for 3½ hrs. at 810° C. and top-chilled.

FIG. 8*a*.—Structure as visible to the naked eye. × ½.

(A) Silver content of horizontal strips immediately below A (Fig. 8*a*).
(B) Silver content of horizontal strips immediately below B (Fig. 8*a*).
(C) Mean composition. (Cf. complete curve.)

specimen. This area assayed 53 per cent., the vertical distribution of silver throughout the specimen being shown graphically in Fig. 8. Thus the evidence of the effect of chilling in reversing the effect due to gravity separation was most marked. The top had been enriched in silver from less than 40 per cent. (cf. previous experiment) to more than 50 per cent., the primaries being driven down to below the limit of the effect of chilling which was abrupt. This abruptness was probably due to the rapid formation of a crust as a result of chilling. Below this limit, a heat balance was set up, the metal of this region remaining above the eutectic temperature for some time without any appreciable temperature gradient. The result was that the primaries already in this region, together with those crowded out from the extreme top area by the severe chilling, had time to become more or less evenly distributed throughout this area, which gradually solidified at a uniform temperature. This region is marked by the lower boundary, which represents the distance to which the secondary effect of chilling is exerted. Below this level, the silver-rich material, from which the primaries had risen during the preliminary soaking, remained much as it was before the chilling was applied to the top. This metal has a lower melting point than the metal above it and was the last to solidify. The lower boundary, therefore, represents the line of demarcation of two liquids, in the upper of which the separated primaries have only just sufficient impulse from the chilling surface to reach this level, but not to penetrate beyond it. The microstructure resulting from this treatment is shown in Figs. 5, 6, and 7 (Plate LIV).

This experiment was repeated under the same conditions with a shorter length of specimen, with similar results, but a specimen chilled from 920° C. (*i.e.* above the liquidus) showed very little segregation.

A specimen " soaked " at 835° C. and chilled by the immersion of a steel rod through the top of the metal showed that, as a result of this form of chilling, the copper-rich primaries tend to move both downwards and outwards, this movement being discernible by both assay and micro-examination.

The above experiments show that the effects of " liquation " and " inverse segregation," observed in ordinary casting practice of copper-rich silver alloys, can be explained by the formation of copper primaries at the chilling surfaces of the moulds at temperatures between the initial and final freezing points of the alloys, followed by their immediate migration towards the hotter portions of the mass.

This effect of the chilling surface of the moulds is strong enough to be manifested in ordinary castings, in spite of the rapid solidification, which is sufficient to inhibit any appreciable gravity separation.

PLATE LIII.

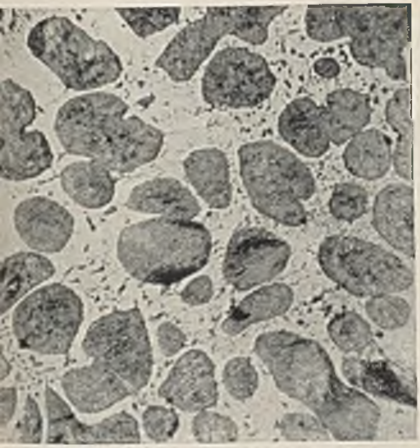

Fig. 1.—50% Ag–Cu. "Soaked" at 810° C. Near top. Silver: 39·0%. × 80.

Fig. 2.—50% Ag–Cu. As Fig. 1. Near bottom. Silver: 57·0%. × 80.

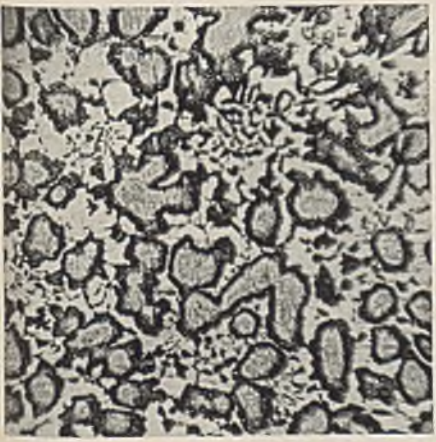

Fig. 3.—50% quaternary alloy. "Soaked" at 905° C. Near top. Silver: 48·0%. × 80.

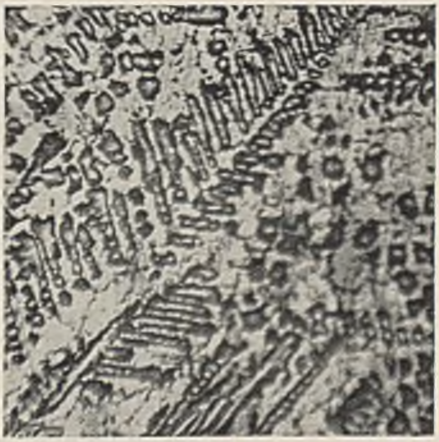

Fig. 4.—50% quaternary alloy. As Fig. 3. Near bottom. Silver: 53·5%. × 80.

PLATE LIV.

FIG. 5.—50% Ag–Cu. "Soaked" and chilled. Upper boundary. Silver: 51·2/49·0%. × 40.

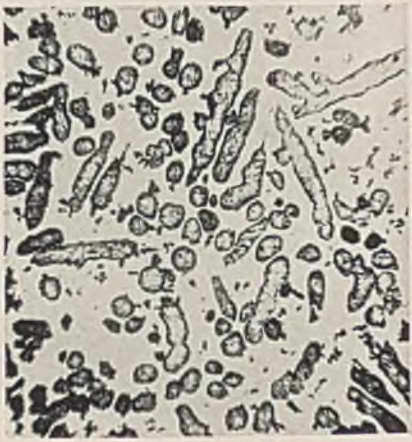

FIG. 6.—50% Ag–Cu. As Fig. 5. Centr portion. Silver: 49·0%. × 40.

FIG. 7.—50% Ag–Cu. As Fig. 5. Near bottom. Silver: 54·0%. × 40.

25 : 75 *Silver–Copper Alloy.*

In still lower grade silver–copper alloys, it might be expected that the copper primaries would suffer from the disability of being so congested that movement was restricted, although it has been known for many years that these alloys exhibit very marked liquation when cast in chill moulds. This was found to be the case, in that there was an enrichment of copper at the top, but only to the extent of 2·82 per cent. The metal, top-chilled by the steel plunger, showed, on the other hand, an enrichment of *silver* at the top of 7·63 per cent., a " turnover " of 10·45 per cent.

The microstructure in each case was similar to that of the corresponding specimen of 50 per cent. alloy, except that the primaries were distinctly coarser and there was little interstitial eutectic.

60 : 40 *Silver–Copper Alloy.*

Experiments with this alloy confirmed previous results. The maximum enrichment of copper at the top of the " soaked " specimen was 18·32 per cent. and in the case of the "soaked " and chilled specimen 6·65 per cent., a reduction of 11·67 per cent. compared with 14·5 per cent. or more in the case of the 50 per cent. alloy. The microstructure was somewhat similar, but no distinct boundaries were observed.

QUATERNARY ALLOYS.

50 : 40 : 5 : 5 *Silver–Copper–Nickel–Zinc Alloy.*

The alloy now used for the Imperial coinage consists of silver 50, copper 40, nickel 5, and zinc 5 per cent., and, in view of its complexity, no prognostication as to its behaviour with regard to gravity separation could be made, although it is known to exhibit a very considerable degree of segregation, which is much greater than that occurring in the binary alloy.

A cylindrical melt, 7 cm. high, was cooled slowly to 905° C., this temperature being held for 4 hrs. (The initial and final freezing points of this alloy are 1025° C. and 765° C. respectively.) A vertical half-section was assayed for silver, copper, and nickel (the zinc being determined by difference) and the results are shown graphically in Fig. 9. There was a considerable enrichment of silver towards the bottom and a corresponding enrichment of copper and nickel towards the top, consistent with the floating-up of the first formed copper–nickel primaries. The zinc showed no segregation, which is in accordance with the conclusion reached on other grounds that, after solidification, the zinc is uniformly distributed between the copper–nickel primaries and the silver–copper eutectic.

Figs. 3 and 4 (Plate LIII) show clearly the distinctive structures at the top and the bottom, the upper portion consisting of rounded copper-nickel primaries in a field of eutectic, and the lower portion of elongated dendritic primaries in a much larger eutectic field. The relative sizes of the primaries confirmed previous observations that the " limiting size " of these primaries is much smaller in the case of a quaternary alloy than in that of a simple binary alloy.

25 : 55 : 10 : 10 *Silver–Copper–Nickel–Zinc Alloy.*

In connection with the liquation of the previous alloys, it is interesting to compare the results obtained in the case of a 25 : 55 : 10 : 10 silver-copper-nickel-zinc alloy chill-cast in a cylindrical iron mould, 16·5 cm. high by 3·0 cm. in diameter. The resulting ingot was sampled by turnings corresponding with rings about 1·5 mm. thick at different parts of the cylinder, and these were assayed. The vertical and horizontal distribution of silver in a half-section is shown in Fig. 10. It will be observed that the chilling effect of the mould has caused a very considerable enrichment of silver on the outside of the ingot, the part poorest in silver being in the middle of the top, as far removed as possible from the chilling surfaces. As regards the base metals, it will be seen that the copper and nickel increase in amount towards the centre to about the same relative extent, whilst the distribution of the zinc is approximately uniform. The facts of liquation observed in the case of this alloy are, therefore, entirely in accord with those observed in the case of the richer quaternary alloy, under slightly

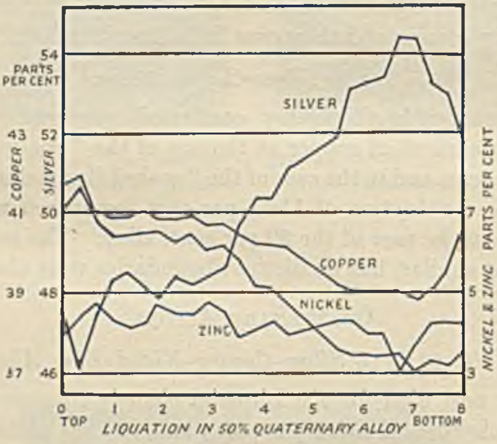

FIG. 9.—Vertical Distribution of Constituents in 50 : 40 : 5 : 5 Ag–Cu–Ni–Zn Alloy " soaked " at 905° C. for 4 hrs.

different conditions of solidification as recorded above. The degree of liquation is, however, greater on account of the increase in the proportion of nickel, which raises the initial freezing point and so widens the solidification interval. This alloy affords an example of the greatest degree of liquation observed in the silver–copper alloys under ordinary casting conditions.

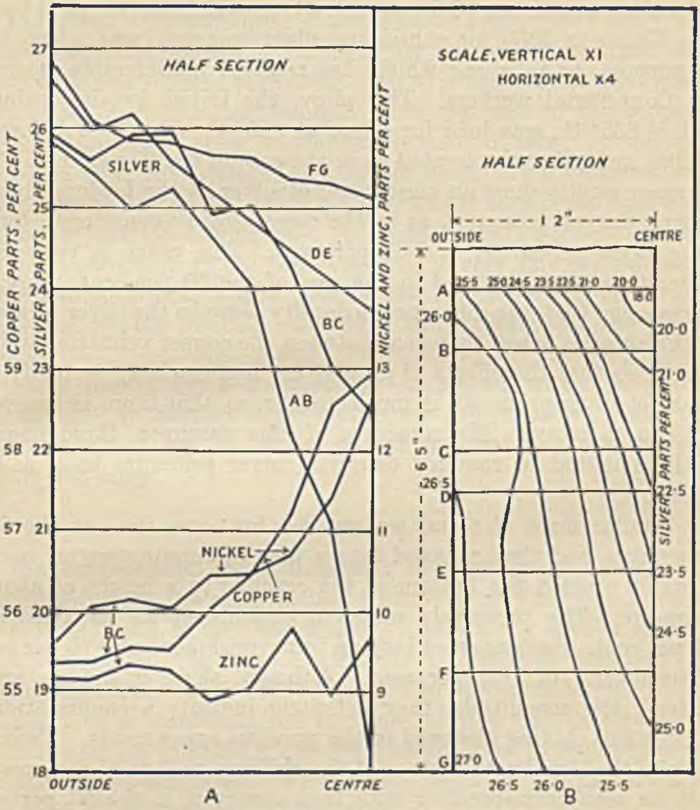

FIG. 10.—Liquation in 25% Quaternary Alloy.

(A) Horizontal distribution of silver in a half-section of a chill-cast cylindrical specimen of 25 : 55 : 10 : 10 Ag–Cu–Ni–Zn alloy at various levels, and of the other constituents at level BC.

(B) Vertical half-section of specimen, showing areas of equal silver content.

HYPER-EUTECTIC ALLOYS.

83·5 : 16·5 *Silver–Copper Alloy.*

It was now necessary to see if the effects of soaking and chilling could be reproduced in hyper-eutectic alloys, but, of course, in the reverse direction. It was to be expected that the primaries, in these cases of silver, being heavier than the surrounding liquid, would sink under the influence of gravity and would migrate upwards under the action of bottom chilling.

An alloy containing 83·5 per cent. silver, which was adopted by the Latin Union in 1865 for subsidiary silver coinages, was selected for this purpose, as it is one which has received considerable attention from Continental workers. This alloy, the initial freezing point of which is 835° C., was held for 4 hrs. at 805° C., *i.e.* 30° C. below the liquidus, and otherwise treated as in the case of the 50 per cent. alloy. The assay results show an enrichment of silver at the bottom, due *not* to rising copper primaries, as in the cases already considered, but to falling silver primaries, of 0·31 per cent. This range is very much smaller than that observed in the case of the 50 per cent. alloy, for two reasons : first, the difference in density between the silver primaries and the eutectic is less than that between the copper primaries and the eutectic, so that the effects of gravity are less marked; secondly, the volume of silver primaries is much greater, so that there is less room for them to move. The structure of this specimen throughout its length consisted of rounded dendritic silver primaries in a field of eutectic.

A similar mass of metal was soaked for some time at the same temperature and then plunged into a dish of running water, so that the water covered the bottom of the crucible to a height of about a centimetre. The previously observed enrichment at the bottom of 0·31 per cent. was converted into an impoverishment of 0·76 per cent., a " turnover " of 1·07 per cent. Although these quantities are of relatively low magnitude, they definitely indicate a confirmation of the effects of chilling observed in the previous experiments. Probably owing to the less drastic nature of the chilling, no line of demarcation could be seen corresponding with that observed in the 50 per cent. alloy. The microstructure was extremely fine and uniform throughout the specimen. Under a high power, this structure was observed to be exactly similar to that seen in the unchilled alloy, but of finer texture. The effects of chilling appear to have been exercised throughout the whole length of the melt.

80 : 20 *Silver–Copper Alloy.*

Similar experiments with this alloy gave results comparable with the above, but rather more accentuated. The enrichment of silver at the bottom of the " soaked " specimen was 1·00 per cent., and the impoverishment at the bottom of the " soaked " and chilled specimen was 1·90 per cent., a " turnover " of 2·90 per cent. The microstructures were similar to those of the specimens of the 83·5 per cent. alloy.

Top-Chilling.

The effect of top-chilling a silver-rich silver–copper alloy should have the effect of increasing the liquation due to gravitational separation. This was found to be the case. An 80 per cent. melt was "soaked" and chilled with the steel plunger, as in the case of the copper-rich alloys. The assays show an impoverishment of silver at the top, as compared with the bottom, of 1·98 per cent. This indicates an impoverishment due solely to chilling, of 0·98 per cent., that due to gravitational separation having been found to be 1·00 per cent. as above. The microstructure at the top consisted of very fine crystallites with definite orientations, whilst that of the lower portion of the ingot, unaffected by the chilling, resembled the structure of the unchilled specimen.

These results again are entirely in accord with the effects of " liquation " in casting silver-rich silver–copper alloys, these effects being explained by the same mechanism that was applied to the copper-rich alloys.

SUMMARY.

The experimental work described above appears to show quite conclusively that the phenomenon which was originally referred to as " liquation," and is now perhaps more commonly spoken of as " inverse segregation," is, in fact, correctly described as liquation in the original and true sense of that term. The procedure adopted has had the effect of accentuating the influence of this gravity separation to an extent far beyond that which could be observed in ordinary practice, and has consequently enabled the movement of the primaries to be confirmed by microscopic examination.

It has also enabled it to be shown that for all the alloys of the silver–copper series, under the influence of a chilling surface, the first formed primaries, whether of silver or copper, move away from the chilling surface, even against the influence of gravity.

Thus in silver–copper alloys having a solidification interval, primaries are capable of migrating upwards or downwards under the influence of gravity, and of being scattered by the influence of a chilling surface, and of undergoing an alteration in shape and size from the same cause.

The failure of the application of the Ludwig–Soret effect to account for segregation in alloys is seen to be due to the very different nature of the phenomenon in which this effect was originally established. In that case, very dilute salt solutions were considered, and the differentiation observed was concerned with the movement of ions. In the case of the segregation in alloys, however, the movements are those of discrete and relatively large particles, to account for which, a physico-chemical mechanism, such as is involved in the Ludwig–Soret effect, is necessarily inadequate.

ACKNOWLEDGMENTS.

The work described above was carried out in the laboratories of the Royal Mint, and the author desires to thank the Deputy-Master for permission to publish this paper. He wishes further to acknowledge his indebtedness to the generous advice given by his colleague, Dr. S. W. Smith, throughout the investigation.

TABLE I.—*Summary of Experiments.*

No.	Silver Content. Parts per cent.	Height of Cylinder cm.	Temperature ° C.	Time, Hours.	Assays (Parts per cent.).		Range (Parts per cent.) (b)–(t).	Remarks (How chilled).
					Top (t).	Bottom (b).		
1	50	4·5	810	4	38·80	57·30	18·50	...
2	50	7·0	810/840	4	40·60	54·80	14·20	quenched
3	50	7·5	890/785	8¼	45·40	63·72	18·32	...
4	50	7·5	820/790 840	4 1½	47·62	54·08	6·46	...
5	50	7·0	835	2¼	Transverse assays			steel rod
6	50	7·0	920	...	49·71*	50·01*	0·30	top
7	50	8·0	810	3½	48·95	53·15	4·20	top
8	50	4·0	810	3¾	47·20	51·83	4·63	top
9	25	7·0	940/800	7½	23·04	25·86	2·82	...
10	25	7·0	940/800	7½	33·00	25·37	−7·63	top
11	60	7·5	795	6	55·55	62·20	6·65	top
12	60	7·5	805	6	47·24	65·56	18·32	...
13	50 (Quaternary)	8·5	905	4	46·10	54·40	8·30	...
14	83·5	6·0	810	4	83·42	83·73	0·31	...
15	83·5	8·5	810	...	84·05	83·29	−0·76	bottom
16	80	8·0	800	4	81·20	79·30	−1·90	bottom
17	80	7·0	800	5¼	78·75	79·75	1·00	...
18	80	7·5	800	5	79·79	81·77	1·98	top

* Mean of eight sections.

DISCUSSION.

Professor T. Turner,* M.Sc., A.R.S.M., F.Inst.Met. (Past-President): The subject of what is called "inverse segregation" is one of considerable importance in connection with the arts, and it is one to which I have given considerable attention. Perhaps some remember that I referred to the subject in my Presidential Address seven years ago.

Work was done in my Department with the object of ascertaining facts in connection with this phenomenon. The difficulty has been to get a proper explanation. We know, of course, that what we call "inverse segregation" occurs when the more infusible material is found collected in the centre of the ingot instead of at the outside. We know that it occurs particularly when we have a considerable interval between the solidus and the liquidus, and when the cooling of the alloy is rapid.

The question naturally arises as to the explanation of what was at first regarded as an extraordinary phenomenon. We now find that it is fairly common, and when it is frequently observed it ceases to become extraordinary. There have been various explanations. The one most commonly adopted is that, during solidification of the mass, a concentrated liquor from the interior is squeezed into interstices between the dendritic crystals on the outside, and that these interstices are due to contraction during solidification.

If a vessel containing water which is hot is allowed to cool, the water towards the outside of the vessel will be colder than that nearer the middle. Any water from the interior mixing with the cold exterior must be cooler than the hot in the middle. It is possible to get past that only on the assumption that during cooling a very rich liquid is produced in the centre—a concentrate. We do not, however, find that such concentration takes place during rapid cooling. If it is desired to get cream from milk the milk is allowed to stand. If a concentration of some particular constituent is required a large body of metal—a big ingot—is cooled slowly and a concentration is then obtained at the centre. Further, there are no voids between the dendrites, when dendrites are formed. These dendrites are surrounded by a liquid, and it has not been proved that there are any voids, so that the explanation starts by assuming that a liquid which does not exist is squeezed into voids which are not there!

Then what is the explanation? I think that Mr. Watson has given us a very great aid in proving that with rapid crystallization the crystals do not form as adherent dendrites, but that they form as very small separate crystals. They may be regarded as something like sand in water. Now, what will happen with sand in water? If a motion is given to the water it will carry the sand with it. If water is allowed to freeze, it will separate the suspended particles, and yield clear ice. I picture, then, that these crystals, which Mr. Watson has shown, are separate, and can be influenced by gravity during the time of their separation. These crystals are pushed forward. There has been the initial natural separation in the first place of the high melting-point material, and these grains, in the form of a powder in the liquid, are pushed forward, by the force of the solidifying material that is behind them, or possibly to some small extent by gravity, although there is not much time for gravity to act; and also partly—and to an amount which at present is quite undetermined—by the fact that a hot body repels solid particles in its vicinity. That is illustrated, for example, in the deposit of dusts by a radiator, on the adjacent walls.

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* Emeritus Professor of Metallurgy, The University, Birmingham.

What the forces are which cause the pushing of these metallic grains towards the centre we are not able to say definitely at present; but the fact that the grains are formed and are able to move; that they do not form parts of a dendrite, all stuck together but that they are able to move and that they are pushed forward towards the centre and thus enrich the centre at the expense of the outside, appears to be a very reasonable explanation. After searching for a long time for a satisfactory explanation, this is the one which to me is most to be commended.

Dr. S. W. Smith,* A.R.S.M. (Member): At this late hour I do not propose to say more than a very few words with regard to this paper, to the conclusions of which I entirely subscribe. The work recorded simplifies, to my mind, a problem which in recent years has given rise to a great deal of hypothetical discussion with very little actual experimental observation to support it. As the author points out, we have long known the main facts regarding the behaviour of the silver–copper alloys in respect to this particular property of unequal distribution of the constituents during solidification. Those who have been concerned with the precise valuation of these alloys and their application in practice have been able, with this knowledge, to make due allowances for these variations, but it has always been a drawback that we have had no actual direct evidence of the mechanism by which this lack of uniformity, or unequal distribution of constituents, occurs. This has been due largely to the fact that differences in composition, which are of extreme practical importance from the point of view of close accounting, are not, as a rule, sufficient to manifest themselves in differences in microstructure. The author, by adopting experimental devices to accentuate the separation of the constituents, has been able to show in polished and etched sections, what actually occurs. The mobility of the first formed primaries and their tendency to move from the cooler to the hotter regions is an observation which should lead to a closer examination of what happens in molten material between the "liquidus" and the "solidus" and to a better understanding of the causes of segregation, not only in the particular cases of the non-ferrous metals, but also in regard to similar occurrences in cast irons and steels and in the wider problem of the variations of mineral concentrations in rock masses.

Mr. E. A. Smith,† A.R.S.M. (Member): I endorse what Professor Turner has said, and am inclined to accept the author's explanation of the phenomenon, known originally as "liquation."

All those engaged in the commercial production of silver alloys have for some time been seeking some more satisfactory explanation of liquation than those hitherto put forward. I should, therefore, like to congratulate Mr. Watson on a very useful piece of work, which has been made possible only by the application of the latest methods of research, thus enabling him to examine much more closely the distribution of the constituents during the solidification temperature range between the liquidus and solidus. In this connection I note that Mr. Watson gives for the 50 : 50 silver–copper alloy a temperature range of 90° C., whilst previous work by Ueno gives a difference of only 75°. Perhaps Mr. Watson has some explanation for this difference? Mr. Watson's data have emphasized the very important part played by the melting and casting conditions in controlling liquation. It has long been recognized in industrial practice that liquation cannot be entirely prevented, and casting conditions have always been regarded as of fundamental im-

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* Royal Mint, London.

† Research Metallurgist, Oakes, Turner and Co., Ltd., Sheffield.

portance, in order that liquation might be kept at the minimum and sterling silver produced that would satisfactorily pass the official test at the Government Assay Offices. Where proper precautions are taken, the difference in silver content in different parts of commercial silver ingots is not great.

It is gratifying to know that this research has been carried out at the Royal Mint, which may be regarded as the birthplace of research on liquation, since the pioneer work of Roberts-Austen, T. K. Rose, S. W. Smith, and others was done there.

Mr. R. GENDERS,* M.B.E., M.Met. (Member): While admiring the careful and interesting experimental work described in the paper, the results of which should be valuable in any consideration of this important problem, I disagree with the author in certain of his conclusions. Gravity liquation effects may occur in very slowly cooled masses of the alloys described, but are unlikely to exert any appreciable influence in rapidly solidified ingots, and deductions from the results of locally chilling a suspension of dendrites are not necessarily applicable to the conditions in a mould where the alloy is initially wholly fluid. From this point of view it would have been useful had the author included the results of chilling experiments on unsoaked melts, at temperatures above the liquidus. The fact that some degree of reversal of liquation can be produced by local chilling, and the evidence of movement of the suspended primaries require explanation, however, and that put forward in the paper suggests that the primaries are repulsed and scattered, even against the influence of gravity, by contact with the cold surface. Such a repulsion effect not only requires a force which so far has not been discovered, but is also in direct opposition to the observed fact that in the solidification of an ingot the primaries are actually formed in contact with the chilling surface. One is, therefore, led to look for other explanations of the experimental results described, and I would suggest that the setting up of convection currents by the chill surface and slight mechanical disturbances during manipulation would be capable of producing the effects observed. The present data are of considerable interest, but do not, in my view, justify any new hypothesis.

Mr. WATSON (*in reply*): I must confess to being extremely gratified to have corroboration from such eminent authorities as Professor Turner, Dr. S. W. Smith, and Mr. E. A. Smith. I was very glad to hear Professor Turner's use of the word "repulsion." I used the word "repelled" in the paper with some misgiving, as I realized that it connoted a certain amount of force, and I was not prepared, and still am not prepared, to say exactly what that force is. Perhaps I ought to have said that the primaries "moved away from the cold surface"; that is rather long-winded, so I boldly said "repelled," and Professor Turner has also used that expression.

I shall have to look up the figures with regard to the 90° C. solidification interval, but I think that although 15° is a considerable amount, it does not affect the conclusions, because the metal was held at various temperatures between the liquidus and solidus without any great differences in the results.

I am surprised that Mr. Genders considers my theory more extraordinary than any others which have been put forward. Mr. Genders suggests that if the primaries are repelled by the cold surface they are repelled by a force—which is quite true, and there are many possibilities as to what this force might be, which I will not go into now. He has also questioned the fact that the primaries do actually move away from the chilling surface, and that this might occur owing to disturbances in the experiment, or to convection currents.

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* Research Department, Woolwich.

If that is so, it is rather remarkable that the disturbances should always be near to and away from the chilling surface. Whether the chilling surface is applied as solid metal to the top, or whether it is effected by lowering the crucible in the water, if the movements were due to convection currents or to mechanical disturbances, they would be more generalized and less differential than they appear to be from the results given in the paper.

[*Note*:—The 90° C. solidification interval queried by Mr. E. A. Smith is taken from Heycock and Neville, *Phil. Trans. Roy. Soc.*, 1897, [A], **189**, 35. The eutectic temperature is here given as 778·65° C. and the melting point of the 50 : 50 alloy by interpolation is 870·7° C., a difference of 92·05° C.]

SOME ATTEMPTS AT MAKING BERYLLIUM–MAGNESIUM ALLOYS.*

By RONALD J. M. PAYNE,† B.Sc., MEMBER, and
JOHN L. HAUGHTON,‡ D.Sc., MEMBER OF COUNCIL.

SYNOPSIS.

A description is given of various methods which were tried for the production of beryllium–magnesium alloys, all of which were unsuccessful.

OWING to the low densities of magnesium and beryllium, and to the remarkable results obtained by the addition of the latter element to copper, various workers have tried to produce alloys of beryllium and magnesium, but so far as the authors have been able to find, without success.

The high melting point of beryllium and the low boiling point of magnesium preclude the melting together of the metals, at any rate under normal pressures, and no action appears to take place between solid beryllium and molten magnesium. Thus, Knoll and Jess § found that lumps of beryllium were entirely unattacked after prolonged heating in boiling magnesium. This was confirmed by the authors.

It was thought possible that if molten beryllium were poured into molten magnesium, the intimate contact of the two metals obtained might result in the formation of an alloy on subsequent annealing of the mixture. Some beryllium was therefore melted (*in vacuo*) in a high-frequency furnace and poured into a pot of molten magnesium; the mixture was well stirred and quickly cast into a steel mould. A portion of the material thus obtained was prepared for microscopic examination, which revealed the beryllium, in the form of small lumps possessing clear-cut edges, irregularly distributed throughout the magnesium. A piece of the casting was then annealed at a temperature of 600° C. for a period of 7 days, and although there were some slight indications of attack at the boundaries of the included beryllium, the

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§ *Wiss. Veröff. Siemens-Konzern*, 1931, 10, (2), 29–32.

mixture was in sensibly the same condition as that which obtained before annealing. Filings secured from the annealed material were given a further short heat-treatment to remove the effects of cold-work and subjected to X-ray examination. From lattice measurements it was concluded that no beryllium was dissolved in the magnesium.

It was considered that the mutual grinding of the surfaces of adjacent pieces of metal, when a mixture of beryllium and magnesium was briquetted in a press in a hydrogen atmosphere, might have the effect of abrading any existing oxide film. This treatment, however, yielded only lumps of beryllium set in magnesium—apparently no diffusion takes place even after prolonged annealing.

The scheme of electrolytically depositing beryllium on to a cathode of molten magnesium was suggested to the authors by Dr. W. Rosenhain, it being hoped that the nascent beryllium might attack the latter metal. It was intended that the magnesium should float on the stock bath of fluorides and oxides used for the preparation of beryllium, and that the latter metal should be deposited on the under surface of the magnesium. The act of adding magnesium to the molten bath, however, caused the bath itself quickly to become pasty and ultimately quite hard. An American publication, "Chemistry of Beryllium," came to hand at this juncture, in which it was stated that magnesium possessed the power of reducing beryllium fluoride, and that in the presence of excess magnesium an alloy would be obtained. The scheme was put forward as a method of preparing beryllium and was protected by patent rights. To test the claim some of the feed material used for the beryllium deposition bath, and consisting of a mixture of sodium and beryllium fluorides, was crushed and added to a crucible of molten magnesium. A slight exothermic reaction appeared to take place, the added material glowing visibly, and a hard infusible residue was left together with the metal in the crucible. The metal so obtained was cast and examined microscopically. Very small black specks were seen on a background of magnesium, but a chemical analysis showed the presence of no more than 0·07 per cent. beryllium, an amount which might readily be present in the form of included fluoride. In another similar experiment a beryllium content of 0·14 per cent. was found. In yet another attempt, this time using pure beryllium fluoride, 0·05 per cent. beryllium was found on analysis.

SUMMARY.

It will be seen that all attempts to introduce beryllium into magnesium have proved abortive. It is just possible, however, that the problem might be solved by the simultaneous electro-deposition of magnesium and beryllium on to the same cathode.

RESEARCHES ON BERYLLIUM.*

By H. A. SLOMAN,† M.A., MEMBER.

SYNOPSIS.

Details of the research on the preparation of pure beryllium at the National Physical Laboratory are described. It is shown that with the progressive elimination of metallic impurities the brittle nature of the early metal was not greatly altered. This brittleness was subsequently found to be due to a beryllium/beryllium oxide eutectic surrounding the metal grains.

Most of the work has been directed towards the elimination of this oxide. Of all the methods attempted and described here, sublimation *in vacuo* has been the most effective. Even by this method it has not been possible to obtain sufficient metal for determination of its mechanical properties in the pure form. Comparatively thin films of the metal of more than 99·9 per cent. purity have, however, been produced. From their properties it is suggested that pure beryllium is likely to be similar in mechanical properties to, for instance, iron—ductile, strong and of medium hardness (Brinell hardness about 55–60).

During the course of the work a successful method of plating beryllium on other metals from fused electrolytes at temperatures of 600° C. and upwards was found.

Certain evidence that beryllium undergoes a transformation at room temperatures has been obtained. Whether this change is associated with the residual impurities or with an allotropic transformation is not yet determined.

INTRODUCTION.

THE objects of the work on beryllium which has been in progress, in the Metallurgy Department of the National Physical Laboratory, for the Minor Metals Committee of the Metallurgy Research Board, Department of Scientific and Industrial Research, may be broadly divided into two sections. Firstly, the preparation of the metal in a pure, compact form, and secondly, an investigation of the constitution and properties of beryllium alloys. The present paper deals only with the former object, but it is hoped in the near future to describe the properties of some of the alloys.

The research on beryllium was commenced in 1923, partly at the suggestion of the then Superintendent, Dr. W. Rosenhain, F.R.S., whose attention had been called to the possibilities which might reside in some

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* Manuscript received, April 30, 1932. Presented at the Annual Autumn Meeting, London, September 13, 1932.

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of the lesser known metals by his participation in the work of the Minor Metals Committee of the Imperial Mineral Resources Bureau (now the Minor Metals Committee of the Imperial Institute). At the request of that Committee, the Department of Scientific and Industrial Research set up a "Minor Metals Research Committee," under which Dr. Rosenhain and his collaborator, then Dr. A. C. Vivian, commenced the study of beryllium. This metal was chosen for investigation because what was known about it suggested that it might have important possibilities in combining strength and lightness, and the problem before the investigators in the first instance was that of producing beryllium metal. Up to a certain point that problem was quickly solved by the work of Dr. Vivian, who by 1926 had succeeded in producing solid electro-deposits by the fusion electrolysis of an electrolyte consisting mainly of beryllium and sodium fluorides. The degree of purity achieved, as described in Dr. Vivian's paper,[1] was approximately 99·5 per cent. From the present point of view the most important fact is that metal of this degree of purity was entirely non-ductile, and it was realized that the production of beryllium of high purity presented problems of an entirely different order from those which had been overcome in the preparation of the metal having the degree of purity indicated above. Dr. Rosenhain, however, strongly maintained that if the metal could be prepared in a sufficiently high state of purity it should possess valuable properties differing materially from those of the impure substance. The fact that the metal possesses a close-packed hexagonal crystal lattice suggests that it should be reasonably ductile, and that the hardness and brittleness observed in the samples so far prepared must be due to impurities. The researches described below were therefore undertaken in order to determine whether beryllium of high purity could be produced by any available method and whether, if produced, it would possess the properties anticipated.

The experimental difficulties which have had to be overcome in the effort to produce the pure metal have proved exceedingly formidable, and as will be seen below it has not yet been possible to produce beryllium of really high purity in sufficient quantities to determine these properties fully, and still less to render feasible the production of ductile beryllium even on the smallest industrial scale. It is claimed, however, that the ductility of the metal has been established and that the impurities which rob the commercial product of this valuable property have been identified and their origin ascertained. It is hoped, therefore, that while, from the fundamental point of view, the present research confirms the anticipation with which it was begun, it may also serve as a step towards the ultimate solution of the problem of the industrial production of high-purity, ductile beryllium.

The present investigation commenced with the publication at the end of 1926 of the paper referred to above, in which was described the method evolved at the National Physical Laboratory for the electrolytic production of beryllium, but before proceeding to an account of the work which has followed, it may perhaps lead to a better understanding of the problems which had still to be faced, if a brief summary of the position at that time is included here.

The paper[2] described the method in detail and pointed out that the metal produced was contaminated by small amounts of iron, carbon, silicon, aluminium, and nitrogen, present in decreasing quantities in the order named, giving a beryllium content of more than 99 per cent. It was not found possible to determine the oxygen. It may be noted that the carbon was present as beryllium carbide and the nitrogen as beryllium nitride.

A study of the source of the above elements was then made. It was found that the Acheson graphite was responsible for the carbon and part of the iron and silicon, whilst the beryllium carbonate or oxide purchased from various sources, and used as the starting point in the preparation of beryllium fluoride, was responsible for the aluminium and the remainder of the iron and silicon. The nitrogen was, of course, derived from the atmosphere.

The method of purifying the graphite from iron and silicon was described, and it was further shown that on remelting the metal, most of the beryllium carbide segregated, by reason of its greater density, to the bottom of the ingot, and could thus be removed by sawing off that portion. A typical analysis of metal so produced was :—

	Per Cent.
Beryllium	99·5–99·6
Iron	0·1–0·2
Carbon	0·05–0·1
Silicon	0·01–0·05
Aluminium	0·01
Nitrogen	0·005
Oxygen	not determined.

The mechanical properties were very disappointing. The metal was brittle, fractured very readily, could not be worked, and had a Brinell hardness of about 140–160. The melting point was given as about 1280° C.

It is now proposed to consider in detail the subsequent attempts which have been made to prepare pure beryllium.

The first step was a complete study of the technique of the actual electrolysis, chiefly with the object of increasing the length of time during which deposition was continuously possible. In the earlier work, the limit was about 7–8 hrs., after which the bath became increasingly high in resistance, whilst disintegration of the auxiliary graphite anode plates occurred. The latter trouble was caused by the burning of the graphite above the level of the melt in that region where the temperature was about 800°–1000° C. The method of protection described in the earlier publication was to evacuate the air from the pores of the graphite under concentrated sodium chloride solution, and allow them to become filled with the salt. After careful drying, a surface glaze was produced by immersion in fused sodium chloride. Several other methods of protection were tried without much success. The original process was, therefore, readopted with the following modification: instead of filling the pores once or twice only with salt solution, this process was repeated several times, allowing the graphite to dry between each. In this way, the pores became completely, instead of only partly, filled with sodium chloride after the water had evaporated. The glaze was then applied as before. Anodes so treated can be used for 15 or more hours before disintegration becomes serious.

The increase in the resistance of the electrolyte noted above was due to a gradual change in composition owing to the removal of beryllium by deposition and to the different rates of volatilization of the fluorides of beryllium, sodium, and barium present in the bath. These losses were not completely compensated by the particular mixture of fluorides added to the bath in the earlier work, but by the use of a more suitable mixture it is now possible to keep the composition and quantity of the bath constant and to operate continuously for many hours, the limit being fixed by the life of the graphite anodes, which, as previously stated, has been increased to more than 15 hrs. This has an important bearing on the commercial production of the metal, where continuous electrolysis is of considerable economic importance. If at the end of, say, every 15 hrs., the auxiliary anodes are changed and a new beryllium cathode tip is inserted, there seems no reason why the deposition cannot be carried on continuously for several such periods, the final limit in this case being the life of the graphite containing crucible, which is approximately 80–100 hrs.

Concurrently with this improved technique, increased purity of the cathode metal was attained. In 1929, a British Patent[3] was obtained covering a method for the production of pure beryllium oxide from beryl and other sources. Full details have already been published.[4]

The use for the electrolysis, of beryllium fluoride prepared from oxide produced by this method, together with a much more careful purification of the graphite parts of the electrolytic furnace, immediately lowered the percentages of certain impurities, so that it now became possible con-

PLATE LV.

FIG. 1. × 600.

FIG. 2. × 450.

FIG. 3. × 250.

FIG. 4. × 75.

[*To face p.* 268.

FIG. 5. × 150.

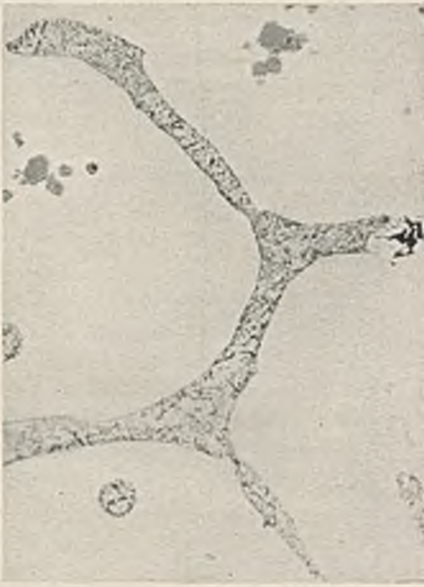

FIG. 6. × 250.

FIG. 7. × 150.

sistently to obtain metal which, after remelting to segregate the major portion of the beryllium carbide, had the following typical analysis :—

	Per Cent.
Beryllium	99·7–99·8
Iron	0·01
Carbon	0·05
Silicon Aluminium	trace
Nitrogen	0·005
Oxygen	not determined

All further attempts to improve the purity beyond this point were unsuccessful, and it became obvious that some subsequent treatment would be necessary to obtain pure metal. Moreover, the properties of these more recent deposits were not very different from those produced much earlier, the chief change being a fall in Brinell hardness from 140–160 to 100–120. This drop in hardness was found to follow the decrease in the iron content (cf. the two analyses given above). The metal was still very brittle, and to obtain it quite pure became of increasing importance, in order to determine whether beryllium itself was essentially a brittle metal or whether this undesirable property was due to one or more of the very small amounts of residual impurities.

A careful microscopic examination of the metal was therefore undertaken to correlate as far as possible the impurities identified under the microscope with those revealed by chemical and spectrographic analyses. It was hoped that if this correlation could be made complete, it would then be possible to ascertain which impurity, if any, was responsible for the brittleness. To avoid confusion, each impurity will be considered separately.

Aluminium.—In the earliest metal, aluminium was determined chemically and found not to exceed 0·01 per cent. Later, as shown in the analysis above, this was reduced to a " trace." The presence of aluminium in these quantities was never demonstrated microscopically, a conclusion which was later confirmed by work on the beryllium-rich aluminium–beryllium alloys, where the solid solubility of aluminium in beryllium was found to be well above the maximum quantity ever found in electrolytic metal. Moreover, slight additions of aluminium up to 0·07 per cent. had no appreciable effect on the general properties of the metal.

Silicon.—The decrease in the silicon content from between 0·01 and 0·05 per cent. to a " trace " closely followed that of aluminium. Among those impurities visible under the microscope was one usually pale blue in colour which occurred as somewhat rounded grains in the crystal boundaries. (Fig. 1, Plate LV.) The fact that the visible amount of this impurity decreased as the purity of the beryllium increased, suggested that it was due to iron, silicon, or nitrogen. It seemed most probable that it was silicon or a beryllium silicide, and accordingly about 1 per cent. of silicon was added to beryllium. The microscope revealed a very much larger quantity of the blue constituent (Fig. 2, Plate LV), whilst the other visible impurities remained unaffected. In the chemical analysis silicon was always found as metal, and not as beryllium silicide. As confirmation seemed desirable, X-ray analysis was employed. Several grammes of beryllium were dissolved in very dilute hydrochloric acid (about 1 in 9) and the insoluble residue was collected, washed, and dried. By sieving through a 200-mesh sieve a small quantity of fine metallic-looking material mixed with a small amount of a brown powder was separated. The latter was very finely divided beryllium carbide (Be_2C). An X-ray photograph of the material gave an excellent spectrum of silicon with fainter lines exactly corresponding with Be_2C.

Attempts were made to determine whether silicon has any solid solubility in beryllium. In the purest metal examined, isolated pale blue grains are visible, which persist even after prolonged heat-treatment near the melting point. It seems probable, therefore, that there is no solid solubility in this case.

Carbon.—Beryllium carbide, Be_2C, formed by the action of the graphite on the metal during electrolysis was the first impurity definitely to be recognized. It occurs in brown or grey, sharply angular crystals or as dendrites (Fig. 3, Plate LV). As already pointed out, remelting allows a segregation of the major portion of the carbide to the bottom of the ingot, and it can thus be removed.

On solution of the metal in very dilute hydrochloric acid, pink crystals are always readily detected in the insoluble residue. These have been separated by hand and analyzed. The composition closely approximates to Be_2C, which was confirmed by X-ray photographs of the same material. During the course of this investigation, a portion of remelted metal with the carbide segregated to one area was obtained and examined (Fig. 4, Plate LV). While with ordinary vertical illumination the colour of the carbide under the microscope was the usual greyish-brown, it was noticed that with a wide angle lens it showed an intense pink coloration. This affords an excellent method of confirming the presence of carbide, which is a very hard, highly crystalline, pink* material similar to carborundum (silicon carbide) in abrasive properties.

Iron.—Under the microscope, traces of a white constituent, usually somewhat in relief, were noticed, and the quantity seemed to vary with the iron content. Like the silicon, it occurred in the crystal boundaries,

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* The pink colour may be due to a trace of iron carbide.

but was never resolved under the highest magnification. It seemed probable, therefore, that it was not a eutectic, but was either iron, or an iron–beryllium compound. A little electrolytic iron was, therefore, added to beryllium. The resulting ingot showed a considerable increase in the quantity of this white constituent (Fig. 5, Plate LVI), which was assumed, therefore, to be associated with the presence of iron. No work on the constitution of the beryllium-rich iron–beryllium alloys has been carried out, with the exception of some heat-treatments of beryllium containing 0·01–0·05 per cent. iron. As a result of this work it was found that the white constituent disappeared on annealing, suggesting a certain, if limited, solid solubility.

Nitrogen.—The presence of nitrogen or beryllium nitride was never observed microscopically. Certain minute specks of a brownish colour have been noted from time to time. These did not show the typical pink coloration mentioned above in connection with the carbide, and it is thought that they were probably due to nitride. In view of the almost negligible quantity (0·005 per cent.) of nitrogen present, it was not considered necessary to investigate the matter further, particularly as it was hoped that nitrogen-free metal would be produced as the result of other work then in progress and to be described later (p. 377, B1).

From the above it will be seen that as far as possible each of the impurities revealed by chemical analysis had been correlated with the microstructure of the metal, and although secondary effects might be expected from their presence, no solution had as yet been obtained to the problems of ascertaining the real cause of brittleness or of identifying one particular impurity always visible under the microscope and not connected with any so far shown by chemical and spectrographic analyses.

This impurity was referred to in the earlier publication, and was there ascribed to iron. This has, however, since been shown to be incorrect. It occurs as a eutectic in the crystal boundaries, and is the one always present in the largest quantity (Fig. 6, Plate LVI). Changes in the purity of the metal seemed to make no difference to this amount. If this impurity could be identified and shown to be of a brittle nature, its presence in varying amounts around each crystal grain would go far towards explaining the brittleness of the metal.

In the course of the investigation of the impurities listed above, some beryllium was, on one occasion, dissolved in very dilute hydrochloric acid (about 1 in 15 to 20). A sponge-like skeleton of greyish material formed which remained insoluble. It was comparatively easy to separate this from the remainder of the residue, which consisted principally of Be_2C. The spongy structure must have been derived from the eutectic impurity, from each cell of which the beryllium had been dissolved. A very careful analysis of this insoluble residue was therefore undertaken. The only elements present were beryllium and oxygen, and the material was definitely identified as a beryllium/beryllium oxide eutectic. Such a metal/metal oxide eutectic is uncommon. This, coupled with the difficulty of directly estimating the oxygen in such a compound as beryllium oxide, may have been the reason why the recognition of this impurity presented difficulties. From its very nature, brittleness would be anticipated from such a eutectic, and it now appeared fairly certain that beryllium itself was not essentially brittle, and that if the oxygen could be eliminated, the resulting metal would be ductile. From the analysis on p. 369, the percentage of oxygen was (by difference) about 0·2 per cent., and if, as seemed probable, all were combined with the beryllium, about 0·3 per cent. beryllium oxide would result, leaving the actual beryllium metal content at 99·7 per cent. The complete analysis is, therefore, as follows:—

		Per Cent.
Beryllium (as metal)		99·6–99·7
Beryllium (as BeO)	0·1	BeO 0·3
Oxygen (as BeO)	0·2	
Iron		0·01
Carbon		0·05
Silicon Aluminium		trace
Nitrogen		0·005

It may be mentioned here that a thermal analysis, *in vacuo*, was carried out with metal of this purity to obtain a more definite figure for the melting point of beryllium. This was found to be 1281° C. (± 2° C.), with a second point at 1265° C. In view of the knowledge of the existence of the eutectic, this second point is of some significance, and the author is inclined to believe that it represents the solidification point of the Be–BeO eutectic. It may, however, be connected with an allotropic change in beryllium itself, a matter which will be dealt with later (p. 386).

The work on the production of pure beryllium now resolved itself into attempts to remove oxygen, and the main portion of the following pages will be devoted to a detailed account of the various ways in which a solution to this problem has been sought. They may be broadly divided into two groups:

A. Preparation of the metal under such conditions as to prevent the formation of oxide.

B. Treatment of metal containing oxide so as to remove the oxygen or render it harmless.

A. ATTEMPTS TO PREPARE OXYGEN-FREE BERYLLIUM.

1.—*Alteration of Electrolysis Conditions.*

The access of air to the molten beryllium during its electrolytic preparation probably accounts for practically all the oxide subsequently found in the metal. If, therefore, the conditions could be suitably varied, oxygen-free metal might be produced in the first stage. An inert or reducing atmosphere was called for, and of the gases available, carbon dioxide seemed the most promising. Nitrogen was avoided on account of the ready formation of nitride when beryllium is heated in it; hydrogen offered possibilities if the danger of explosion could be definitely overcome, whilst argon was considered too expensive. Carbon dioxide was, therefore, selected. This was not ideal, owing to the risk of reduction to the monoxide by a balanced reaction of the following nature :—

$$Be + CO_2 \rightleftharpoons BeO + CO.$$

A preliminary investigation by heating beryllium almost to the melting point in pure carbon dioxide, showed that up to that temperature, at any rate, the risk was very small. Several depositions were, therefore, carried out using a stream of carbon dioxide over the surface of the melt. As had been feared, the electrolysis could not be conducted for any appreciable time, owing to the gradual accumulation of graphite scum, which bridged the electrodes and become entangled in the solidifying metal. The scum is normally burnt away in air. This phenomenon would have occurred with any of the other atmospheres under consideration, and they were therefore not tried. The substitution by other materials of all or most of the graphite offered possibilities, and a large number of trials with different refractory materials was carried out, but none was found which would withstand fluorine attack. Heat-resisting "stainless" steels were examined, but while they did not actually break up, contamination of the melt by iron fluoride was serious at the temperatures involved. All attempts to alter the existing technique were, therefore, discontinued.

2.—*Preparation of Beryllium by Deposition Below its Melting Point.*

As mentioned in the earlier paper, some attention had been given to the deposition of beryllium from fused electrolytes at relatively low temperatures, but with no very marked success. With the failure of the above attempts to produce oxygen-free metal, this type of experiment again came under consideration, and a large amount of work has been carried out on these lines. It was realized that the difficulties inherent in methods employing temperatures above the melting point of beryllium would be much simplified here, and many might disappear completely.

The electrolyte must have a low melting point so that at about 600° C. it shall be reasonably fluid and have a high conductivity. At the same time, serious volatility is very undesirable. Of the compounds containing the beryllium cation, the fluoride is again the only one that can be employed, but as it is a non-conductor in the fluid state, sodium fluoride is added. A mixture of sodium fluoride with twice its weight of beryllium fluoride was found to possess very satisfactory properties. Even below 600° C. it is sufficiently fluid to electrolyse.

In the first trials, a mixture of this composition contained in a graphite or nickel * crucible, heated externally to 650°–700° C. in an electric furnace, was electrolysed using a copper rod as cathode and graphite as anode, with a current density at the former of about 0·5 amp./cm.^{2} at 3 v. It was decided to work without any special atmosphere until the conditions of possible deposition were better understood. In contrast to the earlier experiments described in the previous paper, this led immediately to promising results. After electrolysis for 1 hr., the cathode was removed. The superficial fluoride crust which is readily soluble in water was dissolved off, exposing a definite compact layer of steel-grey beryllium. This film was, however, too thin to polish satisfactorily for examination. In some areas, where the coating was completely removed in the attempt to polish, a yellow material was noticed, which formed a continuous layer between the beryllium film and the copper, and was subsequently shown to be a beryllium–copper alloy formed by diffusion.

Further experiments were then performed with the object of obtaining thicker deposits. The first variable to be altered was the duration of the electrolysis. It soon became apparent that if this was continued for more than about 1·5 hrs., the resistance of the bath gradually increased, and at the end of 2 hrs. it behaved almost as a non-conductor. This tendency could, however, be overcome by stirring by hand up to a limit of about 4 hrs., at the end of which time it had no further effect.

The most obvious explanation of the trouble was change in composition of the bath, but a series of experiments carried out to test this showed that within the limits of experimental error the composition remained unchanged (very little beryllium was being removed by the electrolysis) whilst volatilization of the mixture as a whole occurred at the rate of approximately 1 per cent. per hour under the particular conditions of apparatus design and operation and was not important either as a bath loss or as a factor in influencing resistance.

The possibility of the formation of a high-resistance film around the anode or cathode or both was next investigated. Beryllium was sub-

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* Nickel is unattacked by the melt at these temperatures.

stituted for graphite as anode, but showed no advantages. A rotating anode of graphite was then tried, with excellent results. The resistance remained constant over several hours, as was also the case when the rotating anode consisted of beryllium. It seems certain, therefore, that the increase in resistance is a function not of the anode material itself, but of the anode-bath interface.

Several experiments were conducted with a rotating graphite anode, other conditions such as temperature, current density, &c., being as above. The electrolyses went very smoothly, but the resulting deposits could not be obtained thicker than about 0·01 in., however long the experiment was continued. The only difference between the results of one lasting 1 hr. and another lasting 5 hrs. was that in the latter case the extent of diffusion and the percentage of beryllium in the intermediate alloy layer were considerably greater. It seemed, therefore, that the current density was such as to make the rate of deposition less than the rate of diffusion. The current density was, accordingly, altered within wide limits. An interesting phenomenon was then observed. Below a certain value, variations of current density had no effect whatsoever on the character and thickness of the deposit. Above this value, however, the thin compact film of beryllium was always covered by a mixture of fluorides and coarsely crystalline beryllium particles. On washing in water, these particles fell away, leaving the normal film of about 0·01 in. thickness underneath. The critical value of the current density, therefore, corresponded with a rate of deposition approximately equal to the rate of diffusion.

Further experiments were then conducted in an attempt to find operating conditions which would obviate the non-adherent coarsely crystalline nature of the thicker deposits. A rotating instead of a fixed cathode, substitution of nickel, iron, &c., for copper as cathode, variation of current density within wide limits, alteration of working temperature and beryllium content of the bath over a wide range, were all successively investigated, and found to be unsuccessful.

While disappointing, this result was not altogether surprising, as it had been maintained for some time that in order to produce compact metal from fused electrolytes it was essential to conduct the electrolysis at a temperature above the melting point of the metal required. Moreover, several earlier workers had failed completely to produce compact beryllium at temperatures similar to those employed in this part of the work. The early success in the formation of plated films, therefore, led the author to hope that by a suitable variation of conditions, deposits of any desired thickness could be obtained. It seems, however, that the limiting thickness is of the order of 0·01 in.

and from the point of view of the main objective, which was to produce pure beryllium in large quantities, low-temperature fusion electrolysis is a failure.

The beryllium films which were produced were always too thin to examine for mechanical properties, even by the Brinell hardness test, the figures obtained being representative of the hard alloy immediately below the surface. It is interesting to note, however, that even without the use of special atmospheres the microscope did not reveal any oxide. The metal is presumably protected from oxidation by being deposited beneath the surface of the bath.

Considerable interest in another direction attached to the method from the fact that it represented the first successful beryllium plating that had been accomplished. Deposits capable of taking a high polish were produced on copper, nickel, and iron. They were all strongly adherent and accompanied by diffusion and the formation of alloys beneath the beryllium. It seems certain that the possibility of plating at all is closely associated with this formation of alloy layers. This was confirmed by the failure of all attempts to deposit beryllium on graphite where the possibility of alloy formation is precluded.

If the rate of deposition on, say, copper is adjusted so as to be approximately equal to the rate of diffusion at the temperature employed, electrolysis can be conducted for several hours, and the resulting product will have the usual thin film of beryllium on the outside with a considerable thickness of alloy underneath. By working at about 850°–900° C., the rate of diffusion is much increased so that the current density can be correspondingly raised. In a comparatively short time, this leads to the formation of homogeneous alloys of beryllium–copper containing up to about 2 per cent. beryllium. If the electrolysis is terminated before this stage, a central core of pure copper surrounded by a layer of the alloy is obtained. Such an article, whilst retaining the desirable properties of copper, protected on the outside by a material with the mechanical and elastic properties of the beryllium–copper alloys, should prove useful for certain commercial purposes.

As previously pointed out, it is undesirable to allow the rate of deposition to exceed the rate of diffusion as beryllium flakes begin to be formed round the cathode. These serve no useful purpose and merely represent waste.*

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* The results of a very interesting series of experiments carried out in Germany on these lines have been published (*Wiss. Veröff. Siemens-Konzern*, 1929, 8, (1), 83), which confirm the results given above. The bath mixture is not very different. The author particularly stresses the application of this type of deposition to the preparation of alloys containing small percentages of beryllium.

3.—*Preparation of Beryllium by Deposition from Non-Aqueous Solvents.*

Owing to its position in the electrochemical table, beryllium is one of the metals which it is not considered likely will ever be successfully deposited from aqueous solutions.

Some attention has, however, been directed towards the possibilities of non-aqueous solvents, particularly those which do not contain oxygen. Of these, liquid ammonia is not only easily obtained in bulk, but also possesses many physical properties which ally it closely to water in its behaviour. Several beryllium salts were found to be appreciably soluble in liquid ammonia, but no evidence of deposition was obtained in any of the electrolyses carried out. It was considered undesirable to devote further time to it at this point, in view of other work then in progress.

Since then, however, an interesting note has appeared in an American journal,[5] in which the author claims to have prepared very pure beryllium by electrolysis of dehydrated beryllium nitrate in liquid ammonia. It was hoped that full details would be available later.*

B. ATTEMPTS TO REMOVE OXYGEN FROM BERYLLIUM.

1.—*Preparation of Beryllium by Thermal Dissociation of Beryllium Iodide.*

The method is that first described by van Arkel and his collaborators,[6] and successfully used in the preparation of many metals, in a pure form free from oxygen and nitrogen. The mechanism is essentially as follows: a volatile compound of the metal, usually the iodide, is heated and vaporized in an evacuated Pyrex vessel in which a thin tungsten wire is maintained at a high temperature. Dissociation of the iodide occurs at the temperature of the wire, and the metal is deposited thereon in a pure form. In practice, the iodide of the metal is prepared *in situ* by heating the evacuated vessel containing solid iodine and metal, usually in the form of powder. The temperature of the tungsten wire is read with the aid of an optical pyrometer. A necessary condition for success is that below the melting point of the required metal a temperature region must exist in which the vapour pressure of the metal is lower than the partial pressure of the metal in the gas phase. For any particular metal, the temperature of the tungsten wire is maintained within that region. With beryllium, the tungsten was normally held at about 700°–900° C., and the apparatus was a copy of that used by van Arkel. The beryllium

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* Since the above was written, further publications by Booth and his collaborators have appeared giving more complete details of the method (*J. Phys. Chem.*, 1931, 35, 3111, and 3303). It does not appear, however, that it is likely to prove very important as a method for the production of large quantities of pure beryllium.

iodide was prepared in the reaction vessel by the action of iodine on powdered or massive beryllium at about 350°–450° C. The melting point of the iodide is about 500° C., below which temperature it readily sublimes.

In the course of the earliest experiments, it became apparent that the method would not be successful if conducted in the way described by the Dutch workers. In less than 0·5 hr. after the commencement of an experiment the Pyrex glass became opaque, so that the temperature of the tungsten wire could no longer be read by a pyrometer, and examination of the glass showed that it was deeply etched. A similar vessel containing iodide only was subjected to the same treatment without suffering any damage. This, coupled with the fact that the originators of the method had not apparently experienced corresponding difficulties, confirmed the suspicion that the beryllium iodide as distinct from iodine or other iodides was sufficiently reactive to attack the Pyrex, etching it very rapidly.

The temperature of the vessel was varied over a wide range in an attempt to reduce the attack, but at those temperatures at which the etching action was small there was insufficient iodide vapour pressure to give a deposit of beryllium on the tungsten. A method was therefore sought, by means of which the temperature of the wire could be ascertained in spite of the inability to see it, and ultimately a close approximation to its true temperature was obtained by the use of a molybdenum–tungsten thermocouple sealed through the wall of the vessel, with the junction very near the centre of the wire.

As a result of several experiments, deposits of beryllium were obtained on tungsten wires about 0·1 mm. thick. The deposits, ranging from 1 to 3 mm. in thickness, were coarsely crystalline and very brittle. Analysis revealed the presence of appreciable quantities of silicon and boron, which had been removed from the glass by the action of the iodide and deposited with the beryllium.

Other materials for the reaction vessel were therefore investigated to overcome this serious contamination. Many glasses of different compositions were tried, but even with those which did not contain boron, the silicon was always found as an embrittling impurity in the beryllium. Attempts were made to sputter a protecting film of tungsten all over the interior of the glass vessel, but without success. It was not possible to obtain a tungsten vessel, but certain nickel–chrome steels which could be worked to the required shape were not seriously attacked by the iodide vapour. This attack, however, coupled with the serious problem of insulating the electrodes and thermocouple in a metal vessel, the whole of which has to be vacuum tight at 400°–500° C., led to the decision to discontinue this line of attack, at any rate temporarily.

2.—*Sublimation of Beryllium.*

Sublimation or distillation *in vacuo* has been used at the National Physical Laboratory with success for the purification of several metals, and its earliest application to beryllium was described in the previous publication. Essentially the method is as follows: an ingot of the metal is placed in a small refractory crucible, suitably lagged, on which a similar crucible stands inverted, with a small hole in its base for sighting purposes. These are contained in a vertical silica tube completely closed at the base with a rubber stopper. At the top is another stopper fitted with a small brass tube closed with a glass window, and a second, larger tube, for evacuating the apparatus. The most suitable method of heating is the high-frequency induction furnace, in which the metal itself acts as the heating element, and is thus the hottest part of the system, whilst the silica tube is comparatively cold, being water-cooled on the outside by a helical copper tube which itself forms the induction coil of the furnace. A good vacuum can thus be readily maintained, although the metal may be in the neighbourhood of 2000° C. Moreover, the inverted refractory crucible or hood is heated only by radiation from the small ingot of metal, and remains well below the metal in temperature, thus forming a condensing surface for metal vapour. In the case of beryllium, both the containing crucible and the hood are made of pure beryllia (beryllium oxide).*

The earlier trials were carried out with the beryllium at a temperature of about 1750°–1800° C. and a pressure of 0·1–0·05 mm.† A considerable quantity of material was collected in the hood, chiefly in the form of globules and thin films adhering to the walls. Some of the globules were large enough to examine. Analysis showed the composition to be very similar to that of ordinary remelted metal, except that carbide was very rare. This was confirmed by microscopic examination, which also revealed the intercrystalline Be–BeO eutectic. The Brinell hardness was irregular, being 110–120 (as found for the purest remelted metal) in some globules and as low as 90 in others. The lower figure was found in those specimens having the least intercrystalline impurity. The material was still brittle to a varying degree.

The surprisingly large amount of eutectic strongly suggested that in the main the material was not a true sublimate, but was derived from splashes ejected from the molten metal below.‡ Refractory baffles were

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* See p. 384 for reasons.

† Pressures are given in mm. of mercury throughout.

‡ This effect of the high-frequency field was already known, but its extent in the case of very light metals had not been realized. It is due to the fact that the electrical energy is absorbed by a molten metal partly as heat and partly as movement. With a given metal, the ratio of thermal to mechanical absorption of the energy is more or less constant for a particular frequency. It varies considerably,

therefore introduced between the bottom of the hood and the top of the melt, with the result that in these experiments negligibly small amounts only of material were obtained. (Temperature and pressure as above.) This material, however, was still globular in appearance and contained a certain amount of oxide. The most probable explanation was that it had collected in a region where it had come under the action of the high-frequency field and, owing to lack of cooling, had melted by reason of the currents induced in it. Contamination by residual oxygen would then lead to the formation of the typical eutectic structure on solidification. It became essential, therefore, to prevent this formation of liquid.

Alterations in the design of the induction coil to decrease the intensity of the field in the neighbourhood of the hood were unsuccessful. The application, therefore, of some very powerful form of cooling to the hood offered the only chance of success. After careful consideration, it was decided to attempt the use of a water-cooled hood inside the evacuated system.

The first form of this was a spiral of transparent silica fitting round the outside of the cylindrical beryllia condensing hood. The choice of material was governed by three important considerations: it must be capable of withstanding possibly severe temperature gradients, must be non-porous to water or water vapour, and a non-conductor of high-frequency currents. This last requirement ruled out all metals.

The two ends of the spiral passed out through the top rubber stopper of the silica furnace tube. During sublimation water was circulated through the spiral, whilst a vacuum of about 0·05 mm. and a metal temperature of about 1900° C. were maintained. Considerable reliance had to be placed on the ability of the silica to withstand the severe experimental conditions, as a break would involve cold water coming in contact with molten beryllium a few centimetres below. All possible precautions were accordingly taken to guard against danger should such an event occur. With a later form of water-cooled hood, this did happen, but apart from wrecking the hood and cracking the Triplex glass screen through which the experiment was being viewed, no serious damage was done. The beryllium ingot was of course oxidized to a large extent.

The sublimate produced during the trials with the spiral cooling device was similar to that previously obtained. The cooling action was therefore assumed to be insufficient, owing probably to the poor thermal conductivity of the comparatively thick wall of the beryllia hood. It

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however, with the density of the metal and with the frequency of the field. Hence with a very light metal, such as beryllium, the ratio is low and the agitation of the liquid very violent. It also follows that with a given frequency and power input, beryllium cannot be raised to such a high temperature as a heavy metal such as iron in which the heat absorption is much greater and the movement much less.

was decided, therefore, to go a step further and condense the sublimate on water-cooled silica itself. After some difficulty in design, a double-walled vessel of transparent silica was obtained.* It was essentially an inverted cylindrical crucible with thin hollow walls and base, between which water could be circulated. Inlet and outlet tubes for the water, also of silica, were sealed in and passed through the top rubber stopper of the furnace tube. The vessel was allowed to rest on the refractory baffles above the beryllia crucible containing the metal to be sublimed (Fig. 8). It was during the first trial with this type of hood that the accident referred to above occurred. A second hood was then obtained, and several experiments were successfully carried out with it.

The quantity of sublimate obtained was still negligibly small. There were, however, no indications that it had been molten, although it was somewhat oxidized by the residual oxygen. The question of removing the residual gases was next investigated, and by the use of elaborate precautions, vacua of the order of 0·005 mm. (instead of the earlier 0·1–0·05 mm.) were obtained with the metal at about 1900° C., which represented the limit of temperature and pressure possible with the available resources, and very small quantities of unoxidized sublimate were produced. These experiments definitely showed that the vapour pressure of beryllium at about 1900° C. must be very low.

In view of the impracticability of improving the conditions, it was decided to continue a sublimation experiment for many hours in the hope that the amount of sublimate produced would be sufficient for examination. At the end of about 6–7 hrs. the material in the hood was examined. A few splashes were present, together with a thin cylinder of bright crystalline metal about 1 mm. thick. The surface in contact with the silica was smooth, the other being ragged, representing uneven growth from many centres, of the condensed metal vapour.

This metal was very different in properties from that previously prepared by any other method. The beryllium content was directly estimated as 99·95 to 99·97 per cent. The Brinell hardness number was much more uniform over different parts of the specimen and ranged from 60 to 65. The impressions were accompanied by well-marked slip bands (Fig. 7, Plate LVI), a definite indication of ductility. The specimen itself was not subjected to any mechanical tests owing to the insufficiency of material. It could, however, be bent backwards and forwards many times before the effect of cold-working led to fracture. The microscope revealed a practically plain field of beryllium crystals with very little indication of any impurity.

Many further attempts were made to prepare larger quantities of

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* Messrs. Thermal Syndicate, Ltd.

sublimed metal, but up to the time when this part of the work was discontinued, it had not been possible to prepare specimens suitable for

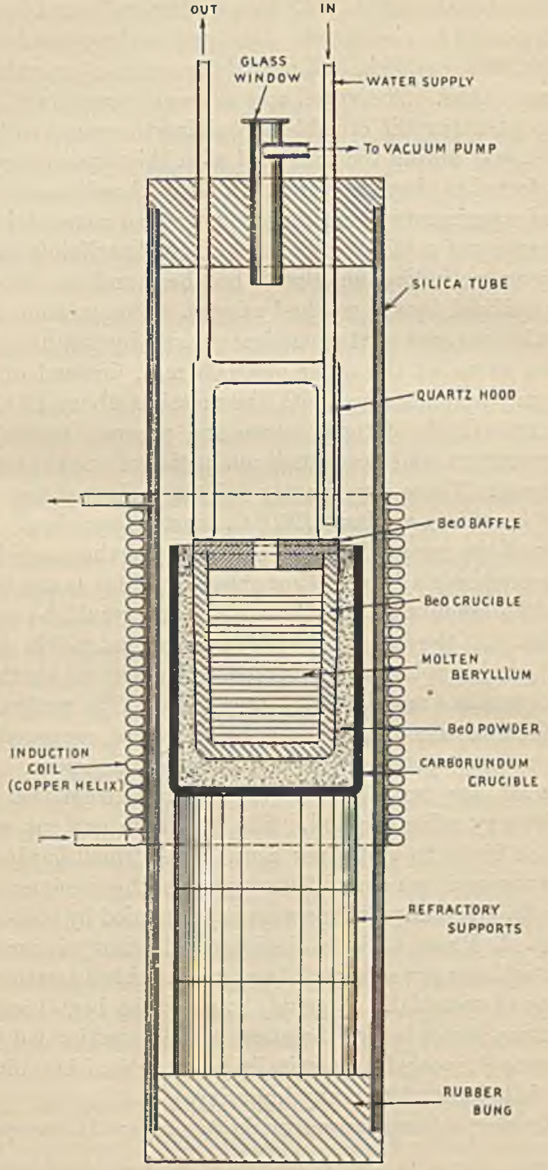

Fig. 8.

mechanical tests. It seems, however, that the essential ductility of beryllium has been established by these experiments on the production of sublimed metal of the above purity. The Brinell hardness of this metal, as stated above, is about 60 (slightly higher than that of pure iron), and it is not likely that any further increase in purity would lower this figure appreciably. Whilst beryllium, therefore, is not so soft a metal as copper or silver, it is ductile in a pure form, and likely to be similar to, say, iron in mechanical properties.

3.—*Attempts to Deoxidize Beryllium.*

The affinity of beryllium for oxygen, both above and below its melting point, is such that it appeared very doubtful if any of the usual deoxidizers would be capable of reducing the residual oxide. Serious attention was, however, given to the use of hydrogen in this connection.

The gas was circulated in a closed system over molten beryllium, contained in a beryllia crucible and heated in a high-frequency induction furnace. Within the system were incorporated water vapour and oxygen absorbers and freezing mixtures (carbon dioxide snow and acetone), together with a means for keeping the gas circulating.

The results of many experiments with different pressures of hydrogen ranging from a few centimetres to 1 atmosphere were to show that no appreciable reduction in the oxide content of the beryllium was obtained. The only difference between melting the metal in an atmosphere of hydrogen and *in vacuo* was the much cleaner upper surface of the ingot in the first case on solidification. This was presumably due to the complete removal by the hydrogen of the residual oxygen normally present in the system during the melting operation. The ingot was not unsound owing to expulsion of hydrogen on solidifying. It was concluded that hydrogen either does not reduce beryllium oxide dissolved in molten beryllium, or that it was not in sufficiently intimate contact with the interior of the molten metal under the above conditions.

A more drastic method was therefore tried, which involved the use of an atomic hydrogen blow-pipe.* The principle is as follows : an arc is struck between two tungsten electrodes held at about 30° to one another, along which a strong stream of hydrogen is forced. The part of the gas surrounding the arc is atomized, whilst the remainder burns, giving a large space occupied by a reducing atmosphere outside the intensely hot central atomized portion.

Some preliminary trials were made with copper containing a known percentage of oxygen. The metal, held in a small crucible, was melted by direct application of the arc from above. After being liquid for

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* A commercial Langmuir atomic hydrogen blowpipe was kindly presented to the National Physical Laboratory by the General Electric Company of America.

about 2 minutes, the metal was cast into a small mould, being kept all the time within the area of the hydrogen flames until completely solid. It was found that by once melting in this way, the oxygen content could be reduced from 1 per cent. to 0·03 per cent. A disadvantage of the method lay in the porosity of the resulting ingot due to hydrogen gassing. The results, however, were of sufficient promise to warrant similar experiments with beryllium, but with this metal no increase in purity was obtained, and after several trials the method was abandoned.

Attempts to remove the oxide by the use of fluxes did not lead to any success. They consisted of various mixtures of alkali and alkaline-earth halides in which beryllium oxide is soluble.

4.—*Crucibles for Melting Beryllium.*

During this work, an investigation was undertaken into the most suitable refractory material from which crucibles to hold molten beryllium could be made. The chief aspect of the case was the risk of contamination of the metal by impurities derived from the crucible. The temperatures involved in melting, and more particularly subliming, were in the neighbourhood of 1900° C., and the choice of refractories seemed to lie between beryllia, alumina, magnesia, and thoria. In each case the purest material obtainable was used for the tests.

Beryllia.—From the point of view of avoiding all possibility of contamination of the beryllium by other metals, beryllia undoubtedly had enormous advantages, but the comparatively ready solubility of beryllium oxide in the molten metal, which has already been stressed throughout these pages, did not make it an ideal material.

Alumina.—Beryllium was melted *in vacuo* in a pure alumina crucible in a high-frequency induction furnace. Analysis of the metal before and after showed an increase from 0·01 to 0·10 per cent. of the aluminium content. A repetition on the resulting ingot led to a further increase from 0·10 to 0·41 per cent. In order to determine whether this aluminium was present as metal or in the form of aluminium oxide derived from the crucible by mechanical scouring, the minimum strength of hydrochloric acid which would attack the alumina from which the crucible was made was first determined. The beryllium for analysis was then allowed to dissolve in acid very much weaker than this. Any aluminium subsequently found in the solution must therefore have been present as metal, and not as oxide.

The figures given above show that an appreciable reduction of alumina by beryllium occurs under these conditions, probably in accordance with the reaction

$$3\,\mathrm{Be} + \mathrm{Al_2O_3} \rightleftharpoons 3\,\mathrm{BeO} + 2\mathrm{Al}.$$

The beryllium oxide formed led to a slight increase in the quantity of the beryllium/beryllium oxide eutectic visible under the microscope.

Magnesia.—Similar experiments were conducted using pure magnesia crucibles. In this case, a trace only of magnesium was found in the metal. The amount of the eutectic impurity, however, had increased considerably, strongly suggesting that reduction had occurred as follows :—

$$Be + MgO \rightleftharpoons BeO + Mg.$$

The very low boiling point of magnesium made it possible that the reason a trace only had been found was its volatility at the temperatures used. Careful examination of the cooler parts of the system revealed the presence of sublimed magnesium.

Thoria.—Owing to the high cost of thoria, the crucible used in this experiment was made of alumina with a thoria lining. Reduction occurred to a larger extent than in either of the two previous cases :—

$$2\,Be + ThO_2 \rightleftharpoons 2\,BeO + Th.$$

The resulting metal was extremely brittle and dense, having a thorium content of about 33 per cent. by weight (about 16 atomic per cent.), whilst the beryllium oxide content rose to about 5 per cent.

The complete failure of these materials to withstand the reducing action of molten beryllium resulted in a return to the use of pure beryllia for all melting purposes.

It was subsequently shown that beryllium oxide which has been heated to about 1600° C., which is normal practice when firing beryllia crucibles at the National Physical Laboratory, is not appreciably soluble in molten beryllium. The metal can therefore be remelted without increasing the oxide content from this source. Oxide, formed by the action of oxygen on molten beryllium or by the reduction of another metallic oxide by beryllium, appears, however, to behave differently, and is appreciably soluble in the molten metal.

5.—*Heat-Treatment of Beryllium.*

A large number of heat-treatments *in vacuo* at different temperatures with and without subsequent quenching have been carried out on samples of beryllium.

As a rule, annealing at 900° C. for a few hours is sufficient to produce two effects which are closely associated. These are a drawing together of the eutectic network into rounded areas which still retain their eutectic structure, and a distinct if irregular lowering of the Brinell hardness number. The total amount of eutectic does not alter, but the fact that it is now irregularly dispersed accounts for some areas being unchanged in hardness, whilst others are much softer. For instance, starting with metal having a Brinell hardness of about 100, we may subsequently find any value from 100 down to about 65 in various parts of the specimen. Examination of the impressions shows that the smallest (highest Brinell number) are those in areas where the eutectic is most concentrated, whilst the largest (lowest Brinell number) are found in places where it has been practically entirely removed. These are usually surrounded by slip-bands.

It thus appears that portions of annealed beryllium are very similar in properties to the thin films of pure metal obtained by sublimation. It has not been possible, however, to obtain uniformity over any particular specimen, despite prolonged heat-treatments under various conditions. The mechanical properties of such metal, being largely determined by the remaining brittle and hard regions, are very disappointing.

6.—*Allotropy in Beryllium.*

Whilst the author feels satisfied that the cause of brittleness in beryllium, prepared even under the best conditions, has been conclusively shown to be due to residual oxide, the possibility of two allotropes of the metal, one of which may be hard and the other soft, has often arisen during the course of this work. In particular, attention was concentrated on allotropy by the following observations.

A specimen of beryllium having a composition similar to that given on p. 372 with a Brinell hardness of about 110 remained unused for about 3 years. At the end of this period, occasion arose for its use for heat-treatments. It was decided to retest its Brinell hardness in order to ensure that the originally recorded figure was correct. It was found, however, that on this occasion the value averaged about 75. The original impressions which still remained on the surface were re-measured, but no doubt could be thrown on the values which had been obtained from them. Microscopic examination showed the normal type of structure (a network of eutectic with a few crystals of beryllium carbide, silicon, and perhaps a trace of iron). Fresh surfaces were cut in different directions and further Brinell hardness figures obtained. The average value was in the neighbourhood of 70–75. Unless one assumed an allotropic transformation in the metal itself, there seemed to be no explanation, other than a solid solubility change in one or other of the impurities, to account for this startling alteration in hardness over a period of time at room temperatures.

An X-ray photograph of the specimen was taken. Normally the structure of the beryllium lattice is found to be a close-packed hexagon, but in the photograph of this particular specimen several other lines appeared, together with those corresponding with the usual structure. It consisted, therefore, of a mixture of normal beryllium and a second unknown phase. Many attempts have been made to correlate the additional lines with one or other of the standard lattice structures, but so far they have proved too complicated and irregular to justify any conclusion. It has, however, been established that they do not correspond with the known structures of beryllium oxide, beryllium carbide, silicon, iron, &c. The X-ray evidence, also, does not distinguish between the possibility of an allotropic change and a phase change due to the impurities.

The fact that the change, whatever its cause, occurred at room temperature suggests that it is a low-temperature effect, and might therefore occur more quickly at a slightly elevated temperature. Moreover, by holding the specimen at a temperature above the transition point, it should be possible to reverse the change completely. Attempts, however, to hasten the production of the change in other specimens by annealing for several weeks at temperatures from 0° C. to 400° C., and also to reverse it in the particular specimen in which it had been observed by annealing and quenching at temperatures up to 900° C., have been unsuccessful. Meanwhile other specimens of similar metal have already been watched over a period of 18 months at room temperatures, but so far no definite changes in lattice structure or hardness have been noted.

Other workers on beryllium have from time to time suggested allotropy as the cause of unexplained phenomena. Lewis,[7] however, definitely claims that his work on the electrical resistivity of beryllium up to 700° C. proves the existence of at least two allotropic forms of the metal. He bases his conclusions on the sudden changes in the slope of the curve of electrical resistivity plotted against temperature. The curve can be divided into three portions having discontinuities between $-50°$ C. and $+20°$ C. and between 550° C. and 650° C.

The lower of these two transition points revealed by electrical conductivity measurement is very significant when considered in conjunction with the change in hardness and lattice structure at room temperatures found by the author. Somewhat disturbing, however, is the fact that whereas the electrical measurements show the change to be readily reversible, all attempts to control the lattice structure and hardness have, as pointed out above, failed.

With regard to the transformation at about 600° C. noted by Lewis, no X-ray or other evidence has so far been obtained to confirm this. It is possible, however, that if it is a true allotropic change, it might be more readily found in beryllium-rich alloys than in the pure metal.

It appears to the author that while allotropic transitions must always produce sudden changes in the values of such properties as electrical conductivity, the converse is not necessarily true. Other causes, such as the effects of impurities, may produce equally marked changes in the value of such a property. It may be pointed out that the complete analysis of the metal used by Lewis is not given in the account of his work (the total metallic impurities are said to be about 0·5 per cent.). Sufficient impurity is, however, admittedly present to make it unsound in the author's view to conclude on the available evidence that the phenomena must necessarily be due to allotropy in the beryllium, and not to the effects of impurities.

At this point, reference may again be made to the second arrest point found in the thermal analysis of beryllium at 1265° C. As previously stated, it is not thought that this has any bearing on the present problem, as it is difficult to see how a change at such an elevated temperature could affect the metal when held at or near room temperatures for any length of time whatsoever.

ACKNOWLEDGMENTS.

The work described above was carried out under the supervision of Dr. W. Rosenhain, F.Inst.Met., F.R.S.—until recently Superintendent of the Metallurgy Department of the National Physical Laboratory—to whom the author offers his thanks for his great interest and encouragement throughout and for his many valuable suggestions towards the solutions of the problems involved. Within a few months of the publication of his paper, which forms the commencement of the present work, Dr. A. C. Vivian resigned from the staff of the National Physical Laboratory. The author acknowledges his association with the work for that period, during which he was chiefly responsible for many of the attempts to prepare beryllium by the dissociation of its iodide. Thanks are also due to Messrs. W. E. Carrington and H. E. Bennett, who gave valuable help as laboratory assistants throughout the investigation.

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JOINT DISCUSSION.

DR. W. ROSENHAIN,* F.Inst.Met., F.R.S. (Past-President): I cannot add very much to what has been said in these papers. A good deal of the work was carried out while I was in charge of the Metallurgy Department of the National Physical Laboratory, and I was consequently very intimately associated with it at that time.

Mr. Sloman is to be congratulated on having carried out what I am almost inclined to call a losing battle with great skill and perseverance over a large

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* London.

number of years. It has been, I can assure you from the experience of a lengthy series of researches, without exception the most heart-breaking piece of work I have ever seen anyone attempt. Every promising method that one could think of (and we thought of a great many and tried them) seemed to fail for some reason which one could not have anticipated. Take, for instance, the method by which certain Dutch investigators at Eindhoven had succeeded in preparing a number of pure metals which had never been produced before. They did that by the decomposition of the vapour of the iodide of the metal in contact with a hot filament, initially a very fine wire of tungsten, which gradually grew by the deposition of the other metal, and as a result delightful samples of pure material—chromium, tungsten, zirconium, and others—were obtained. I have a piece of zirconium which is quite ductile. It was hoped that beryllium could be prepared in the same way, and a great deal of time was spent in setting up an apparatus for that purpose. Dr. A. C. Vivian began it, and Mr. Sloman carried it on. It was hoped to obtain a corresponding result, but we found that, unfortunately, the volatile beryllium iodide attacked the glass-containing vessel, and, instead of depositing pure beryllium, both silicon and boron out of the glass were transported on to the filaments, rendering the resulting deposit impure and brittle. So far no one has been able to devise for this process a containing vessel which is at once an insulator electrically, strong enough to hold a vacuum at the temperature which it attains, and incapable of being attacked by beryllium iodide. When that problem is solved, the making of high-purity beryllium on a laboratory scale will be possible.

Then, again, this question of sublimation was hedged about with the most appalling difficulties not anticipated. Quite a good deal of what was believed to be sublimed beryllium was obtained, but it was found that instead of being sublimate it was splashed metal from the boiling beryllium below.

Then an attempt was made to condense it on a mass of refractory made of beryllium oxide; the molten metal promptly dissolved oxide from that body. The metal was molten where it condensed because it was still in the field of the induction furnace. The result was a very exciting experiment. It sounds quite simple to talk about a water-cooled silica condenser placed immediately above a mass of more or less boiling beryllium at 1800° C. in a high vacuum, but I can assure you that the first time it was used Mr. Sloman had a good deal of respect for that piece of apparatus. I certainly had. However, after a good many failures it was got to work, and the nearest approach to pure ductile beryllium that has ever been produced was the result. Mr. Sloman is to be congratulated on a very well-deserved success; in fact, I think that he deserves a good deal more success than he has yet achieved.

With regard to the future of the whole thing—and that, after all, is perhaps the most interesting point—it is highly important (from the scientific point of view rather than from the practical viewpoint) to endeavour to produce pure ductile beryllium. Until a great many other problems are solved, the use of beryllium as a basis metal—that is to say, as constituting the major portion of any alloy which is used—is impracticable. The question of cost alone is at present many times prohibitive. That question is for the future to solve, and if beryllium passes—and I think that it very likely will do—as aluminium and tungsten have done, from the stage of pounds per ounce to shillings per cwt. we shall get what we want. Nevertheless, it is very important to have some idea of the fundamental properties of the substance in its pure state, and it is in that direction that this work has been aiming.

The uses of beryllium, on the other hand, are likely to be very important—and important in the near future—as an alloying element. There, of course, a very high degree of purity is not so important, and it offers a tempting path to research on alloys which, I am almost sorry to say, the investigators at the National Physical Laboratory have been obliged to follow under the pressure of economic necessity. It was, I think, felt that the amount of money spent on research for the production of the pure metal had been sufficient, and that work of this kind would have to give place to the more immediately practical, or potentially practical, research on alloys. I am afraid that the search for the pure metal is not likely to be continued for the present, although I do not know whether other counsels have prevailed during the last twelve months. It is a pity, but at the same time there is no doubt that the immediate practical interest does centre in the alloys of beryllium where that metal is, so to speak, a minor constituent in regard to quantity and to cost, although of major importance in regard to its effect on the properties of the material.

Mr. Sloman (*in reply*): I should like to thank you for the kind way in which this paper has been received, and in acknowledging the remarks of Dr. Rosenhain, to say that had it not been for his interest in the work and perseverance in the face of all the difficulties with which we were faced, I am sure that it would not have been possible to carry it to a successful conclusion.

CORRESPONDENCE.

Dr. C. B. Sawyer,* B.A. (Member): Mr. Sloman is to be congratulated on the completion of a difficult laboratory research which, although apparently non-commercial in itself, will have a very great effect on the development of the beryllium metal industry. The discovery that beryllium can be ductile is a matter of the first magnitude to the metallurgical world.

Work done at the laboratory with which I am associated has produced single crystals of quite pure beryllium, which possess a degree of cold malleability. Such malleability seems to increase after melting the individual crystals in hydrogen, even though the resulting pellets are coated with a skin of oxide due doubtless to impurities in the hydrogen. Except for this skin of oxide, these and other results of ours confirm those of Mr. Sloman.

While Mr. Sloman has adhered to the use of fluorides, and obtained a maximum duration of electrolysis of 100 hrs., I may state that using chlorides in a modification of the method first described by Borchers,† we have carried on continuous electrolysis for 250 hrs. without any indication that the limit had been reached, or that a limit exists. The graphite anodes were not visibly impaired.

I am in hearty accord with Mr. Sloman's emphasis of the need for purity of all chemicals (compounds of beryllium and otherwise) entering into the manufacture of beryllium metal. This thought, coupled with that of maximum commerciability, has dominated our efforts. The purity of our beryllium oxide was of fundamental importance in bringing out the finer properties of beryllium oxide refractories in the pioneer work in the United States by the U.S. Bureau of Standards.‡

Mr. Sloman (*in reply*): I am very glad to learn that the single crystals of beryllium obtained by Dr. Sawyer possess cold malleability. This undoubtedly confirms the results recorded in the present paper.

With regard to Dr. Sawyer's remarks on the maximum duration of electrolysis, I should like to make it quite clear that the limit of 100 hrs. referred to in my paper represents the life of the graphite crucible and is in no way associated with any change in electrical resistance or in composition of the bath after 100 hrs. continuous running.

* President, The Brush Laboratories Company, Cleveland, O., U.S.A.

† Wilhelm Borchers, *Z. Elektrochemie*, 1895.

‡ Wm. H. Swanger and Frank R. Caldwell, *U.S. Bur. Stand. J. Research*, 1931, 6, 1131–1143.

MODERN WORKS PLANT AND EQUIPMENT FOR THE HOT-WORKING OF NICKEL AND NICKEL ALLOYS.*

By W. R. BARCLAY,† O.B.E., Vice-President, G. A. V. RUSSELL,‡ Wh.Ex., and H. WILLIAMSON.§

Synopsis.

This paper describes a modern plant erected in this country as the result of experience in the hot-working of nickel and its alloys and a close study of the conditions under which similar work is carried out in Europe and America.

The main features of the plant are :—

(1) Hydraulic forging press.

(2) Hot-rolling mill, consisting of :—

- (a) a three-high universal type mill with horizontal and vertical rolls for the production of sheet-bar and strip.
- (b) a three-high Lauth type mill for the rolling of sheet-bar and small rectangular ingots into sheets.

A detailed description of each section is given with diagrams and illustrations.

Various prevailing methods of practice in other countries are compared and underlying principles discussed.

The text includes an outline of the methods of production adopted in working the plant.

The heating of sheet-bar for rolling into sheets is carried out in a specially designed electric resistance furnace which is described and illustrated.

The paper concludes with some general remarks on the hot-working of nickel and its alloys.

CONTENTS.

1.—Introduction.

Metallurgical problems in the production of metals and alloys in what may be termed semi-manufactured forms, *e.g.*, sheets, strips, tapes,

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

‡ Assistant Chief Engineer, I.C.I. Metals Ltd., Birmingham.

§ Engineer, Henry Wiggin & Co., Ltd., Birmingham.

rods, wires, tubes, &c., are so intimately bound up with engineering considerations of plant and equipment that it appeared to the authors that a somewhat detailed description of a modern installation * for the production of metals and alloys necessitating high-temperature work (and therefore somewhat special conditions) would be of interest to the Institute, especially since such an account will serve to show the close interdependence of the metallurgical, engineering, and operating factors.

2.—GOVERNING FACTORS IN DESIGN OF LAY-OUT AND PLANT.

It is necessary to point out in the first place that in contemplating the mill and equipment below described certain difficult fundamental conditions had to be borne in mind. The general object was to provide facilities for the production of pure nickel and alloys of varying nickel content, but obviously such a field necessarily covers metals and alloys having widely different properties, ranging from materials such as the binary nickel–chromium alloys possessing a strength at high temperatures almost equivalent to the commoner non-ferrous metals at normal temperatures, to materials such as the lower grades of German-silver which are reasonably comparable to the brasses and bronzes.

A further factor of importance was that the new plant must tie-in so far as possible with existing plant and ensure at least a modicum of continuity in tradition and progress of operations.

Prior to the inauguration of the new scheme in the works described, hot-rolling of nickel and its alloys had been for the main part carried out on a two-high reversing mill of conventional design, and it was necessary to use this mill for every class of finished product whether sheets or strips, and whatever the width or gauge.

In addition to the problem of designing plant capable of dealing with materials of so wide a range of properties, the added difficulty existed that nickel and its alloys, and indeed the whole class of high-temperature materials, were relatively in their infancy, and the field of their use was rapidly broadening, that new alloys were continually entering the field and demanding either to be included in the present scheme or to be considered as more or less formidable competitors.

Obviously the foregoing position could only be met by designing equipment which not only covered all existing requirements but possessed the maximum degree of flexibility for future demands.

A careful study was made of rolling mill practice in Great Britain, on the Continent and in America, and particular attention was given

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* Works of Henry Wiggin & Co., Ltd., Birmingham.

to mills carrying on production which bore any resemblance to the foregoing requirements.

A number of rolling mill plants exist in all these countries which, *inter alia*, deal with nickel and its alloys and the conditions in these mills were studied, and the experience gained used in working out the final plans.

For clearness it will be advisable to describe briefly current practice in other countries. Broadly, it may be said that there obtain two classes of opinion in regard to the production of sheet and strip work in these high-temperature alloys. One is represented mainly by practice adopted in Central Europe, the other by the methods in vogue in America. The essential difference between these is fundamentally in the form of ingot used, but it is an *important* difference since it involves both metallurgical and engineering considerations.

In the former case ingots are usually cast in rectangular slab moulds in dimensions differing from works to works but having approximately the following as an average :—

	Inches.
Length of slab	30 to 45
Width of slab	8 to 12
Thickness of slab	3 to 5

These slabs after the usual machining and surface treatment are hot-rolled direct from the ingot, on two- or three-high rolling mills of conventional design. Roughly this may be considered as following general non-ferrous methods. In the latter case the procedure adopted is much more in line with steel works practice. Ingots used are larger and heavier and follow the usual form adopted in steel ingot casting, *i.e.*, square in cross-section with a slight longitudinal taper. The approximate measurements range from ingots of 5 in.^{2} to 14 in.^{2}, varying in length from 40 or 45 in. to 60 in. The smaller range of ingots weigh from 500 lb. to 600 lb., the larger may weigh from 1 to 2 tons. The ingots are not usually rolled direct, but after machining pass through a forging or cogging process and are reduced to slabs or sheet bar before rolling into sheet or strip.

It was finally decided, after considering all factors of the case, that it would be advisable to adopt in general outline the second of these alternative methods. This decision was arrived at in view of the probability, or at least the possibility, that demands would increase for the high-temperature alloys of the type of the nickel–chromium series, and it was further considered that on metallurgical grounds alone the argument was definitely in favour of what may be called the " sheet bar " scheme rather than the " cast slab " scheme. Had it been contemplated to deal only with materials like pure nickel itself or the lower nickel-containing binary alloys with copper, undoubtedly the adoption of the cast slab scheme of operating would have involved a somewhat lower capital expenditure. A factor, however, which weighed very considerably in the final decision was the constant necessity for machining whichever type of ingot is produced. This is an unsatisfactory factor in the production of sheet metal from cast slabs since slabs must be thoroughly machined over a fairly considerable area and scrap losses are therefore appreciably higher in percentage than when large square ingots are made and the area of surface machined is less in relation to the nett weight of the ingot. As hinted earlier, however, close attention was given to the purely metallurgical problems involved, and it was mainly on this ground that the decisions were ultimately reached.

Much has been written and more said on the methods of the production of sound ingots, particularly in the metallurgy of steel, and while the case is by no means closed, the weight of evidence does undoubtedly tend to show that within reasonable limits the best results are obtained in alloy steels with square tapered ingots of reasonable dimensions. The conditions of crystallization from liquid to solid are more favourable in this type of ingot than in the slab type and unquestionably feeding of " pipe " can be carried out with greater certainty and uniformity. Still further, a good deal of experimental evidence exists in the production particularly of nickel–chromium alloys showing that if ingots are subjected to a forging operation prior to hot-rolling the resulting product is distinctly superior to material rolled direct from the ingot. This point, of course, finds analogies in certain steels.

The scheme as finally adopted therefore provided for a forging operation interposed between ingot production and hot-rolling with the aim not only of subjecting material to this form of hot-working prior to rolling but to converting a square tapered ingot to a form more suitable for rolling, *e.g.*, a rectangular section of requisite thickness and length for its ultimate purpose. Since, however, in the present scheme the forging press and hot-rolling mill are in close juxtaposition in the same building, the forging process may be omitted for such materials as can be hot-rolled direct from the ingot, and in actual practice a large proportion of the present production of malleable nickel is so hot-rolled without forging, the hot-rolling plant being sufficiently elastic to admit of this method of working even with tapered ingots such as described above. It should be pointed out, however, that unless the ingots are exceptionally sound and free from slag inclusions or cold laps (insufficiently cleared in machining) it is very difficult to obtain sheets of a first class surface by this direct method, and it will be clear to those who have had experience in such work that the process of reducing large square ingots of this type to sheets of the order of 3 ft. or 4 ft. in width necessitates some intermediate "frazing," "scurfing" or "grinding" treatment in order to remove internal defects which only reveal themselves in the later stages of sheet production.

Scheme and Lay-Out. On the basis of the foregoing arguments and conclusions a scheme and lay-out was decided upon in which the sequence of operations is :—

(*a*) Casting of ingots
(*b*) Machining of ingots
(*c*) Forging
(*d*) Fettling or frazing
(*e*) Hot-rolling to sheet bar or strip
(*f*) Hot-rolling of sheet bar to sheets

The flow of operations is illustrated in Figs. 1 and 2.

Ingot practice for sheet and strip work is standardized on the basis of production of two sizes of ingots of 5 in.^{2} and 8 in.^{2}, weighing approximately 600 to 1600 lb. respectively. For the production of rod and wire, which operations are carried out in an adjacent plant, smaller ingots are made (approximately 100 to 200 lb.) using the same casting equipment. Fortunately one disadvantage of the square type of ingot, namely, cost of, and time occupied in, machining, has been appreciably reduced by the introduction of the square turning lathe which machines a square ingot in exactly the same manner that a round ingot can be treated, *i.e.*, by a simple turning operation. In the present scheme a square turning lathe supplements the operation of planing machines.

From the machining operations ingots pass directly either to the forging plants or to hot-rolling. For intermediate overhauling of forged or rolled surfaces pneumatic fettling hammers are provided and also a "frazing" or "scurfing" machine. Since the latter type of machine is more common abroad than in England a short description is inserted here :—

The machine is specially constructed for the overhauling of nickel alloys, and is of a particularly robust design. The principle of operation is that of the ordinary milling machine with a circular cutter, except that the cutter mounting is not rigid but flexible and driven entirely independently of the moving table. The latter, of course, is capable of traversing either transversely or longitudinally, and the pressure of the cutter itself is regulated by means of balance weights.

The machine is largely automatic, but the operator can control operations of frazing in such a way as to deal with any inequalities in the surface or abnormal flaws or roaks in the metal. For the treatment of deep slivers or flaws the machine can be stopped and the milling cutter held in any position until these are completely removed so as to leave a smooth-edged indentation.

The method of driving the cutter is by separate motor mounted on a swinging arm through a double worm gear, running in double ball bearings. The cutter itself is very accessible and can be quickly and readily changed.

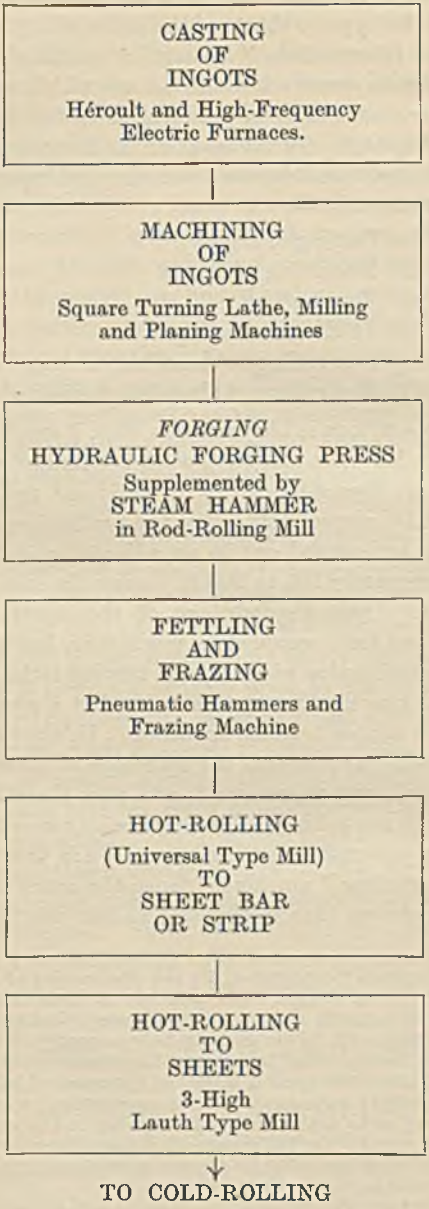
CASTING OF INGOTS
Héroult and High-Frequency Electric Furnaces.
MACHINING OF INGOTS
Square Turning Lathe, Milling and Planing Machines
FORGING
HYDRAULIC FORGING PRESS
Supplemented by STEAM HAMMER in Rod-Rolling Mill
FETTLING AND FRAZING
Pneumatic Hammers and Frazing Machine
HOT-ROLLING
(Universal Type Mill) TO SHEET BAR OR STRIP
HOT-ROLLING TO SHEETS
3-High Lauth Type Mill
TO COLD-ROLLING

Fig. 1.

Broadly, the facilities provided enable forgings both in bloom and shaped form, rolled billets, slabs, sheet bar and strip, together with sheets and light plates, to be made as required and in accordance with the special properties of the materials being handled.

The principal productive units described in the following pages comprise :—

(*a*) A 750 ton high-speed steam-hydraulic forging press.
(*b*) An 18 in. three-high universal type mill.
(*c*) A 52 in. Lauth type sheet mill and the requisite auxiliary equipment for heating and for handling and disposing of the rolled product.

3.—Buildings and Services.

In ordinary circumstances the design of the building for the accommodation of operations and equipment as here indicated would present no serious problem but in the present case the site conditions created certain difficulties. The land available consisted of a narrow elongated area bounded on the one hand by the space necessary for other contemporaneous factory developments and on the opposite by a canal. Under previous ownership the site had been excavated in such a fashion that the differences in level were both acute and considerable.

After a careful study of the existing conditions which was much facilitated by the method developed by one of the authors and described by him elsewhere * of employing a plasticine model, it was decided to house the new department in a long building roughly parallel to the canal and containing under one crane service the metal storage, melting, machining and forging sections as well as the rolling-mill equipment and with space available for a future annealing plant. The building as finally designed is a compromise between the limitations imposed by the site and the technological requirements of the manufacturing operations. It consists of a main bay 80 ft. wide and 540 ft. long having a height of 30 ft. to the crane rails and 35 ft. to the eaves. This is flanked on the canal side by a partial length lean-to for the electric equipment of the melting furnaces and the steam boiler plant also by a short perpendicular bay or annex housing the shear and coiler belonging to the universal mill plant. The general arrangement of the building and of the equipment it contains as well as its relationship to the contiguous sections of the works is shown in Fig. 2 whilst Fig. 3 (Plate LVII) gives a good idea of the interior appearance.

The design of the steelwork follows conventional lines but is exceptionally heavy. The roofs, where not glazed, and the side walls

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* H. Williamson, *Engineer*, 1928, 146, 711.

down to a distance of 8 ft. from the floor level, are covered with asbestos protected corrugated steel sheets. Below this point brick curtain walls have been built. The natural lighting has been liberally arranged for by glazing approximately 30 per cent. of the roof area and providing an almost continuous belt of glazing along the wall under the crane girders on the canal side. The artificial illumination has been designed to secure a sufficient general intensity of lighting, the illumination value at floor level being 6 ft. candles, without necessitating recourse to supplementary local intensification.

The shop floor consists principally of cast iron plating laid on ashes but the section allotted to machining operations and the area beyond the sheet mill are laid with wood block paving.

The building foundations call for no comment, but those for the heavy plant are interesting in being built in hard blue brick set in cement in lieu of the more usually adopted concrete construction. Owing to the complexity of many of these foundations it was considered that this type would be no more expensive than concrete since the elaborate shuttering required with the latter could be eliminated. It would also possess the advantages of better bonding and comparative facility for making alterations during construction should a mistake occur.

The main bay is served by a 10-ton electric overhead crane which is provided with a 3-ton auxiliary hoist, later a second crane will be added. The shear and coiler annex is commanded by a 1-ton floor controlled electric overhead crane having a double lift. The track for this crane is extended from the annex into the main building below the main crane to enable the direct transference of loads to be made. (See Fig. 2.)

Electrical energy is derived from the City of Birmingham Electric Supply, which is now in course of being changed over from 25 cycles to 50 cycles periodicity to bring the area in line with the standardized frequency adopted by the Electricity Commissioners. At present a 1,500 kw. frequency changing set has been installed which will be taken out of service as soon as the change-over has been effected. High tension current at 11,000 v. will then be transformed down to 400 v., at which pressure it will be utilized throughout the new plant. To reduce conversion losses it was decided to adopt alternating current for all auxiliary motors.

The steam requirements for the forging press and other miscellaneous purposes are met by a multi-tubular dry-back oil-fired boiler with an evaporative capacity of 8000/9000 lb. of steam per hour at a pressure of 150 lb./in.^{2}

The water requirements are taken from the town supply.

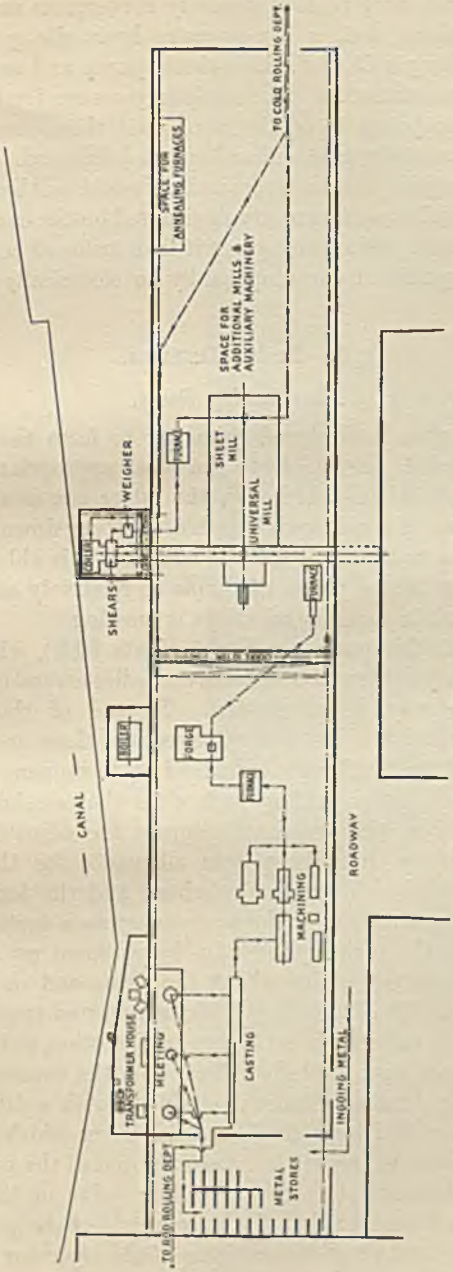

FIG. 2.—Flow Sheet and General Arrangement.

For the operation of various auxiliary movements on the mill and for furnace pushers, &c., a low-pressure hydraulic power plant is installed comprising a 15 H.P. three-throw pump and an 8 in. × 8 ft. weight loaded accumulator. The working pressure for this system is 700 lb./in.^{2} The pump is of the horizontal three-throw type with all working parts totally enclosed and splash lubricated.

The fuel oil required for the press and universal mill heating furnaces and boiler is stored in a main reservoir situated on the canal side with a capacity of 37 tons. From this point it is distributed to service tanks placed near the points of consumption by an electrically driven rotary pump.

4.—PLANT DETAILS.

The Forging Press.

The forging press is designed primarily to form the cogging unit and serves to reduce the ingots to the most appropriate sections for feeding the universal mill, although the latter can as already stated, when such a course is considered desirable, itself cog down ingots having a cross-section up to 9 in. × 9 in. In addition, it is able to undertake the production of forged pieces of simple or relatively easy shape, the demand for which in some nickel alloys is growing.

The design of this press, see Fig. 5 (Plate LIX), whilst following conventional practice in main essentials, embodies several improvements, some of which may be mentioned. Instead of the usual press "columns" or tension bolts of circular section, these are made square over the length traversed by the crosshead guide slippers. This affords a much larger and better guiding surface for the crosshead, especially as, in this instance, the crosshead slippers are adjustable and can, therefore, be set-up to make proper allowance for the differential expansion occurring between the crosshead and the top and bottom plattens of the press. One of the press columns is further utilized as the inlet pipe to the main cylinder by being bored up hollow, which reduces the amount of piping about the press and imparts a clean appearance to it. The intensifier is of the inverted type arranged for the working stroke to be made in the upward direction, so that the return stroke is more easily accomplished than when the reverse procedure is adopted. The hydraulic cylinder is equipped with a differential ram. The press is controlled by a single-handing lever which is coupled to the steam admission valves of the intensifier and of the press crosshead pull-back cylinders and also the pre-filling valve of the main press cylinder in such a manner that the movements of the press crosshead follow accurately and at all times those of the operator's hand. The

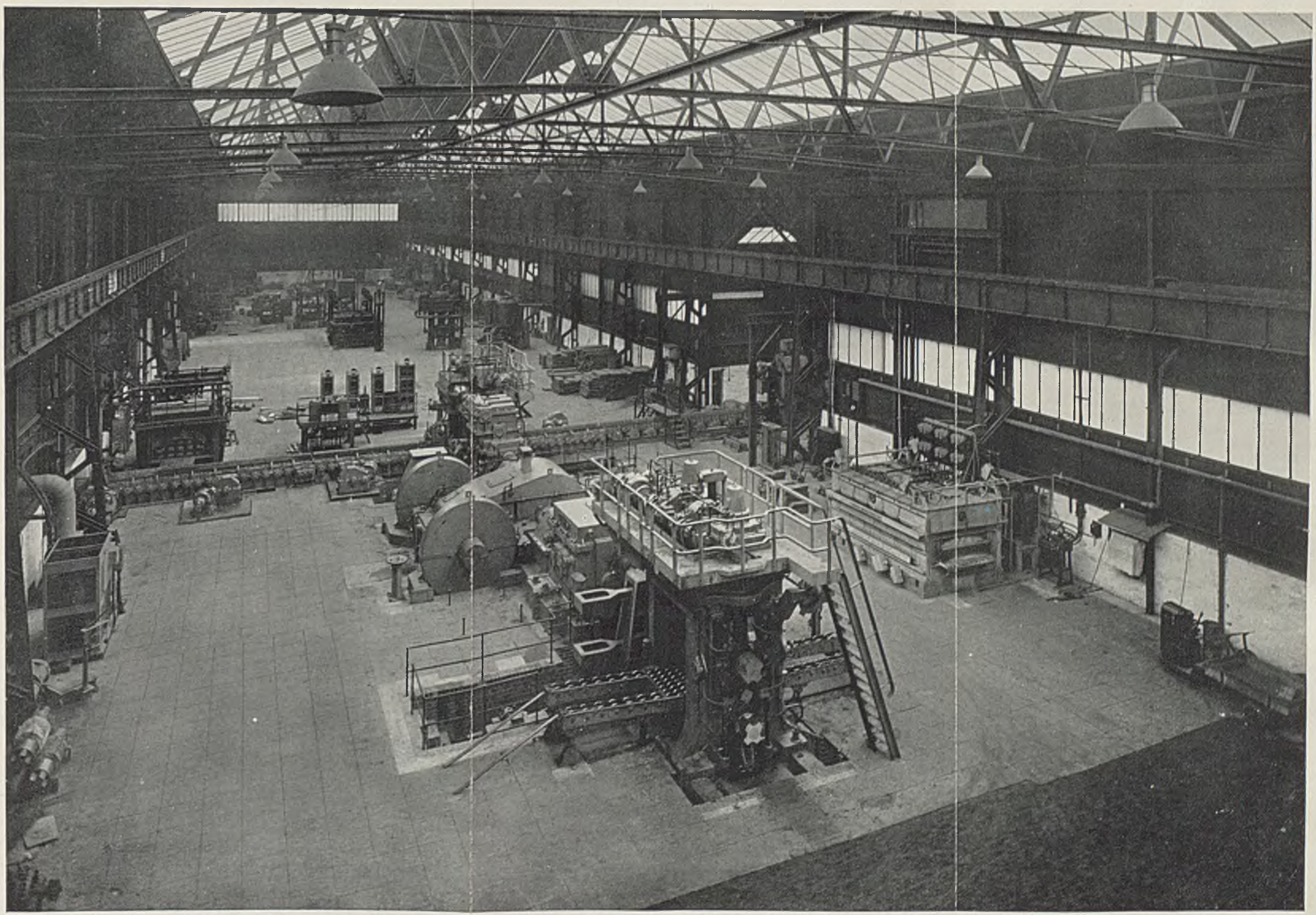

FIG. 3.—General View of the Plant.

[To face p. 400.

PLATE LIX.

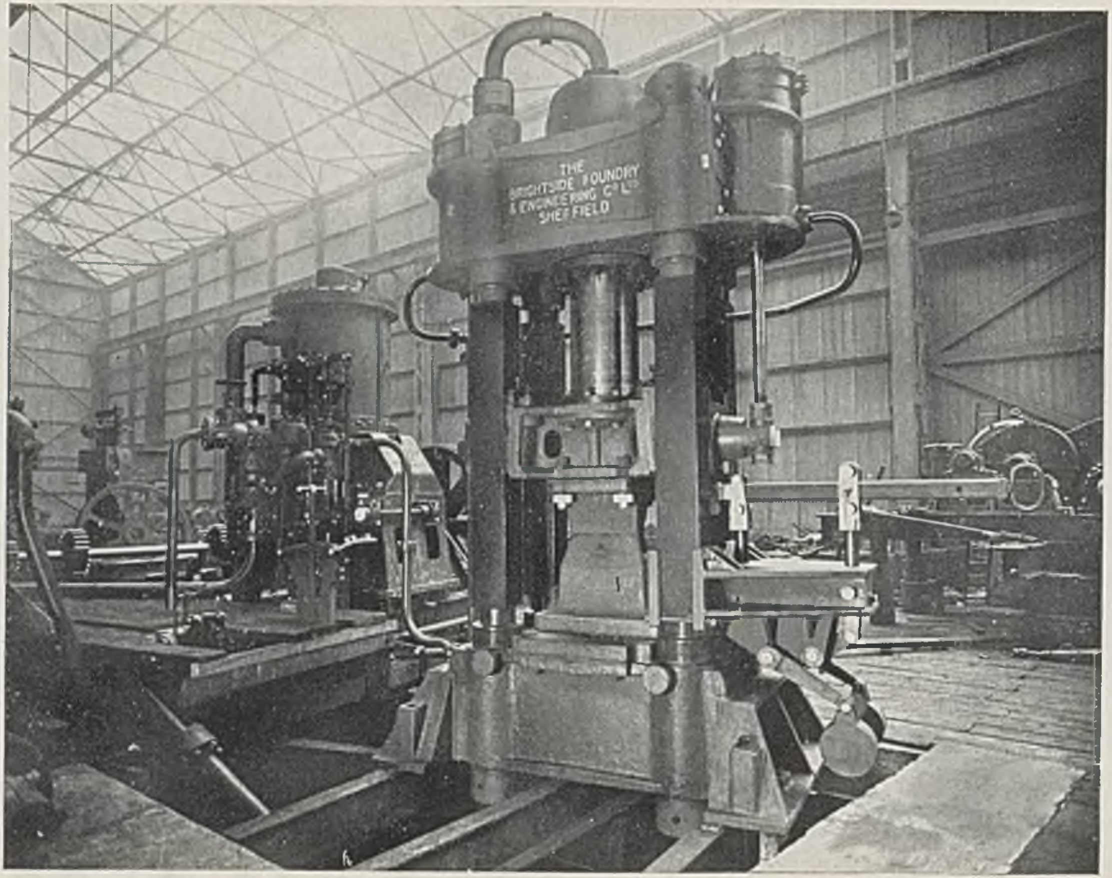

FIG. 5.—Forging Press and Intensifier.

[*To face p.* 400.

PLATE LX.

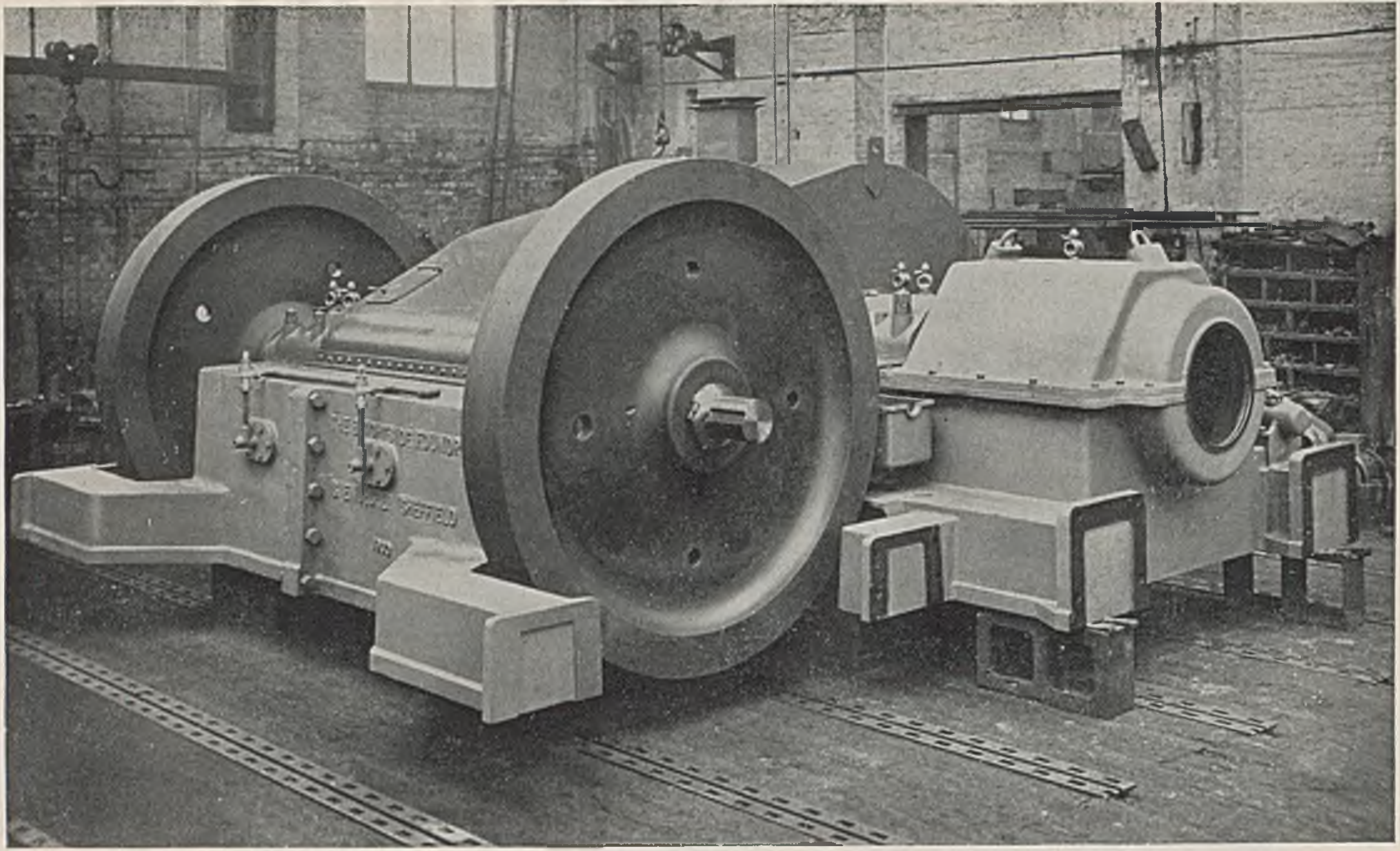

PLATE LXI.

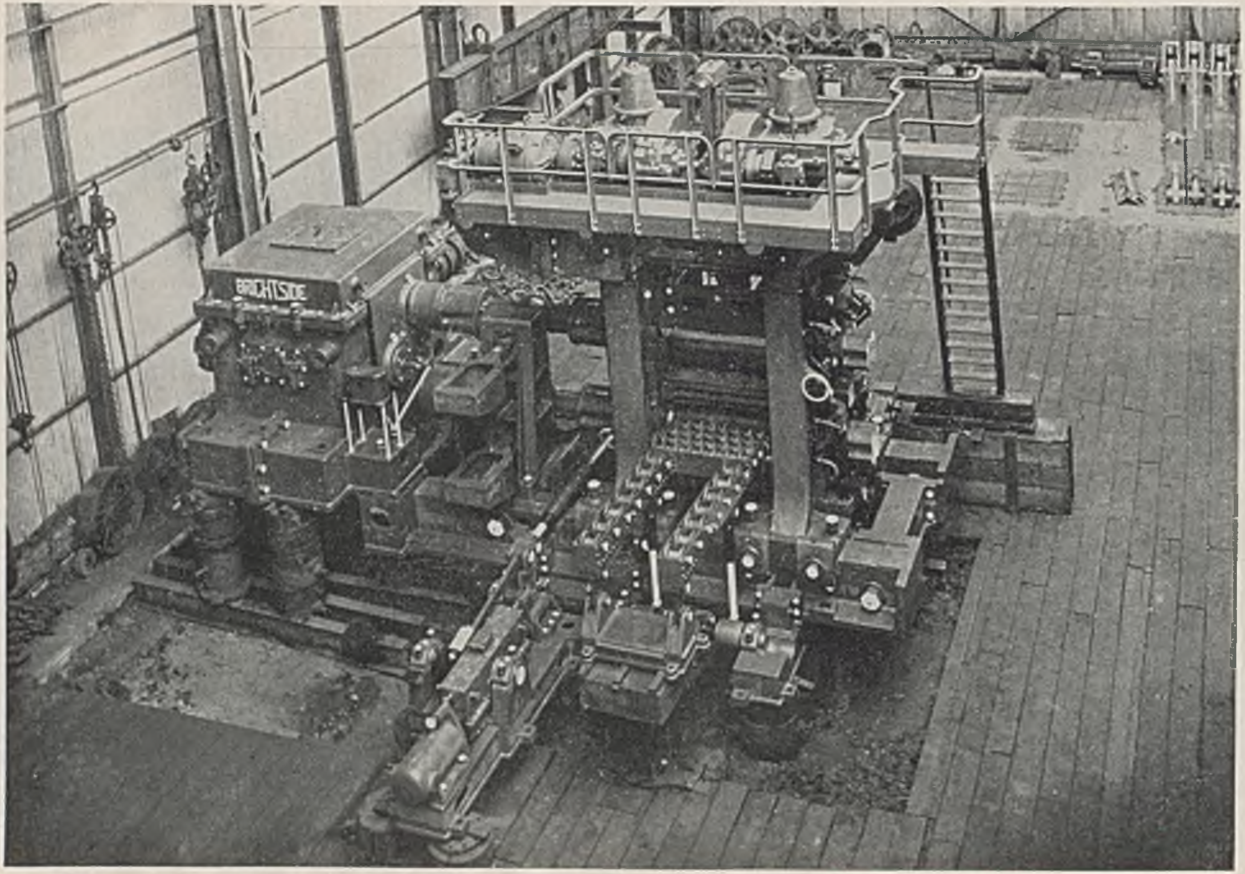

FIG. 7.—Lauth-Type Sheet Mill.

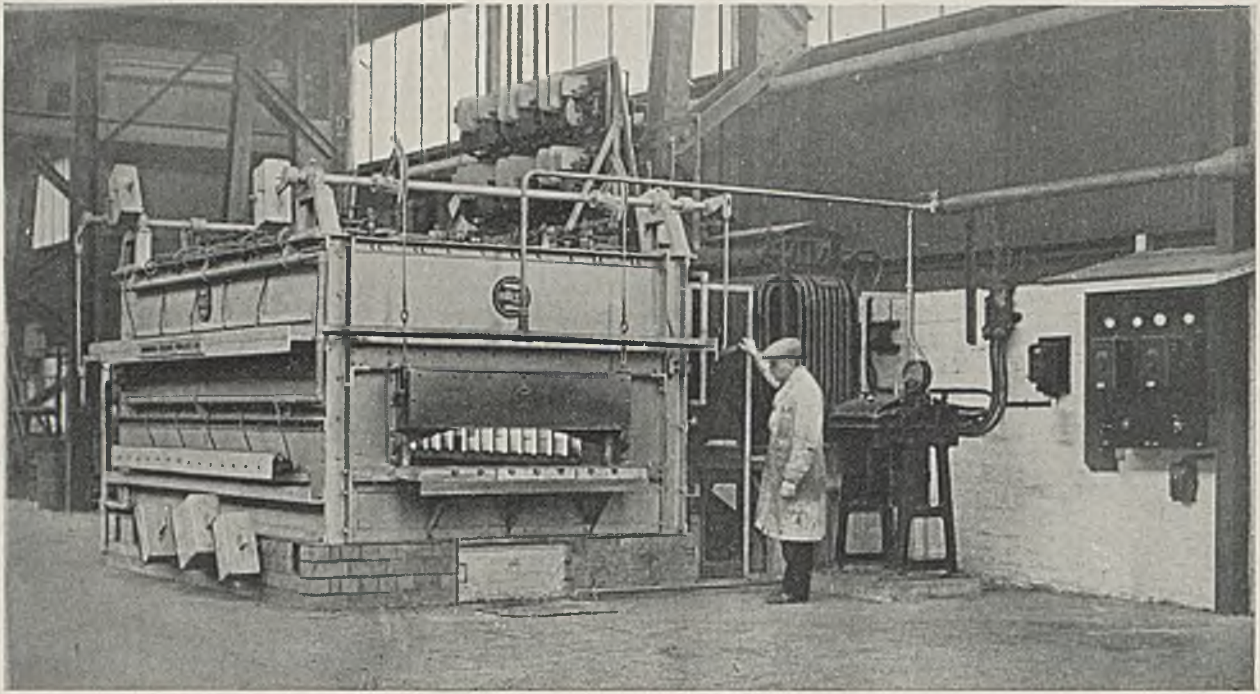

FIG. 8.—Electrically Heated Sheet Bar Furnace.

PLATE LXIII.

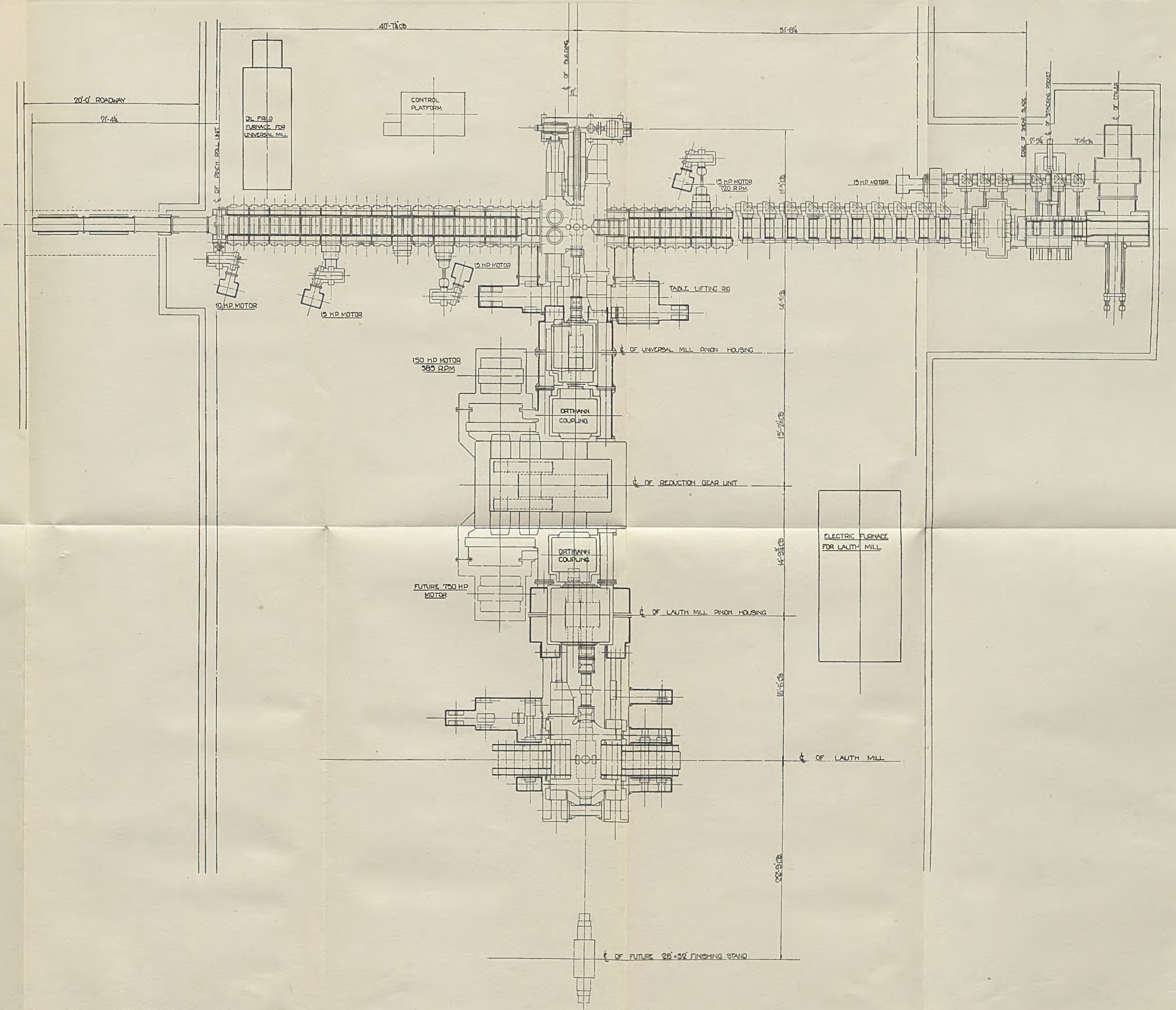

Fig. 9.—General Lay-out of Rolling Plant.

[*To face p.* 400.

principal shafts of the control gear are mounted in ball bearings and these coupled with the equilibrium type valves employed for controlling the steam admission render the operation of the press extremely easy and call for practically no muscular effort on the part of the driver.

The press is at present served by a single hearth-type oil-fired reheating furnace with a hearth area of 6 × 8 ft. Space has been left for the installation of a second unit. Manipulation of ingots at the press and furnace is controlled by a 1-ton electrically-operated self-contained jib crane. At a later date the forging plant will be completed by the installation of a simple type of press manipulator which will at least double its productive capacity.

The Hot-Rolling Mill Plant.

The two hot-rolling mills mentioned above are arranged on either side of a common gear reduction unit. At present this is driven by a single 750 H.P. forced ventilated induction motor with a synchronous speed of 585 r.p.m. which provides adequate power to operate one of the mills at a time. When the production required is such as to call for the simultaneous running of both mills, a duplicate motor running in parallel with the first machine will be added at the other end of the driving pinion shaft of the gear unit. The gear unit is designed to transmit a normal horse power of 1,500 and peak loads of up to 4,500 H.P. The gearing ratio is 9·6 : 1 giving a speed of 61 r.p.m. to the final drive shaft.

Between the gear unit and the pinion housing of each mill is interposed a hydraulically operated main coupling of the improved Ortmann type, cradle supported, totally enclosed and continuously lubricated. These couplings enable either mill to be connected or disconnected from the drive in about 2 minutes. The casing of one of these is shown in the general view of the gear unit reproduced in Fig. 6 (Plate LX).

The gear unit is of the double reduction type with symmetrically arranged gearing and a pair of flywheels over-hung on the motor pinion shaft. The first reduction comprises a pair of single helical gears, the pinions being integral with the pinion shaft, and the gears lying on either side of the single double-helical second reduction pinion. The advantages of the symmetrical disposition are the equal loading of the bearings carrying each shaft which results in the maintenance of the alignment and consequently of the tooth contacts when eventually some wear occurs. The gearing is mounted in a massive bedframe and is of course totally enclosed, below, by the bedframe constituting a pan, and above by means of a heavy welded steel casing. The total weight of this gear is approximately 100 tons.

The lubrication of the gear unit is effected from a central automatic gravity return lubrication system which also serves the disengaging couplings, the two pinion housings, the screw down gear mechanisms of the two mills and the vertical roll drive for the universal mill. About 30 gall. of oil are circulated per minute. The oil gravitates from a high-level storage tank, carried from two of the shop columns, to the points to be lubricated and is sprayed on to the various gear teeth and fed into the bearings. The supply to each point is individually adjustable and visible. After use the oil is drained away by gravity to the main return tank located in a special cellar in the mill foundations. This tank is equipped with settling compartments and duplicate filters to clean the oil and remove water and sludge. The oil is circulated by a pair of rotary pumps, one driven from the gear unit and the other, a standby, by an independent motor. The extensive employment of such a lubrication system is fully justified commercially by the reduced oil consumption, less wear and tear on the plant resulting from the continuous lubrication of the important working parts with oil in good condition, coupled with their thorough enclosure, also by the saving in attendance and increased reliability.

(a) *Three-High Universal Type Mill.* When the decision to employ relatively large ingots of square section had been taken, it became necessary to investigate the most economic equipment for the production of both the requisite sheet bar and strip. As has already been indicated, the normal practice is to utilize the forging press for the preliminary reduction to a convenient slab section. In view of the diversity in requirements for semi-finished material the flexibility of the universal type of rolling mill appeared likely to afford the most rational solution, as by its means it is feasible to produce stock of any cross-sectional dimensions within the capacity of the mill without changing rolls or making any other lengthy adjustments. Hitherto the intermediate or semi-finished products for sheets in alloys of the type under consideration have been rolled in mills with fixed grooved rolls, following the conventional methods for the production of steel sheet bar, with the drawback of limitation in range of section without roll changing. One of the authors has already drawn attention to the advantages in sheet bar production attendant upon the adoption of a universal mill and references are given below to the sources where these arguments have been more fully developed.*

It was considered that in addition to rolling sheet bar of the various

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* G. A. V. Russell, "Possibilities in Re-habilitation of Existing Rolling Mill Equipment in British Steel Works," *Iron and Coal Trades Rev.*, 1928, **116**, 555, 665; and *Engineering*, 1928, **126**, 243, 274, 379.

weights required for further processing, the universal mill should be capable of rolling strip up to 15 in. in width. The maximum length of product to be taken care of was fixed at 65 ft. In view of the relative hardness of the majority of the alloys to be dealt with the question of stiffness and rigidity of the mill became most important and for this reason a departure from the usual design of universal mills was made by arranging the mountings of the vertical rolls on the outside of the roll housings. This permits of the horizontal of main rolls being made of such a length as to deal satisfactorily with the maximum width of product desired without reference to the need further to lengthen the barrels to provide space for the accommodation of the vertical rolls and their mountings between the roll housings as in the normal design of universal mill. To keep the distance between the centres of the vertical and horizontal rolls of the mill to that usually obtaining in universal mills, the shape of the roll housing posts on the side upon which the vertical rolls are mounted is of a special form. In this case the horizontal rolls have a barrel length of 21 in. All rolls have a diameter of 18 in. and are positively driven from the pinion housing. The rolling speed of the mill at the synchronous speed of the main driving motor is 300 ft./minute. The vertical rolls have a diameter of 14 in. These rolls are carried in a novel fashion on the extremity of stiff rectangular rams sliding in guides cast with the roll housings. They are driven from fixed mitre gears totally enclosed through the intermediary of flexible spindles. This arrangement is superior to the usual method of driving the vertical rolls of universal mills in that it permits the gearing to be more liberally proportioned and effectively enclosed and lubricated. Furthermore, with the type of mounting above described, the liability for scale and dirt to damage the bottom guiding surfaces of the vertical roll frames is entirely eliminated. The appearance of these new developments in universal mill design is well shown in the general view of the mill on the builder's erecting floor reproduced in Fig. 4 (Plate LVIII).

Several improvements have been embodied in connection with the mounting and adjustment of the main rolls. To reduce power consumption, roll neck and bearing wear and increase accuracy of product, the main chocks are of the totally enclosed type, having compound wearing surfaces of white metal and phosphor bronze, and further the chock bodies are made hollow for water cooling. The lubrication of the roll necks together with that of the chocks in the housing windows is effected positively by grease under pressure from a mechanical grease pump with independently adjustable multiple feeds operated from the vertical roll driving shaft. The screw down gear is of the two-motor type. Each motor is connected to the worm gear operating one screw by a train of reduction gearing but the two sets of gearing can be connected at will by means of an electromagnetic coupling so that either screw or both may be operated as desired. The movements are controlled by a six-point push button type master controller situated on the operating pulpit. Further, two screwing speeds are provided, the higher speed of 40 in./minute for sheet-bar rolling and the lower of 12 in./minute for strip production. The screwing torque available at the slow speed is sufficient to enable the operator actually to screw down on the metal during a pass to correct a tendency for the stock to curve.

The necessity of maintaining the surfaces of the rolls in first class condition has been fully appreciated and to facilitate frequent grindings the roll changing procedure has received special consideration. The main rolls complete with their chocks are removable axially through the window of the outer roll housing by means of an hydraulically operated shifting device to a position sufficiently far away from the roll stand to afford easy access of the shop crane to the assembly. All the subsidiary operations in roll changing have also been made equally convenient so as to be speedily accomplished.

The pinion housing rests directly on the foundations and is connected to the bedframe of the gear reduction unit through the disengaging coupling bedframe and on the other side the mill bedplates are rigidly attached to it, thus the whole train is self-contained. The lower portion of the housing which accommodates the pinions for the horizontal rolls is constructed on the usual lines with the pinion bearings located in deep jaws or windows at either end, but the upper part which contains the gearing for the vertical rolls drive is built up on the layer system with a joint at the axis of each shaft.

The drive is by the central pinion and to equalize the rate of wear on the teeth a separate zone on the faces of the pinions is reserved for the transmission of power to the vertical rolls drive. The intermediate gear in the latter transmission is arranged as a " free-wheel " drive to permit the slippage of the vertical rolls when the piece has been engaged by the horizontal rolls and thus relieve the drive of any undue strain.

The total weight of the universal mill with its main tilting tables and their operating mechanism amounts to 165 tons.

The general arrangement of the universal mill and its auxiliary equipment will be gathered from Fig. 9 (Plate LXIII). On either side of the roll stand are tilting tables. These tables are hydraulically operated. With the operating mechanism is associated a hydro-pneumatic balancing device, which entirely eliminates all shock and jar in spite of extremely rapid motion of the tables, a complete stroke of which in either direction takes less than 1 second. The movement for the raising and lowering of the middle roll is also derived from the operating mechanism of the tilting tables. The rollers of all roller tables in the plant are carried in roller bearings and the gearing is totally enclosed and bath-lubricated.

Beyond the tilting tables the roller gear is extended on the entry side to the discharge from the reheating furnace and further to a pinch roll unit leading to a subterranean strip chute running under the road which parallels the new building, and on the delivery side to an electrically driven cropping and cutting up shear. Beyond the latter is located a stacking pocket for cut-to-length material up to 5 ft. long. This pocket is hydraulically displaceable in a transverse direction. When "cut-to-length" stock is being produced the pocket is positioned directly behind the shear where it remains until full when it is traversed to one side to permit of discharging by means of the special 1-ton floor-controlled crane operating in the shear annex. Strip material is required coiled and for this purpose an automatic electrically driven strip coiler is located beyond the stacking pocket. When coiled stock is being produced the latter is moved into its discharging position which simultaneously brings up a short length of driven roller gear into line with the approach table to the shear to conduct the stock into the coiler.

The shear is designed for a maximum blade load of 110 tons and can cut either flats, billets or sheet bar within its capacity. It is of the up-cutting type with the bottom blade and bolster flush allowing piling to take place directly behind the blades. The motor reduction gearing and clutch are mounted in a housing carried directly over the shear approach table to economize space. The driving mechanism, including the hydraulically operated automatic disengaging clutch, is totally enclosed and lubricated on the automatic gravity return system. A stop and measuring gear to deal with lengths up to 5 ft. is provided. The shear is driven by a 20 H.P. motor geared to give a speed of 30 cuts per minute.

The coiler is located below the run-out table to permit of stock running out beyond it, should it be advantageous at a later date to roll increased lengths. For this purpose provisions have been made to instal further live rollers in the coiler frame and also to add a hinged chute with dead rollers capable of being swung outwards over the adjacent canal. The strip is diverted downwards into the coiler by a deflecting switch, arranged between adjacent table rollers and passes through pinch rolls into the circular space bounded by a nest of six positively driven rolls. Here it is coiled up, the rolls gradually opening out into an ever increasing circle. The radial movement of the guide rolls is controlled by an adjustable weight counter-balance which can be varied within limits to modify the radial resistance imposed upon the strip to suit its character and the desired degree of closeness of wrapping of the coil. When the strip is completely coiled up the rollers are opened out still further against the resistance of the balance weight by an hydraulic cylinder, whereupon the coil drops on to a centrally disposed core and hangs there until a hydraulically-operated stripper ejects it on the coil receiving stand from which batches of coils are removed by the annex crane. The coiler is capable of dealing with strip up to 15 in. wide and 0·375 in. in thickness at the full delivery speed of the universal mill. It is driven by a 50 H.P. induction motor through totally enclosed and automatically lubricated reduction and transmission gearing.

The mill is served by a continuous-heating furnace of the end-discharge type having a hearth length of 15 ft. and equally adapted to the heating of ingots or forged slabs. This furnace is equipped with dual means of firing by oil or town's gas. The stock is pushed through the greater portion of the hearth length upon nickel–chromium skids by a hydraulic pusher. Towards the exit end the skids are discontinued and the material enters the equalizing or soaking zone from which it is at present withdrawn manually on to a sloping skid plate which discharges it on to the approach table of the mill. Provision has been made, however, to mechanize this operation when desired.

(b) *Three-High Lauth Sheet Mill.* This mill is intended for the production of sheets up to 48 in. wide. Initially both roughing down and finishing will be performed on the one stand. At a later date if it is found necessary to put down a second stand for finishing it is intended to instal a two-high type arranged in line and driven from the bottom roll of the present stand through a connecting spindle of sufficient length to permit of the incorporation of a common roll changing device to serve both stands. The connecting spindle would be hydraulically movable transversely after sliding off the coupling boxes to provide the requisite space for the withdrawal of the rolls. The present three-high stand has also been designed to roll heavy sheets or light plates in lengths up to 12 ft. and from slabs ranging up to 1½ in. thick. The top and bottom rolls have a diameter of 26 in. and the middle roll 16 in. while the common barrel length is 52 in. The normal speed of the main rolls is 37 r.p.m. giving a rolling speed of 250 ft./minute. The reduction in speed from that of the slow speed shaft of the main gear drive of the plant is obtained by the employment of a speed-reducing pinion housing, the central or driving pinion of which is offset to maintain a sufficient diameter by the increased gearing centres.

The general character of the detailed design of the Lauth mill is similar to that of the universal mill. A view of the plant is given in Fig. 7 (Plate LXI). The screw down gear is operated by a single 30 H.P. motor which is coupled to hollow driving pinions of individual reduction gears for each screw by electro-magnetic couplings to permit of simultaneous or independent operation of the screws. For serving the rolls a pair of substantial tilting tables is provided equipped with dead rollers. These tables are sufficiently robust to stand up to the heaviest work the mill is called upon to perform whilst not being too cumbrous to impede the manipulation of the ordinary weights of sheet produced. As in the case of the universal mill they are hydraulically operated in conjunction with the middle roll of the mill. The Lauth mill plant with its tables weighs 170 tons.

The heating of sheetbar for this mill is carried out in a special semi-continuous electric furnace, see Fig. 8 (Plate LXII). The furnace is double-ended and the material is carried through by a walking beam conveyor. This conveyor is not worked continuously but is actuated through push button control when required. When a heated bar has been removed for rolling, a cold one is placed in at the charging end and the mechanism set in motion. The bars in the furnace are moved forward the width of one bar, and the conveying mechanism then automatically stops. In order to prevent any possibility of grit sticking to the material, metal rods and not refractory materials support the charge in the furnace.

The furnace is heated by means of silicon carbide (" Globar ") elements arranged vertically in each side of the chamber. Electrical contact with the elements is obtained by means of spring-loaded (water-cooled) terminals. A pump circulation system is employed for circulating the water through the " Globar " terminals, thus preventing waste.

The furnace is designed for operation at temperatures up to 1300° C., and can deal easily with an output of half a ton per hour. The electrical rating is 300 kw., which is divided into two separately controlled zones. The supply taken at 400 v., 3-phase, 50 cycles, is stepped down to a lower voltage at the furnace by means of a transformer. This transformer is provided with tappings so that the voltage on the elements can be increased as their resistance increases, and their usual life prolonged. Control of temperature is entirely automatic; the two zones being controlled within close limits by means of two potentiometric controllers.

The furnace chamber is 12 ft. long inside the doors and 4 ft. 6 in. wide. The heat losses are small, as the furnace is well insulated with 12 in. of highest quality insulating brick (Kieselguhr) and powder.

5.—GENERAL REMARKS ON THE HOT-WORKING OF NICKEL AND ITS ALLOYS.

The hot-working of nickel and such of its alloys as are intended for service at high temperatures gives rise to certain special problems which centre mainly round two points :—

(*a*) The necessity for obtaining and maintaining temperatures of the order of from 1000° C. to 1300° C. during working.

(*b*) The heating of ingots, billets, &c., in an atmosphere as free as possible from deleterious gases (*e.g.* containing sulphur) with the avoidance of excessive oxidation.

(*a*) In the range of temperature indicated most of the high nickel-content alloys of commercial compositions can be fairly readily forged or rolled, but it is characteristic of some of them (*e.g.*, nickel–chromium alloys) that round about 700° C. or 800° C. they pass through a brittle range and develop edge-cracking and other similar faults which give rise to much trouble in later stages of working.

It is therefore very essential that the metal to be forged or rolled shall be thoroughly and uniformly heated throughout to the required temperature, and the speed of "working" be such as to maintain the temperature well above this brittle range so long as hot-work of any kind is being applied.

These remarks relate in some degree also to coiling operations if such are to be carried out hot, although, of course, strip and rod in the thinner gauges may be coiled in the cold. It is obvious therefore that a close study must be paid to such factors as :—

(1) Heating methods and practice;

(2) Percentage reduction per pass or per press or hammer stroke in rolling and forging operations respectively;

(3) Speed of deformation;

(4) Quickness of manipulation.

(*b*) The problem of heating furnace design is vitally important for the successful hot-working of these materials, and it is, unfortunately, not yet possible to say that it has been satisfactorily solved. In general, coal-fired furnaces are cheaper if regard is paid only to cost of fuel, but these are not as a rule convenient to use or satisfactory so far as furnace conditions and atmosphere are concerned.

Oil or gas-fired furnaces are more convenient, but even in the best of these it is difficult to get an atmosphere sufficiently non-oxidizing. More important, however, is the question of a satisfactory degree of freedom from sulphur. It is well known that sulphur is very deleterious to nickel and its alloys, and this fact is of supreme importance in hot-working practice. If the material to be worked is attacked by sulphur, at high temperatures, nickel sulphide is formed, and immediately gives rise to local surface cracking. This is aggravated if the metal is covered by a layer of oxide, since nickel oxide readily reacts with sulphur. Under such conditions surface interpenetration of crystal grains by nickel sulphide takes place and serious troubles ensue.

Electric heating is unquestionably the most satisfactory method of heating, but to bring it within the possibilities of reasonable economic practice considerable skill in designing the furnace is essential. The type described and illustrated on p. 407 and Fig. 8 (Plate LXII), so far as the present authors are aware, is one of the best yet evolved, and is giving satisfaction in practice.

Acknowledgments.

In conclusion the authors would like to record their indebtedness for advice and assistance to many friends and colleagues. They are particularly grateful to Mr. A. F. Dixon, of Messrs. Brightside Foundry & Engineering Co., Ltd., builders of the forging and mill plant, and to Mr. A. Glynne Lobley, of Messrs. Birmingham Electric Furnaces Ltd., for valuable co-operation. They also desire to thank Messrs. The Mond Nickel Co., Ltd., through its Delegate Director, Mr. D. Owen Evans, for permission to publish the paper.

DISCUSSION.

Dr. W. J. P. Rohn [*] (Member): I should like to congratulate the authors on the work described in this paper, which shows very clearly the nature of the development which may be expected in future so far as non-ferrous metals are concerned. The fact that the alloys with which the authors have been dealing are of greater strength than steels at rolling temperature, and that their output must, of course, be much smaller than that of iron and steel, makes the problem even more complicated and difficult, and I think that we must all admire the way in which the authors have dealt with it.

This kind of work seems to me to be a sort of link between iron and steel and the non-ferrous metals, so that this paper forms a very suitable introduction for a joint meeting of the two Institutes. Perhaps it may be of special interest to look again into the same subject after another decade, and to see then whether the general line of development has followed that described in the present paper or the other one dealt with in the paper presented to the London Local Section in November 1931.

Dr. W. H. Hatfield [*] (Member): I have read this paper with very great interest indeed. I am one of those members of both Institutes who fully appreciate the great value of these joint meetings. We in the steel world have much to learn from those who are working in the non-ferrous industries, but, if the authors will forgive me for making the observation, we are not so much interested in the precious metals. Nickel is one of those metals which has a great affinity for gold! It seems in a mysterious way to follow the fortunes of gold; and, speaking now as a member of the Iron

[*] Director, Heraeus Vacuumschmelze A.G., Hanau a. M., Germany.

[†] Director of the Brown–Firth Research Laboratory, Sheffield.

and Steel Institute, I think that I may say that we shall be far more interested in the authors' researches on nickel when the economic aspects of nickel are such that we can really take a practical interest in that metal. I hope that the authors will pass that on to those concerned, who can be the means of encouraging this greater interest which we should like to take, since we know that nickel is quite a valuable metal to add to iron with a view to modify its properties.

With regard to the paper itself, there are only two points which I should like to mention. First of all, a very important point arises in Section 2 of the paper, where the authors say that they found it necessary to plane all the nickel ingots, to machine the surfaces. That is probably one reason why the metal is at such an uneconomic level; but it would be interesting if the authors would explain technically what the difficulties are as regards the surface of these nickel ingots which necessitate these machining operations. Is it cold lapping or trapped slag, or is it a case of occluded gas being given off under the skin with the formation of subcutaneous blowholes? In other words, if the authors can state the nature of the defects which make it necessary to remove this metal, members of both Institutes will probably learn a good deal. Incidentally, it is conceivable that members of the Iron and Steel Institute may be able to give the authors some helpful comments.

The only other point that I wish to mention is that emphasis has been placed on the desirability of keeping these nickel ingots and nickel metals away from sulphurous gases. I believe that that is necessary, but we do find in ferrous metallurgy 10, 12, 15, or 20 per cent. of nickel may be added, and it would appear that those alloys are immune from action from the sulphurous gases. That is a very interesting fact.

Mr. RUSSELL (*in reply*): I thank you for the very kind reception you have given to our paper. We should have welcomed a critical discussion of some of the features embodied in the plant, but perhaps in the written discussion members will be good enough to give us the benefit of their reactions to our ideas.

Mr. BARCLAY (*in reply*): We thank Dr. Rohn very much for his kind remarks. I will see that Dr. Hatfield's comment is passed on to the proper quarter; personally, I am not responsible in any shape or form for the particular matters to which he refers.

With regard to the necessity for planing nickel ingots, it is possible to produce quite respectable-looking material without planing at all, but the trade requires an extraordinarily high standard of finish of sheets, and one of our difficulties, particularly with pure nickel and very rich nickel alloys, is due to the fact that we are using magnesium as a desulphurizing and deoxidizing agent. Anyone who has had experience in casting rich nickel alloys to which magnesium has been added will be familiar with the difficulty of getting perfectly clean ingots. The metal pours, as the caster says, "more like treacle than like water," and it is difficult to get a perfectly clean surface. We do get a very high standard, but we find that the operation of planing is a profitable one from the point of view of getting a very high-grade finish on sheets and strips.

With regard to sulphur, I quite agree with Dr. Hatfield that when nickel is present in alloys to the extent of only 10 or 12 per cent. the sulphur problem is by no means so serious as we find it to be in the case of the rich nickel alloys. In the plant described in the paper, we are dealing *inter alia* with alloys of from 70 to 90 per cent. nickel content, and with pure nickel itself, and I am sure that Dr. Hatfield will agree with me that with that class of material the problem of sulphur is serious.

OBITUARY.

Robert Bowran, J.P., died on October 24, 1932, at his home in Gosforth, Newcastle-upon-Tyne, at the age of 64. He had been active to within a few days of his death, for, as Chairman and Managing Director of Messrs. Robert Bowran & Co., Ltd., he was at his office as recently as Thursday, October 13.

Mr. Bowran founded his Company in 1893, and on its incorporation in 1909 became its first Chairman and Managing Director, which offices he held until the time of his death.

For the past five years he had been President of the Newcastle Chemical Industry Club, and was a Member of the North-East Coast Engineers and Shipbuilders.

For many years he was interested in the public life of his native town of Gateshead, being for some years a Councillor, and for over 20 years a Justice of the Peace. In this public work his chief interest was concerned with the Education Committee. Apart from this, his main interest lay in musical circles, and he was for over 30 years musical director of the Primitive Methodist Psalmody Association and conducted massed choirs of the district in the Newcastle City Hall.

Notwithstanding his intense application to his business, Mr. Bowran found time to be of service in many directions of value to others, and in addition to that already stated, his work as Chairman of the Newcastle Branch of the National Commercial Temperance League is worthy of mention.

His funeral, which took place at Gosforth on October 27, was attended by representatives of practically every firm and institution connected with the engineering world, and the Institute of Metals was represented by Mr. H. Dunford Smith and Mr. J. W. Craggs, both Past-Chairmen of the Local Section. Mr. Craggs also attended as a Director of Robert Bowran and Co., Ltd.

It can be truly said that Mr. Bowran spent his life in the service of others. The evidence of all this is in the affection with which his Staff spoke of him as the "Guvnor." They recognized in him not only master, but friend.

Mr. Bowran joined the Institute of Metals in 1911, and was always enthusiastic in promoting its welfare.

Professor Dipl.-Ing. Dr. Rudolf Hoffmann died suddenly on September 7, 1932, on his return from a long excursion with a party of his students.

He was born in Ingurtosi, Sardinia, on July 23, 1873, and studied at the Bergakademie at Freiberg i. Sa., where he took his metallurgical degree in 1898. In 1903 he was appointed Deputy Director of the chief works of the Staatlich Sächsischen Hütten- und Blaufarbenwerken. He obtained his Assessor's examination by means of his theses "Advances of the Last Twenty Years in the Extraction of Zinc by Dry and Wet Methods and their Application to Conditions in Freiberg" (*Jahrbuch für Berg- und Hüttenwesen in Kgr. Sachsen*, **1904**, pp. 19, 107) and "The Care of the Worker in the Government Foundry."

On November 1, 1906, he was appointed Professor of Metallurgy and Electrometallurgy at the Staatlichen Bergakademie, Clausthal-i. Harz, and held this post for more than twenty-five years.

Professor Hoffmann visited many districts in Germany in order to study foundry conditions, and came to England in 1909, when he took part in the

International Congress of Applied Chemistry in London, and in 1911 made a journey to Austria, the United States of America, Mexico, and Canada. He took part in the Great War, and won the Iron Cross, Second and First Class.

He was the author of many scientific papers, dealing chiefly with rolling processes of which he was the inventor and density determinations of metals in the solid and liquid states, his most notable publications being the section on the metallurgy of the metals arsenic, lead, cadmium, copper, nickel, cobalt, silver, zinc, and zinc white in Ullmann's "Encyclopädie der technischen Chemie," and the section on "General Metallurgy" in Kögler's "Taschenbuch für Berg- und Hüttenleute."

Professor Hoffmann was a member of the American Institute of Mining and Metallurgical Engineers, the Electrochemical Society, Gesellschaft deutschen Metallhütten- und Bergleute, the Deutsche Gesellschaft für Metallkunde, the Verein deutscher Eisenhüttenleute, the Verein deutscher Chemiker, the Verein deutscher Giessereifachleute, and the Bunsen Gesellschaft.

He was elected a Member of the Institute of Metals on March 8, 1926.

HARRY ARTHUR RUCK-KEENE, an Original Member of the Institute, a Member of Council from 1922 to 1930, and Chief Engineer Surveyor of Lloyd's Register of Shipping, died at his home in Finchley, London, on October 14, 1932, at the age of 66.

The third son of the Rev. B. Ruck-Keene of Copford, near Colchester, he was educated at Cheltenham and on the Continent. He served his apprenticeship on the Tyne with Sir W. G. Armstrong, Mitchell & Co., and R. and W. Hawthorn, Leslie & Co., Ltd. He remained with the latter company on the completion of his apprenticeship until 1890, when he was appointed an engineer surveyor to Lloyd's Register. After serving the society at Middlesbrough, London, and Antwerp, he was appointed in 1907 as a principal surveyor on the staff of Dr. James T. Milton, then the chief engineer surveyor. In December 1908 he was promoted to be assistant to the chief engineer surveyor; and in October 1921, on the retirement from active service of Dr. Milton, he succeeded him as chief engineer surveyor.

Mr. Ruck-Keene was a vice-president of the Institution of Naval Architects and of the Institute of Marine Engineers, and he was a member of the Institution of Civil Engineers, the Iron and Steel Institute, the North-East Coast Institution of Engineers and Shipbuilders, and the British Association of Refrigeration. He was one of the pioneers in the development of autogenous welding for boiler repairs in Great Britain, for, so far back as 1907, he contributed a paper to the Engineering Conference of the Institution of Civil Engineers on this subject. This paper was the first contribution to a British technical society dealing with the possibilities of this method of repair. In the same year he followed it by a further paper on the subject, entitled, "New Methods of Effecting Boiler Repairs," read before the Institute of Marine Engineers.

In his long term of high office in the service of Lloyd's Register of Shipping he was recognized as a leading authority on the far-reaching effects of the developments which occurred in marine propulsion, and was prominently associated in the many amendments and additions made to various important rules of the society. He coupled his wide technical knowledge and experience with a personal charm of manner which endeared him alike to his colleagues and his many business friends. Mr. Ruck-Keene was an enthusiastic sportsman. He was a keen golfer, and he also took a great and active interest in the affairs of Lloyd's Register cricket and rifle clubs.

MR. LA VERNE WARD SPRING died on March 23, 1932, at the age of 56.

He was born in Coldwater, Michigan, and attended the University of

Michigan, from which he graduated with an A.B. degree in chemistry. After serving for some time as chemist with the Illinois Steel Company, South Chicago, Ill., he accepted a similar position with the Wolverine Portland Cement Company. Later he returned to the Illinois Steel Company to undertake metallurgical and superintendency work in the plate mill. In 1906 he became connected with the Crane Company, Chicago, with whom he remained to the day of his death. Here he served first as chemist, and was later placed in charge of the laboratories. In 1914 he was promoted to chief chemist and metallurgist.

Mr. Spring, jointly with J. J. Kanter, received the Charles B. Dudley Medal in 1929. The medal was awarded by the American Society for Testing Materials, following the presentation of a paper on research on engineering materials. He was presented with a posthumous John A. Penton Gold Medal by the American Foundrymen's Association for outstanding service to the foundry industry.

He was the author of an interesting book on " Non-Technical Chats on Iron and Steel " and of many papers for the technical press, one of which was an American Foundrymen's Association exchange paper on " Considerations and Tests for Cast Materials for High-Temperature High-Pressure Service " for the Institute of British Foundrymen, which was read in 1931.

Mr. Spring was a member of the American Foundrymen's Association committees on cast iron, non-ferrous metals, and malleable iron, and represented that association and the American Institute of Mining and Metallurgical Engineers on the advisory committee to the U.S. Bureau of Standards. He also served on various committees of the American Society for Testing Materials and was a member of the joint American Society for Testing Materials–American Society of Mechanical Engineers committee on research on the effect of temperature on the properties of metals. He was also a member of the American Society for Steel Treating, the American Chemical Society, and the American Institute of Mining and Metallurgical Engineers.

Mr. Spring was a great lover of art; photography was one of his greatest hobbies and some of his landscape photographs won recognition in nation-wide contests. He was also an expert player of several musical instruments.

Mr. Spring was elected a Member of the Institute of Metals on March 8, 1926.

INDEX TO AUTHORS AND SPEAKERS.

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