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THE JOURNAL OF THE INSTITUTE OF METALS

VOLUME LXI

EDITED BY

G. SHAW SCOTT, M.Sc.

SECRETARY

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36 VICTORIA STREET, LONDON, S.W.1
1937

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[Entered at Stationers' Hall

Form A.

(Membership Application)

No.....

Recd.....

The INSTITUTE of METALS

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

Founded 1908. Incorporated 1910.

To the Secretary.

The Institute of Metals.

I, the UNDERSIGNED*

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

*Name of applicant in full

Address.....

†Business or Profession

Qualification.....

Degrees and/or honorific distinctions.....

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

.....

.....

.....

.....

Signatures
of three
Members.

The Council, having approved the above recommendation,
declares the applicant to be duly elected as.....
Member of the INSTITUTE OF METALS.

To be filled up
by the
Council.

36 VICTORIA STREET.

Chairman.

WESTMINSTER, LONDON, S.W.1.

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

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

Name and address of firm (or other body) should be stated, as well as position held.

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

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 [17–26 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 3s. per annum, and of each Student Member £1 1s. per annum. Ordinary Members shall pay an Entrance Fee of £2 2s. each and Student Members an Entrance Fee of £1 1s. each. (Entrance Fee for Students has been temporarily suspended.)

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.



P.99/37/2

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Sir WILLIAM HENRY WHITE, K.C.B., LL.D., D.Eng., Sc.D., F.R.S.,
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THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS.

AUTUMN MEETING.

THE TWENTY-NINTH AUTUMN MEETING of the Institute of Metals was held in Sheffield from September 6-9, 1937, by invitation of the Sheffield Local Section and other local friends of the Institute.

Monday, September 6.

The meeting opened in the evening, when members and their ladies attended a Reception by the Lord Mayor of Sheffield (Councillor Mrs. A. E. Longden, J.P.) and the Senior Pro-Chancellor of the University of Sheffield (Lieutenant-Colonel Sir Henry Stephenson, Bart., D.S.O., D.L., LL.D., J.P.) in the Mappin Hall of the University.

WELCOME TO SHEFFIELD.

The LORD MAYOR, in extending a welcome on behalf of the City, said that it was a very great pleasure to have the privilege of meeting those who were attending that important conference. She offered to each one of them, on behalf of the City, a very hearty welcome to Sheffield. She hoped that they would find the environment of the city conducive to good judgment, and that their deliberations might be of mutual benefit and would lead to the cementing of friendships.

Metals were something about which many Sheffield men knew a great deal, and questions relating to their use should afford ample scope for discussion and provide many themes of interest during the members' stay in the City. They in Sheffield had recently had some very lean years, but fortunately to-day trade had improved wonderfully, and they rejoiced that the effects of that improvement were showing themselves in the happiness and contentment of their people. They were delighted that the members of the Institute of Metals had come to visit them at such a time, and to share the happier period that had come to Sheffield. She sincerely hoped that the members would spend a very pleasant time in Sheffield, and that when their meeting was ended they would feel that it had been well worth while.

SIR HENRY STEPHENSON said that he would like to echo, on behalf of the University, the welcome to Sheffield which had been given to the members of the Institute by the Lord Mayor. It was a very great pleasure to the University to afford facilities to scientific and learned bodies when they came to the City, and it was, he thought, in that home of iron and steel a particular compliment that those who were interested in the non-ferrous metals should make Sheffield their place of meeting. He wished the members a very happy visit to Sheffield.

The PRESIDENT, in reply, said that the members of the Institute and their ladies were very grateful for the welcome which had been given to them so warmly that evening. In view of the efforts of the Reception Committee,

under Professor Andrew, and by the citizens of Sheffield, the meeting could not possibly be other than eminently successful.

They were particularly happy to meet in Sheffield, with its wonderful traditions of industry and science. None of them could fail to recall, as they stood in that Hall and in that building, the names of those who made the old Sheffield Technical School, the University College of Sheffield, and afterwards the University, and he would particularly like to remind the younger members of the Institute how deep was our debt to one of Sheffield's greatest citizens, Dr. H. C. Sorby, who gave us one of the most wonderful instruments for the investigation of metallurgical problems which there had ever been, namely the metallurgical microscope. He was quite sure that the city of Sorby and Arnold, and of the School of Metallurgy which was founded in those early days and which had been carried on by Dr. Desch, and by Dr. Andrew, would continue to be a Mecca for metallurgists.

BUSINESS MEETING.

After the Reception, a business meeting was held in the Department of Applied Science of the University of Sheffield, the President, Mr. W. R. Barclay, O.B.E., occupying the chair.

The PRESIDENT: The holding of a business meeting before the Autumn Lecture is a departure from precedent, but I am sure the members will agree that it is an advantage to hold the business part of the Autumn Meeting at an early stage.

The Minutes of the General Meeting held in London on May 5, 1937, were taken as read and confirmed.

NOMINATIONS OF OFFICERS FOR 1938-1939.

The SECRETARY (Mr. G. Shaw Scott, M.Sc.) read the list of members nominated by the Council to fill vacancies as Officers for the year 1938-1939, as follows:

President.

Dr. C. H. DESCH, D.Sc., Ph.D., F.R.S.

Vice-President.

Professor J. H. ANDREW, D.Sc.

Members of Council.

J. W. DONALDSON, D.Sc.

Engineer Vice-Admiral G. FREECE, C.B.

H. S. TASKER, B.A.

The PRESIDENT: I know that the members of the Institute will share the gratification of the Council that Dr. Desch has accepted our offer of the Presidency for 1938-39. Those of you who know Dr. Desch will not need me to say anything about him, but I should like to remind those who may have forgotten that Dr. Desch is an Original Member of the Institute and was one of the first contributors to its proceedings. Those of you who care to refer to the first volume of our *Journal* will find his name as the contributor of a most valuable paper on a subject then little known, namely intermetallic compounds. Dr. Desch has served the Institute very faithfully and loyally ever since. He has been a member of our Council for some years, and a Vice-President, and I feel sure that the traditions of the Institute of Metals will be upheld very worthily by him.

We shall all welcome Professor Andrew as one of our Vice-Presidents, as also the new Members of Council. I am sure that, although we are losing greatly

esteemed members of the Council under our retirement scheme, we shall be strengthened by the addition of these new ones.

As my predecessor said two years ago, this Institute is a democratic body. Sometimes it may not seem so, but it is so. Any ten members have the privilege of nominating any other members for the vacancies on the Council provided that the nominations are received by the Secretary by 12.30 p.m. to-morrow. If any such nominations are received there will be a ballot, the result of which will be declared at the General Meeting in March.

ELECTION OF MEMBERS AND STUDENT MEMBERS.

The SECRETARY read a list of members and student members elected on July 8 and August 26, 1937, as follows :

MEMBERS ELECTED ON JULY 8, 1937.

BOWDEN, Frank Philip, Ph.D., D.Sc.	Cambridge.
BRADLEY, Harold, M.Met.	Runcorn.
CASTLE, George Cyril	Solihull.
COOPER, W. L., M.C., M.A.	Bristol.
DELPORT, Vincent Paul, B.Sc.	London.
GOETZ, Professor Alexander, Dr.-phil.	Pasadena, Cal., U.S.A.
ISELL, William Tren, M.S.	Bonne Terre, Mo., U.S.A.
RUSSELL, Reuben Sussex, B.Sc.	Melbourne, Australia.
SMALDON, Henry Oliver	Sutton Coldfield.
WEEBER, Karl Hermann, Dipl.-Ing.	Manchester.
WOODHEAD, Percy	Wakefield.

STUDENT MEMBERS ELECTED ON JULY 8, 1937.

BURDEN, Walter Henry Aldwyn	Wolverhampton.
CHILD, Frank Carr, B.Sc.	Durham.
COTTON, Raymond Frederick, B.Sc.	Birmingham.
DRASIKOTZY, Ratibor, B.Sc.	Birmingham.
HYSEL, Victor Barclay, B.Sc.	Coleshill.
MOUNTFORD, Norman Duncan Gerard	Heaton, Newcastle-upon-Tyne.
NORRIS, Leonard Matthew	Birmingham.
PARKER, Robert Stanley	Newcastle-upon-Tyne.
RITCHIE, Peter	Low Fell, Co. Durham.
THORNHILL, Raymond Spencer, M.A., Ph.D.	Cambridge.
TRUMPER, Arnold Frederick	Birmingham.
TUXFORD, Harry Weston	Darlaston.
WRIGHT, Norman Gardner, B.Sc.	Ponteland, Northumberland.

MEMBERS ELECTED ON AUGUST 26, 1937.

van ARKEL, Hendrik Jacobus	The Hague, Holland.
BANCELIN, Jacques, Dr.-ès-Sc.	Levallois (Seine), France.
CARLISLE, Charles George	Sheffield.
CARPENTER, Francis William Alan	Calcutta.
COLBECK, Eric Winearls, M.A.	Northwich.
DUPUY, Eugene Louis, Dr.-ès-Sc.	Paris, France.
FALMOUTH, The Rt. Hon. Viscount Evelyn Hugh John	London.
GILLOTT, George Francis, B.Met.	Oxford.
GORDON, Frederick Felix, Assoc.Met.	Sheffield.
GRENINGER, Alden Buchannon, A.B., Met.E., Sc.D.	Cambridge, Mass., U.S.A.
GRIFFIN, Ronald Ernest	Birmingham.
HARBORD, Vernon, A.R.S.M.	Kenley.
HARRIS, Herbert, Ph.D., B.Sc., A.R.C.S., D.I.C.	Renfrew.
HERGENROETHER, Ernst J.	Detroit, Mich., U.S.A.

MATTHEWS, Stanley Edward	London.
MILLER, James Edwin	Chesterfield.
NEWALL, Archibald Park	Glasgow.
PARKYN, Roderick William, M.A.	Alderley Edge.
POPE, Ernest Legh	Gorseinon, Swansea.
REICHWALD, Otto F.	London.
SWARUP, Professor Daya, B.Sc., Ph.D.	Benares, India.
VOGEL, Julius Leonard Fox	Widnes.
WERNING, Karl Hermann	Berlin-Borsigwalde, Germany.
WICKERSHEIMER, Ernest, D.M.	Strasbourg, France.
WILLIAMS, Enoch	Sidecup.

STUDENT MEMBERS ELECTED ON AUGUST 26, 1937.

BANFIELD, Thomas Arthur, Ph.D., A.R.C.S., D.I.C.	Birmingham.
BRIMLOW, Ernest Irving, B.Eng.	South Farnborough.
CLARK, William Davidson, B.A.	Lancaster.
DARRAH, Brian Douglas, B.A.	London.
DOWSON, Arthur Gordon, B.A., Ph.D.	Cambridge.
DOYLE, John Davis, B.Met.E.	Richmond.
DOYLE, William Michael, B.Eng.	Farnborough.
FAIRFAX, Ernest	London.
JONES, David John, B.Sc.	Neath.
KACÍREK, Milos	Prague, Czechoslovakia.
KING, Robert, B.Sc.	Birmingham.
LEVICK, Ronald Herbert, B.Sc.	Sheffield.
LLEWELLYN, Geirionydd, B.Sc.	Cumgorse, G.c.G., Glamorgan- shire.
MATHIAS, Ernest Victor, B.Sc.	Swansea.
MILNES, Aubrey Henry, B.Sc.	Sheffield.
MORDEN, John Frederick Charles	Ilford.
NEWMAN, Ernest George Vincent, B.Sc., A.R.S.M.	London.
PEARSON, Robert John	Melbourne, Australia.
REES, Taliesyn David, B.Sc.	Swansea.
ROADLEY, John Arthur, B.Sc.	Loughborough.
SMITHAM, William	Swansea.
STANLEY, Douglas Gordon	Leeds.
TEDDS, Dennis Frederick Bernard	Coventry.
THOMAS, George Lorraine, B.Sc.	Kettering.
WORNER, Hill Wesley, B.Sc.	Melbourne, Australia.

FUTURE MEETINGS.

The PRESIDENT: The Annual General Meeting of the Institute will be held in London on March 8, 9, and 10, 1938. I am also entrusted with the most important announcement that the next Annual Autumn Meeting of the Institute will be held in the United States of America in October 1938, jointly with the Iron and Steel Institute, and by the invitation, most cordially given, of the American Institute of Mining and Metallurgical Engineers, the American Iron and Steel Institute, and the American Society for Metals. I have, both orally and by letter, received warm assurances of a very hearty welcome to the members of the two Institutes, and I hope that the meeting in the United States will be very strongly supported by the members of this Institute.

AUTUMN LECTURE

Dr. D. R. PYE, C.B., M.A., F.R.S., Director of Scientific Research, The Air Ministry, then delivered the Autumn Lecture on "Metallurgy and the Aero-Engine."

At the conclusion of the lecture (which is printed in full on pp. 19-34 of this volume), Professor J. H. Andrew, Member of Council, proposed a hearty vote of thanks to the lecturer, which was passed with acclamation.

Members and their ladies then adjourned to the Mappin Hall for light refreshment, music, and dancing.

Tuesday, September 7.

Morning.

The morning session, for the reading and discussion of papers, was held in the Mappin Hall at the Department of Applied Science of the University, Mr. W. R. Barclay, O.B.E., President, occupying the Chair.

The PRESIDENT at the commencement of the proceedings extended a very cordial welcome to the overseas members and friends who were attending the meeting.

PAPERS.

Papers by the following authors were then presented and discussed: W. O. Alexander and D. Hanson; W. O. Alexander and N. B. Vaughan; L. Kenworthy; D. W. Ginns; and B. Chalmers.

At the conclusion of the session, the President proposed, and there was carried with acclamation, a hearty vote of thanks to the authors.

In the morning the ladies left Sheffield for an all-day visit to the Dukeries and Firbeck Hall Club.

Afternoon.

After lunch at the Royal Victoria Station Hotel, members visited, by invitation, the works of Messrs. Brown Bayley's Steel Works, Ltd., Messrs. English Steel Corporation, Ltd., Messrs. Mellowes and Company, Ltd., and Messrs. United Steel Companies, Ltd.

Evening.

Members and their ladies were the guests of the Lord Mayor of Sheffield at a Reception at the Town Hall.

Wednesday, September 8.

Morning.

The meeting was resumed in the Mappin Hall of the University, Mr. W. R. Barclay, O.B.E., President, occupying the Chair.

PAPERS.

Papers by the following authors were presented and discussed: H. A. Unckel (in the absence of the author), C. Sykes and H. Wilkinson, D. Hanson and W. T. Pell-Walpole (two papers), and G. B. Brook and A. G. Waddington.

At the conclusion of the session, the President proposed, and there was carried with acclamation, a hearty vote of thanks to the authors for their papers.

VOTES OF THANKS.

The PRESIDENT: We are indebted for the arrangements for this meeting to a large number of friends, and I therefore propose:

That the best thanks of the members in General Meeting assembled be accorded to:

(1) The Sheffield Local Section and the Sheffield industrialists, for their invitation to hold this meeting.

(2) The Lord Mayor of Sheffield (Councillor Mrs. A. E. Longden, J.P.).

the Lady Mayoress (Miss Mary Longden), and the Senior Pro-Chancellor of the University of Sheffield (Lieut.-Colonel Sir Henry K. Stephenson) for their cordial welcome to Sheffield, and for their hospitality.

(3) The following firms, who have granted permission to members and their ladies to visit their works, and for their hospitality :

Edgar Allen and Company, Ltd.
Brown Bayley's Steel Works, Ltd.
English Steel Corporation, Ltd.
Thos. Firth and John Brown, Ltd.
Hadfields, Ltd.
Mellowes and Company, Ltd.
United Steel Companies, Ltd.
Walker and Hall, Ltd.

(4) The Dukeries and Firbeck Hall Club, Arthur Davy and Sons, Ltd., and the Snowite Laundry for their hospitality.

(5) Professor J. H. Andrew, D.Sc., Chairman, Mr. E. J. Thackeray, Honorary Secretary, and the members of the Local Reception Committee for their hospitality and for their most valuable work.

(6) Professor and Mrs. Andrew for their hospitality to members and their ladies on the occasion of the all-day tour to some of the beauty spots of Derbyshire.

(7) The authorities of the University of Sheffield, for their kindness in placing rooms in the Department of Applied Science at our disposal, and for the many facilities given us for carrying on the business of our Autumn Meeting.

In these votes of thanks we have not hitherto made special reference to the ladies and to the work of the Ladies' Committee. This time I feel that you would regard it as a serious omission if we did not do so. The ladies of the Reception Committee, under Mrs. Andrew and Mrs. Kenneth Gray, have undertaken a great deal of work and organization in making most generous provision for the entertainment of the visiting ladies.

Professor R. S. HURTON, M.A., D.Sc., Fellow : I appreciate very much the honour of seconding the resolution, because, like the President, I look back to the days when we both lived in this city. It is particularly interesting to return on such an occasion as this and to note the great advances which have been made, and the great changes which have taken place, in Sheffield. We have all appreciated very deeply the arrangements made in connection with this meeting, and the splendid hospitality which our Sheffield friends have offered to us. In listening to the names included in this resolution, it was brought home to me what alterations have taken place in Sheffield since last we were here; even the names of the firms who have offered us hospitality have in most cases changed out of all recognition.

We hope that we have come to Sheffield at a moment when the renaissance of the non-ferrous metal industries of this city will commence. Many of our members may not be aware what a very important centre of the non-ferrous trades the city of Sheffield represents. There are many thousands of workers here who are engaged in the silver and other non-ferrous metal industries, and those who have had an opportunity of visiting some of the works will appreciate what an important branch of our non-ferrous metal industry exists in this centre.

The business meetings then terminated.

In the morning the ladies visited the food factory of Messrs. Arthur Davy and Sons, Ltd.



Afternoon.

After lunch at the Royal Victoria Station Hotel, members and their ladies visited the works of: Messrs. Edgar Allen and Company, Ltd., Messrs. Hadfields, Ltd., and Messrs. Walker and Hall, Ltd., and the Snowite Laundry.

Evening.

Members and their ladies were the guests of the Local Reception Committee at a Banquet and Dance at the Royal Victoria Station Hotel.

Thursday, September 9.

Members and their ladies took part in a whole day excursion through some of the places of beauty in Derbyshire, lunch being served at the Palace Hotel, Buxton.

The party was entertained to tea at the Rising Sun Hotel, Bamford, by Professor and Mrs. J. H. Andrew, and returned to Sheffield, where the meeting terminated.

AUTUMN LECTURE, 1937.

METALLURGY AND THE AERO-ENGINE. 78

By D. R. PYE,* C.B., M.A., Sc.D., F.R.S.

SIXTEENTH AUTUMN LECTURE TO THE INSTITUTE OF METALS, DELIVERED SEPTEMBER 6, 1937.

SYNOPSIS.

The remarkable increase of recent years in the power of aero-engines has been largely due to improvements in the quality of the fuel available, but it could not have been achieved without many parallel improvements of a metallurgical character. The increase of power has involved thermal and mechanical problems, and of the former, those associated with the piston and exhaust valve are the most formidable. On the mechanical side, the problem is that of maintaining two surfaces at high temperatures rubbing without seizure. It is of importance to consider what treatment of the metal surfaces themselves will render them less liable to seizure when the lubricant can no longer provide sufficient protection. Metal surfaces, normally crystalline in their atomic structure, can in some circumstances be rendered amorphous, and there are reasons for thinking that in this state they form more satisfactory bearing surfaces. A study of the ultimate structure of metal surfaces, such as is provided by the physicist, may be expected to afford valuable assistance in the engineer's problem of bearing surfaces.

MAY I first say how much I appreciate the honour of being invited to deliver this annual Autumn Lecture to the Institute of Metals. The President, in conveying the invitation of your Council, intimated that I might address you upon any subject I chose; but it is probable that when the Council decided to invite me they had in mind more specially my connection with the Air Ministry and aeronautical research; and when casting about in my mind for a subject on which I might hope to interest the members of the Institute of Metals, and at the same time avoid putting too great a strain upon the patience of their ladies, it seemed to me that a review of some of the changes in aero-engine design and construction during the last five years, more especially from the metallurgical point of view, would enable me to place before you some of the outstanding problems which face the aeronautical engineer at this moment, and for the solution of which we need the assistance of your expert knowledge.

If one compares two aero-engines of roughly the same type and

* Director of Scientific Research, Air Ministry.

cylinder capacity, the one of 1937 vintage and the other of about six years earlier, the outstanding fact is that in six years the maximum power output, expressed as horse-power per cubic foot of cylinder capacity, has increased by amounts which vary in different designs between 50 and 100 per cent.

In outward appearance the engines are very similar. How, then, does one achieve an output nearly twice that of its predecessor of six years ago? Many people would reply that this satisfactory result is almost entirely due to the improved quality of the fuel supplied to it, because this allows the combustible mixture to be supplied at a much higher temperature and pressure, and at the same time to be more highly compressed in the cylinders, without the combustion taking on the characteristics of a detonation which is destructive in its effects. It is true that without this improved fuel only a small part of the 100 per cent. increase of power could have been achieved; but it is of interest to enquire in what respects the engine itself has had to be developed, step by step, with the improvement in the fuel and the greater quantity of combustible mixture supplied to each cylinder per stroke, to enable it to withstand this forcible feeding and to digest the special diet. We shall see that for the most part it is the metallurgist who has been called in as the physician.

You must understand that if the present-day fuel had been available five years ago the power of the engines could not have been safely increased by more than a comparatively small amount. It is impossible to say just where the engines would have failed—probably half a dozen engines would each have failed in a different way—but fail they would, either in bearings, cylinder bolts, valves, pistons, sparking plugs, or what not; for in the aero-engine the design is trimmed to the power within so fine a limit that one might almost compare it to the Deacon's masterpiece, the wonderful one-horse shay, that

Was built in such a logical way
It ran 100 years to a day

and on the stroke of the century the Deacon's grandson found himself deposited in the road amid a pile of chips which a moment before had been the one-horse shay.

Of the two pairs of engines shown in Figs. 1 and 2, each outwardly so similar, there is hardly one major component of which either the material or its treatment has not been modified and improved in the last five years to meet the far more severe conditions of to-day.

The problems introduced by an increase of power one may classify broadly as thermal and mechanical. On the thermal side the problem

can be stated in general terms by saying that an internal combustion engine draws into its cylinder per minute a certain weight of combustible mixture which depends upon the product of the engine speed and the density of the air supplied. Combustion of the mixture then generates an amount of heat per minute in direct proportion to its weight, and of this total heat generated a certain fraction—which we call the engine's thermal efficiency—is converted into mechanical work at the crankshaft.

Now the possibility of increasing this fraction of the total heat generated which an engine converts into mechanical work is strictly limited. It is fundamentally impossible to increase it very greatly, and as between the engines of to-day and of six or seven years ago the increase has in fact not been more than about 10 per cent. The important conclusion from this fact to which I want to direct your attention is that an increase of power of 100 per cent., is inevitably accompanied by an increase, in nearly the same ratio, of the *waste* heat, which must be got rid of with the exhaust gases and by conduction through the various metal components of the cylinder.

The greater part of this increase of waste heat goes out with the exhaust gases; but for 100 per cent. increase of total heat generated per minute there is at least a 40 per cent. increase of that communicated to the cylinder walls and other components, to be got rid of by conduction. Moreover, that conduction has to be effected without allowing rises of temperature in the various components which will prejudice their mechanical working one with another, for example, the pistons with the cylinder walls, and the valves in their guides. So far as direct conduction through the cylinder walls is concerned we find that in order to dissipate this heat without an excessive rise of temperature in the cylinder barrel and head, the fin area on air-cooled cylinders of the same size has been increased by about 95 per cent. in the last five years. Even so there has probably been some increase in the average temperature of the inner surface of the cylinder barrel which may now be as high as 180° C.

The material employed for cylinder heads of air-cooled engines has not changed much in recent years, and development has been rather towards improving the forging and machining qualities. The light alloys have good conductivity compared with steel in any case, and as compared with the thermal problems inherent in pistons, valves, valve seats, and sparking plugs, those of the cylinder head itself are less acute. As regards steel for the cylinder barrel, the essential requirements are good machining qualities combined with the possibility of special treatment of the working surface. The question of surface condition

as affecting friction and lubrication I propose to return to later on. Although operating temperatures are vitally important, the subject falls more appropriately into the class of mechanical problems, to be dealt with later.

Of all the many components in which a weakness may cause breakdown of an engine, there are two which remain, perhaps, the major preoccupation of the designer: the piston, and the crankshaft and its bearings; the problems of the piston being chiefly thermal, and of the crankshaft, mechanical. The problem of the piston and its ailments must have something of the same difficulty to the experimental engineer as the human brain has to the physician and surgeon. It is the most sensitive and vital part of the organism, and at the same time the least possible to observe in operation, or to treat. Let me first outline its problems in the face of the 100 per cent. increase of power for the same size of cylinder to which I have referred. It cannot avoid receiving as much as 40 per cent. more heat per minute over its top surface, and all the heat it receives must be dissipated either to the cylinder walls across an oil film, or from the under-side to the air and oil in the crankcase. Cooling from the under-side of the piston is comparatively small, and the only possibility of avoiding a big rise of temperature in the material is to have a higher thermal conductivity in the material, or to increase the thickness of the piston crown, so that the heat is rapidly transferred to the periphery without large differences of temperature along the radius. The change from a cast iron to an aluminium alloy piston, under the same full throttle conditions, caused a fall of the maximum temperature in a 4-inch diameter piston from about 450° to 250° C., owing to the better heat conductivity and the greater thickness allowable of the light metal. It is typical, however, that these figures can only be given as rough approximations, because of the virtual impossibility of direct observation under real working conditions. Temperature observations by thermocouples have been successfully made up to about 1500 r.p.m. with the aid of elaborate gear on a single cylinder engine, but the difficulty of leading out the electrical connections to stationary measuring points outside the engine is extreme, and to do so would be impossible on a complete aero-engine. Even on a single cylinder engine the number of connections limits the number of thermocouples to about 6. From examination of the re-crystallization of aluminium alloy pistons after use, we guess that the temperature at the centre of the crown, even with this material, may nowadays reach temperatures in the neighbourhood of 450° C. What it really is, is perhaps not very important, because whatever the horrid truth may be the aero-engine designer will always force piston temperatures as high

as the design and the material permit. In the last five years the ability of piston materials to maintain the necessary strength at high temperatures has undoubtedly improved, although reliable figures would be difficult to put before you. Nevertheless, for the sake of the necessary strength, and also to allow of an adequate rate of heat-flow to the periphery, it has been necessary to thicken the piston crown and put up with a heavier piston. A point which I wish to leave in your minds is that any new material of specific gravity not greater than 3.0—but the lower the better—and of thermal conductivity not inferior to Y-alloy, which at the same time is able to maintain its mechanical properties better than Y-alloy at temperatures of 300° C. and over, will be of major importance to the aero-engine of the future.

The 100 per cent. increase in the waste heat from the cylinder has profoundly affected the design and metallurgy of the exhaust valve in the last five years. It would surely be difficult to find anywhere so many thermal, chemical, and metallurgical problems concentrated in so small a space. The difficulty of direct observation is not so great with the valve as with the piston, but the problem is far more complex. The successful development of the poppet valve and the seat on to which it closes calls for the most expert observation, and a critical analysis of the facts based upon wide knowledge of materials and engine design. For example, suppose an attempted run of 100 hrs. at high output has been stopped through a failure such as that illustrated in Fig. 3, which one describes loosely as “burning” of the valve. There is a variety of possible causes: overheating by itself, if sufficiently severe, might do it; but it is more probable that local overheating was due to some distortion of the valve or its seating ring in the cylinder head, on account of unsymmetrical expansion with temperature. This prevents perfect closure of the valve and allows an escape of burning gas under the full cylinder pressure. Or again, the imperfect closure may have been of a more accidental character caused by the pinching of a little piece of carbon or scale between the valve and its seat; and besides these mechanical and thermal possibilities, there is the chemical aspect introduced by the presence of tetraethyl lead in the fuel.

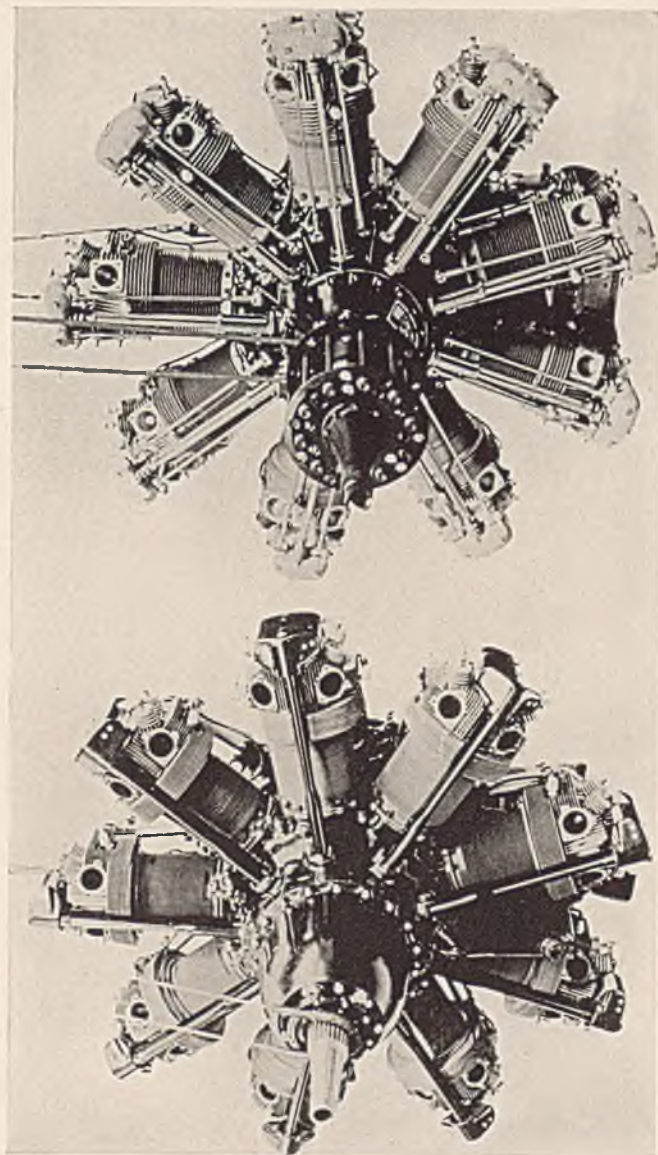
All the fuels demanded to-day by engines of the highest output owe their quality in some degree to the presence of the well-known “ethyl fluid.” This is a mixture of tetraethyl lead with ethylene dibromide and other substances, and it introduces a whole series of problems for the exhaust valve. It decomposes during the combustion in the cylinder with the formation of lead oxide and lead bromide, and the former of these, at the temperature of the exhaust gas, has disastrous effects upon the steel of the valves. These are effects which are not

serious in the automobile engine—do not, I pray you, take this as a warning not to use ethyl petrol in your car, or I shall get into trouble with my friends who produce it. The effects of the lead compounds on the exhaust valve are very much dependent on the valve temperature, and hence on engine output, and only become very serious when the valve is working under conditions far more severe than are ever met with in the automobile engine. Engine conditions, indeed, are extraordinarily critical. It has been found that a cylinder which will survive a hundred hours running quite happily when developing a brake mean effective pressure of 180 lb. per sq. in., will consistently fail through exhaust valve trouble when the power is increased by 10 per cent.

The most popular valve steel in use to-day is one containing 12 to 14 per cent. each of nickel and chromium, but in spite of a high innate resistance to corrosion attack it is not able, by itself, to withstand oxidation in the presence of lead oxide at high temperatures. To get over this, advance has been along two lines: firstly, a complete re-design of the valve to maintain better cooling; and secondly, the covering of the seating ring, and now even the whole head of the valve, by Stellite, a very hard alloy composed of cobalt, chromium, and tungsten, with about 2½ per cent. of carbon, which has a better resistance to the effect of the lead.

The problem of cooling the valve is, like that in the piston, one of transferring the heat from the point where it is received—the head—to some point where it can be got rid of; ultimately, of course, to the surrounding air, but immediately to the metal of the cylinder body. With the mushroom valve there is little hope of getting rid of the heat directly from the head, and the problem is that of transporting it to the cooler stem, and thence across the working surface between the stem and the valve guide.

Twenty years ago, experiments were made at the Royal Aircraft Establishment on the removal of heat from the head to the stem by making the valve hollow and filling it with a fluid which was shaken up and down by the valve's motion. At first, mercury was tried, and later a eutectic mixture of potassium and lithium nitrates. The suggestion was at that time premature, because the steel-makers were able to produce better and better non-scaling steels which could work for long periods at a red heat, prior to the introduction of tetraethyl lead. In the last five years the introduction of the chemical problem has forced designers to find means for getting better cooling, and to face the complication and expense of the hollow valve, containing metallic sodium as its heat carrier, which is now becoming universal in high-duty engines. In Fig. 4 are shown cross-sections of three slightly varying



A

B

FIG. 1.—A. Bristol Pegasus XXII (1936). Power for "Take Off" 1010 H.P. B. Jupiter VII F (1929). Power for "Take Off" 460 H.P.



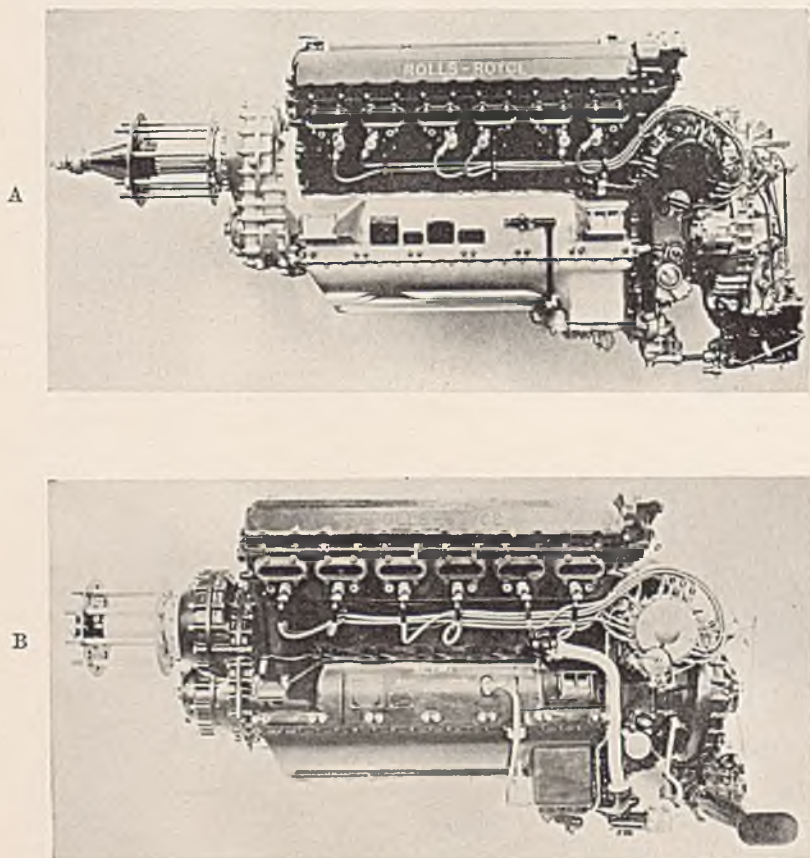


FIG. 2.—A. Rolls Royce Kestrel XVI (1937). Power for "Take Off" 870 H.P.
B. Kestrel II S (1931). Power for "Take Off" 534 H.P.



FIG. 3.—“ Burnt ” Exhaust Valve.

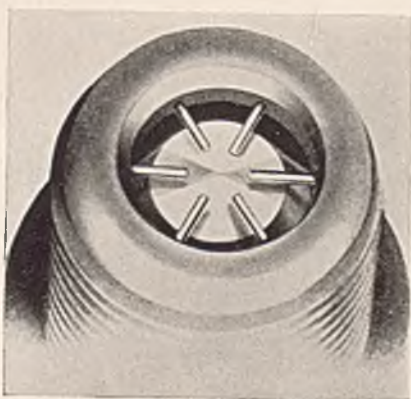


FIG. 5.—Sparking Plug with Negative Electrode of Platinum-Iridium Wire.

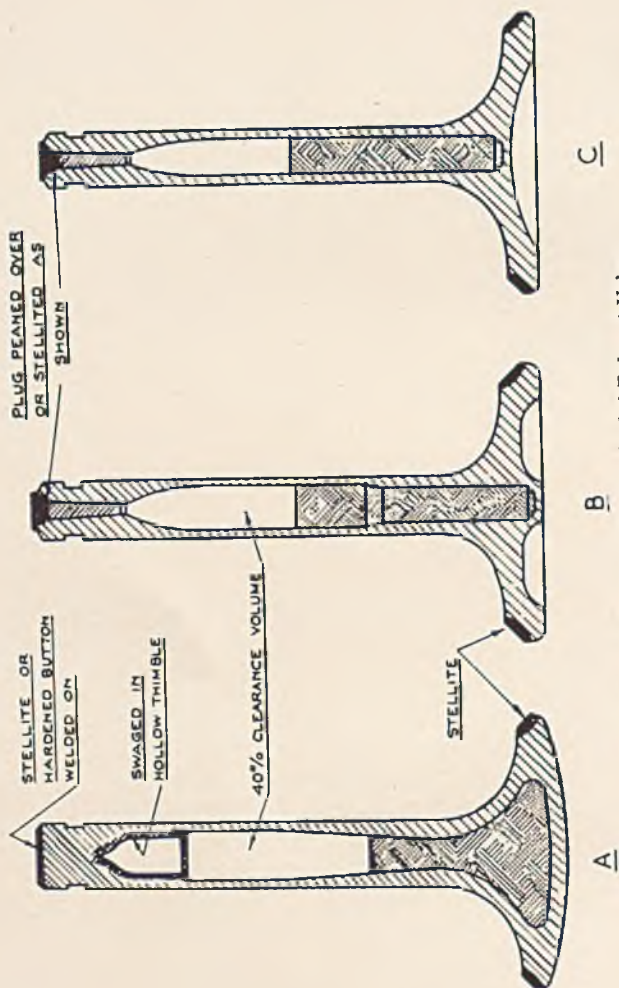


FIG. 4.—Three Types of Sodium-Cooled Exhaust Valve.

types of "liquid-cooled" exhaust valve. The sodium is solid when cold, but melts at about the temperature of boiling water.

Even this complex design, however, combined with the Stellite surface treatment, has not sufficed to cure the troubles of the exhaust valve. There is evidence of a rapid increase in the rate of attack even on Stellite, in the presence of lead oxide, between 600° and 700° C. and again above about 900° C. The practice of covering the whole top surface of the valve, moreover, to prevent scaling, has led to trouble owing to a difference between the coefficients of expansion of the steel and the Stellite which has been found to cause cracking of the Stellite over the head surface, so that the covering has completely disintegrated after 50 or 100 hrs. of high-duty running. A new material composed of about 80 per cent. nickel and 20 per cent. chromium has recently been tried for the same purpose and appears not to suffer in the same way when spread over the valve head. A possible further development is the fabrication of the entire solid parts of the valve from this non-ferrous alloy, thus avoiding the difficult welding processes involved in the composite valve. Finally, although the liquid sodium filling suffices to convey heat more rapidly from the valve head to the stem, it still remains to get this heat across the rubbing surface between the stem and the valve guide. Here also is an interesting problem, mechanical and metallurgical, which I shall deal with in the second half of my lecture.

I have compared the piston to the human brain, from the difficulty of observing it in operation, and one might almost compare the sparking plugs to one's teeth from the frequency with which they need attention. Here again the problems are thermal and chemical, and although they centre mainly on the insulating material, mica or porcelain, and are therefore outside the scope of this lecture, there are also points of great metallurgical interest on which the co-operation of the pure physicist might be of value.

The magneto is called upon to produce a spark across the plug points in a gas at about 10 atmospheres pressure, while itself surrounded by air which may be at only $\frac{1}{2}$ to $\frac{1}{3}$ of normal atmospheric pressure. The necessary sparking voltage is increased by supercharging, while surface leakage and corona discharges are promoted by the low pressure outside the cylinder. It is obvious, therefore, that the magneto problem becomes more and more severe with highly supercharged engines at great heights and that all possible means must be used of reducing the minimum voltage which the magneto has to supply across the plug points. It is found that this voltage is very much greater when it is of an "impulsive" character—that is, rapidly rising and falling again

as it is in a magneto—than when a steady voltage is gradually increased until a spark passes; and moreover that the magnitude of the impulsive voltage depends very much on the metal of which the plug points are made. For example, the “impulse ratio,” that is the ratio of the impulsive to the steady voltage, was found to be only 1.1 with nickel as compared to 1.6 with tungsten points. It depended also upon whether the high tension lead was positive or negative.

The choice of materials must take other things into account also. The sparking voltage depends on the length of the spark gap, and erosion of the plug points under the electric discharge produces in service a steady increase of the gap and of the voltage. The increase in length of the gap under comparable conditions was found to vary in the ratio of nearly 20 : 1 from $\frac{1}{1000}$ in. in 100 hrs. for tungsten up to $\frac{20}{1000}$ in. for nickel.

The frequency of sparking plug replacement will depend upon the rate of erosion, and it is clear that the metals we should choose from the point of view of voltage impulse ratio are not the best from the point of view of erosion. In the matter of erosion the chemical problems of fuel containing tetraethyl lead come in also. There is definite evidence of an increase in the rate of erosion on a change over to leaded fuel. These very practical problems of impulse ratio and rate of erosion are seen to take us straight away to problems in pure physics in which the relative ease of throwing off the atoms of different metals from the plug points under the electric forces, and of electrons from the atoms themselves, needs to be studied.

Apart from the electrical aspect, the sparking plug has to be designed to fulfil two contradictory conditions: it has to be so hot that any lubricating oil splashed on it will be burned away, and yet so cool that there is no danger that ignition of the fuel-air mixture can occur at the hot points before the spark passes. These are, indeed, the overruling conditions, for hitherto the magneto, although hard pressed, has been equal to the electrical problem. An interesting new development is a plug on which the negative points are formed from fine platinum or platinum-iridium wires $\frac{1}{80}$ in. in diameter placed radially and close to the flat-topped positive electrode as illustrated in Fig. 5. The fine wires eventually erode away, but being parallel to the flat top of the central electrode, this does not alter the size of the gap. Furthermore, the fineness of the wire probably allows rapid cooling of the sparking points during the induction stroke of the engine, and this prevents pre-ignition. The plug seems to have an uncanny power, also, of clearing itself when oiled up. An interesting point in connection with the erosion is that when platinum-iridium wire was used it was

mainly the platinum which was removed, leaving the iridium behind; but when pure platinum wire was used the resistance to erosion was greater than that of the platinum-iridium alloy under similar conditions.

Let me turn, now, to the problems where the emphasis is mechanical rather than thermal, although the temperatures at which things work are at all times a vital factor. In this part of my lecture, I propose to leave aside for the most part the comparison of present and past designs and materials, and to consider some of the basic questions in physics and metallurgy which lie behind the engineers' problems of the future as I see them. Before I leave the practical engine, however, it is of interest to point out that the mechanical problem of maintaining two surfaces rubbing without seizure occurs in a variety of forms in the internal combustion engine. There is the crankshaft in its bearings, in the first place, and the piston in the cylinder; but equally important and interesting to the metallurgist is the problem of wear between the valve stems and their guides, and of the camshaft and other parts of the valve gear. In each one of these directions the last five years have brought changes in the material and the technique used in the preparation of the working surfaces, always in the direction of providing greater hardness to resist wear and "pick-up" under heavy loads. In both liquid- and air-cooled engines we find, for the cylinder surfaces, either a change to special steels capable of extreme hardening or to chromium-plated surfaces. Similarly, the so-called lead-bronze has almost entirely replaced white metal as the bearing material, and this in its turn has involved the use of a hardened steel shaft to prevent excessive wear.

The problem of wear, seizure, and "pick-up" between metal surfaces obviously cannot be considered apart from the question of lubrication, which under ideal conditions may preclude metallic contact entirely. Indeed, turning to the other end of the scale, it may be said that every surface, unless it has been chemically cleaned with the greatest care, is lubricated in some degree. Many of you will be familiar with the embarrassing manner in which a teacup will slide about in a dry saucer, and you may have learnt by experiment that a splash of hot tea will make it stick. The explanation is that even in the best regulated households it is normal for the supposedly clean, dry cup and saucer to be covered by a grease film, which is dispersed by the presence of water.

Having digressed into the realm of teacups, I am now going to continue the digression still further from everyday engineering and talk about metal surfaces in terms of molecules and molecular dimensions. Any surface, solid or liquid, is composed of molecules in motion, and a perfectly smooth surface would be one in which any irregularities were of molecular dimensions. We can picture the free surface of an

undisturbed liquid as being smooth in that sense. It was the view of the late Lord Rayleigh that the difference between a liquid and a finely polished solid surface was not great, and that elevations on the solid surface would be of molecular dimensions. At the same time it must be remembered that our finest test for the flatness, as distinct from smoothness, of a surface would only detect hills and valleys equal to a height of about a thousand molecules. While accepting Rayleigh's view, therefore, that the smoothness of a solid surface may approach that of a liquid, we may yet picture the most perfectly prepared plane surface as rather like a good golf green, smooth, but with ups and downs; and almost any bearing surface met with in engineering as being like a piece of smooth rolling downland. Fig. 6 is intended to

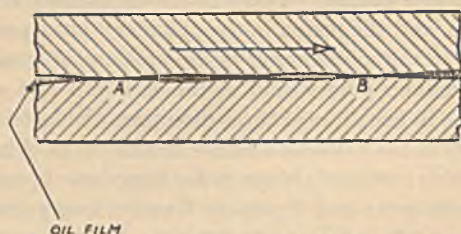


FIG. 6.—Surfaces in Contact with Oil Film Between.

give some idea of what two supposedly flat surfaces, pressed together with an oil film between, would look like if sufficiently magnified. They touch only at the two points A and B.

When two surfaces slide past one another they may, in effect, be floating past one another on an almost continuous film of oil. This would be the state of things in a well lubricated crankshaft bearing. On the other hand, the conditions may not be favourable to the maintenance of a continuous oil film. This is true between the piston and the cylinder, and more especially between the piston rings and the cylinder. In these circumstances the metal surfaces, as they slide past one another, come into contact, but only intermittently, and at points which are constantly changing. Remembering Fig. 6, we can say that there is contact at the hilltops when these come opposite to one another, but that between-whiles the surfaces are separated by an oil film thick enough to contain many thousands of oil molecules. Thirdly, the surfaces may carry no visible lubricant at all, like the tea-cup, as may happen between a valve stem and its guide; or the load may be so concentrated, as on the working surface of a cam, that any thick film of oil is instantly squeezed away. I will mention, in passing, an interesting case of invisible lubrication between a steel valve and

its bronze guide. It was on a well-known radial air-cooled engine. No special lubrication was provided for the valve-stem, but it was quite able to run for some hundreds of hours without appreciable wear of the guide. Then some experiments were made, running the engine on a very economical fuel-air mixture so that there was insufficient fuel to use up all the oxygen of the air, and it was found that the engine could not be run for more than 20 hrs. on account of excessive wear of the valve guides. The explanation appears to have been that under normal conditions a minute quantity of oil, or perhaps only oil vapour, was finding its way down by the valve stem and providing an invisible lubricating film. But when there was any free oxygen left over by the fuel, the oil vapour was burnt up and the wear increased by many hundreds per cent.

We must now touch upon what friction and wear really are and why they are reduced by a lubricating film. It used to be thought that the force of friction which opposes the sliding of one surface over another was always due to a sort of interlocking of minute asperities at the points of contact, however perfectly the surfaces might be polished. That view is now given up and we believe that the resistance to motion is due to cohesive forces between the molecules themselves acting across the interface between the surfaces; and that these forces are of the same kind as the cohesive force between the molecules of a solid on which its strength depends. These cohesive forces between the molecules are very powerful at short range, but the range is extremely small. Remembering the "golf green" character of any smooth surface when considered in terms of molecular dimensions, it is clear that it is only over a small fraction of the apparent area of contact of two surfaces that the molecules will be brought within each other's range of attraction and that owing to the short range of action of the cohesive forces even a single and quite invisible layer of oil molecules between two surfaces will suffice to prevent the molecules in each from getting to grips with one another. Whenever and wherever they do so, however, they will cohere with a force equal to that of the metal itself and some molecules of one surface will be torn away, held firm by the molecules of the other: in other words, either wear or "picking-up" will occur. It is of interest that even in a well-lubricated shaft bearing, minute adhesions have been observed to take place between the shaft and the bearing metals without these adhesions having proceeded to the point of a seizure. The experimental evidence is that a sliding of one surface on another will always cause some slight abrasion, due to this metallic cohesion, unless the surfaces are protected by a layer of oil molecules. Even when they are so protected, temperatures are produced in the

surface layers, wherever there is contact, which are so high as to decompose the oil, and we have to imagine an extremely rapid succession of break-downs and repairs of the oil film. It may be that the force of friction, once complete fluid lubrication has ceased, is due to the cohesion and parting again of innumerable pairs or groups of molecules, and that the observed value of the force is really an average result derived from a rapidly alternating state. If this is so, the likelihood of wear or of seizure must depend ultimately on the magnitude of the cohesive forces between the molecules on the two surfaces. Now the nature of these molecular forces which may be fatal to a bearing are essentially the same as the forces of chemical affinity, and just as the elements show a wide diversity in their eagerness to form chemical compounds with one another, so bearing surfaces must differ in their readiness to cohere when lubrication has failed. There are, of course, plenty of instances of two metals, A and B, which will work harmoniously together when A and C, under exactly the same conditions of load and temperature, will produce a seizure.

Our ability to preserve metal surfaces rubbing without seizure, in spite of heavier loading and rising temperatures, is vital to progress with the high-duty internal combustion engine, and I propose now to refer in more detail to the nature and behaviour of surfaces and their influence on the engineer's problem.

So long as a complete unbroken oil film is maintained, this question of the proper "pairing" of metals does not arise, but even in a well-lubricated bearing there are the humps and hollows already described, and whenever two humps pass one another so that they are helping to carry the load on the bearing, then the oil is squeezed away until there is no more than a single layer or so of oil molecules between the surfaces; very high temperatures are produced, and intermittent failure of the oil film and metallic cohesions will occur. So long as this state persists, the two surfaces are said to be in the state of "boundary lubrication."

It is easy to understand why high temperatures of the metal surfaces make the danger of seizure more acute. In the first place the rate at which the oil is squeezed away from between the surface humps as they approach will depend on its viscosity. As temperatures rise the viscosity falls, the thick film of oil is more quickly dispersed and the dangerous condition of boundary lubrication is earlier established. Besides this, however, there is the effect of a higher temperature on the danger of metallic cohesion when the oil film breaks down. At a higher temperature all chemical activity is enhanced and there is, therefore, *prima facie*, likely to be a direct effect of temperature in the direction of promoting metallic cohesion and seizure.

Accepting that between two heavily loaded surfaces in contact a condition of boundary lubrication, though intermittent, is constantly recurring and that however good the oil, opportunities for metallic cohesion will occur, it is of great interest to consider what it may be possible to do to the metallic surfaces themselves to obtain relief and reduce the danger of seizure.

I have spoken already of the parallel between the forces of metallic cohesion and of chemical affinity and of the engineer's experience that some metals show less readiness to seize together than others. I want now to speak of the light thrown by recent research work on the ultimate nature of surfaces, and how they may differ, and from that to suggest how the special treatment of surfaces may perhaps assist in the engineer's problem. The normal condition of a smooth metallic surface may be described as a crystalline aggregate with the atoms or molecules within each crystal arranged in a regular manner according to a "space-lattice" which is characteristic of the metal. On the surfaces of most liquids, on the other hand, the molecules, if we could see them, would appear completely without order of any kind, and there are many solids also which have this amorphous atomic structure.

Beilby—one of your Past-Presidents—after a careful microscopic study 35 years ago of the process of polishing, suggested that this did not consist simply of a rubbing away of asperities to smaller and smaller dimensions, but that the act of polishing produced a fundamental change in the character of the surface either of a metal or non-metallic crystal, during which the crystalline character is lost and the molecules become arranged "all higgledy-piggledy" in the way characteristic of a liquid surface. The correctness of Beilby's conclusion and the frequent occurrence of this amorphous layer, now known as the "Beilby layer," on a polished metal, is generally accepted. It has received remarkable confirmation from the work of Bowden, and more recently from that of Finch and others with the electron camera. Bowden showed that when two metals were rubbed together, even quite lightly, temperatures could be recorded electrically at the surface which quickly rose to the melting point of one of the metals, and that by no increase of load and rubbing speed could the temperature be made to rise higher. He has since extended his observations more particularly to polishing, and finds evidence that the surface temperature, when a surface is rubbed with a polisher, always rises to the melting point of the polished surface. It must be understood, of course, that the very high temperatures are confined to an excessively thin layer on the surface, and do not spread perceptibly throughout the body of the metal.

An obvious deduction from these observations is that during the act of polishing, a liquid or semi-liquid layer of the metal is smeared over the underlying crystalline surface and, hardening again immediately, retains the amorphous character it had as a liquid.

Finch has confirmed this conclusion, but has further reached the extremely interesting and important one that this amorphous layer left by polishing may or may not remain amorphous according to the material polished and how it has been treated. I shall return presently to the practical importance of this conclusion. The thickness of the amorphous layer varies widely according to the material and the amount of polishing, from a layer only 20-30 atoms thick up to one of 100,000 or more. By examination of some new and some used aero-engine cylinders, Finch found that the "running-in" process between the piston and cylinder results in an extremely thick Beilby layer being formed: so thick, that several rubbings with fine emery paper were necessary to remove the hard amorphous layer and re-expose the crystalline substratum.

It is, of course, common knowledge to the engineer that he must not allow an engine to give its full power until the "running-in" process is complete, or scoring and seizure between the piston and cylinder will infallibly occur. This conforms with the physicists' observations upon the Beilby layer, that metal in this amorphous condition is in general harder and tougher than the crystalline variety. Moreover, what is probably more important, so long as the surface is crystalline one must expect its ultimate nature to be, as it were, a forest of minute crystalline peaks, rather than of the nature of a liquid at rest on which the surface irregularities are of molecular dimensions. It is fairly obvious that a metal surface of this latter type will be much more easily protected by an exceedingly thin oil film than a surface on which there are crystalline peaks each hundreds of thousands of atoms high, which will pierce the oil film and make metallic contact, with local high temperatures and an immediate danger, or even certainty, of some metallic cohesion.

Now let me return to Finch's observation that polished surfaces may or may not remain amorphous. The forces exerted by the atoms in the underlying crystal always try to rearrange the atoms in the amorphous Beilby layer, and in some materials they succeed, so that the polish layer is found to show some crystalline character under the electron beam. On other materials the amorphous layer shows a great reluctance to recrystallize. The forces of order exerted from the underlying crystal fail to bring about any rearrangement. I may mention in passing, as a matter of some interest, that the diamond is in a class by itself. Professor Finch was never able to detect the slightest trace

of surface flow as a result of polishing. The polish on a diamond appears to be simply a rubbing down of the crystalline excrescences to smaller and smaller dimensions without their ever losing their typically crystalline character.

Diamonds seem a long way from the internal combustion engine, and yet it is quite possible these phenomena we have been discussing may prove of great importance, if they lead to means for controlling the condition of the surface layer of metals used as bearing surfaces.

One of the substances which exhibited a stable amorphous layer after polishing was spinel, which is a magnesium aluminate with aluminium oxide in solid solution. Finch has suggested that if a suitably oxidized magnesium-aluminium alloy surface is used, it is possible by polishing this "to form spinel with a permanently amorphous and therefore smooth Beilby layer." The usual aluminium alloys used for pistons, on the other hand, become spontaneously covered with a thin layer of very hard aluminium oxide. This oxide layer is, or can be made, amorphous; but Finch's observations gave evidence that during the process of running-in, the oxide layer, instead of settling down into a smooth amorphous bearing surface, became converted into a layer of minute sapphire crystals. It has long been known that the wear of the cylinder barrel is more severe with an aluminium than with a cast-iron piston in spite of the greater softness of the former. It has hitherto been supposed this was due to the embedding of abrasive particles in the soft aluminium piston, but the explanation of Finch that aluminium forms its own peculiar kind of grinding surface with sapphire teeth, is not only more picturesque, but probably more true also.

Cast iron is an example of a material long known to be in the first rank as a bearing material, and here recent research has shown conclusively that it owes its quality to a unique faculty for preparing its own bearing surface. Cast iron contains minute particles of free carbon in the form of graphite. The methods of X-ray and electron diffraction have shown that the carbon atoms in graphite are built up together in the form of thin flat plates or flakes, and that when a smooth surface of cast iron is polished, this has the effect of bringing out the occluded graphite flakes and of spreading them out over the iron surface so that their slip planes are parallel to it. In this way they act as a lubricating layer protecting the iron from abrasion. It is this unique power of forming a good bearing surface which keeps cast iron supreme as a piston ring material in spite of its being entirely unsuitable from almost every other point of view. It has poor elastic properties, it is brittle, and it conducts heat badly, but the essential thing is that a piston ring *must* continue to rub without seizure under conditions in which satis-

factory lubrication is impossible, and therefore we put up with the shortcomings of cast iron because of its peculiar virtue in this one respect.

A piston ring may seem an insignificant trifle in the whole design, but it is, perhaps, the most critical element in the piston, and this I have likened to the brain of the whole mechanism. I think I shall not be far wrong if I suggest that more money has been spent in bringing the modern piston ring to its present imperfect stage of development than on any other single element of the design, and the problem is still one in which there is great scope for the metallurgical physicist. The reason why piston ring development is so expensive is that nothing short of prolonged tests at nearly full load in the actual engine will search out its weakness, and the failure, if it comes, may be the starting point of widespread damage.

I have said enough now to show you that engine development is almost synonymous with development of the material the engine is made of; an improved fuel may allow a higher supercharge, but full use cannot be made of it without parallel improvements in a hundred other directions to meet the more severe conditions of heat flow and mechanical loading. The new problems range from the call for a 150-ton steel to the need for a more stable lubricating oil or an improved insulator for the sparking plug; but undoubtedly it is the metallurgist who must chiefly and always be at hand to advise, and he in his turn must be ready to listen to what the pure physicist can tell him.

I have emphasized the importance of a knowledge of surface conditions and the ultimate structure of metal surfaces in terms of atomic arrangement, because I think I see there the necessary line of advance in the crucial problem of rubbing without seizure. Hitherto we have been able to rely safely upon an oil film to keep down the extent of the metallic contacts; but as the temperatures of the working surfaces increase the viscosity of the oil gives less and less protection, and the nature of the metal surfaces will play a more and more important rôle in the avoidance of seizure.

The line taken by the engineer to-day is to make use of one of the recognized methods, of which there are several, of producing a hardened surface; but do we know accurately, in terms of the ultimate atomic structure, *why* one surface is hard and another soft? If the physicist would tell us that, we might make a big step towards the goal of the perfect piston ring and the unseizable bearing surface. And there are plenty of other problems about which we engineers will continue to grope in our blinkers if we do not get the physicist to teach us the ultimate nature of the materials with which we work.

INVERSE SEGREGATION: A REVIEW.* 780

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SYNOPSIS.

The literature relating to inverse segregation is reviewed. The nature of the phenomenon is described, and a selection is given from the published experimental data to illustrate the influence of the various factors which have been found to affect the extent of inverse segregation; these factors include: composition of the alloy, casting temperature, pouring speed, mould material and temperature, and the relative size of ingot to mould. The papers from which the figures quoted have been chiefly taken are by Woronoff, Bohner, Claus and Goeke, and Genders.

The numerous theories which have been advanced to account for inverse segregation are summarized, and the main supporting evidence is indicated. The principal theories are those of Smith (Le Chatelier's law), Benedicks (Ludwig-Soret effect), Masing (undercooling), Kühnel (contraction pressure of solidified shell), Bauer and Arndt (interdendritic flow), Masing and Haase (crystallization pressure), Genders (gas evolution), and Watson (dendrite migration). No attempt has been made, however, by the author to appraise the different theories.

THIS review of published information relating to the phenomenon of inverse segregation has been prepared as the initial step in an investigation of the subject which is being undertaken by the British Non-Ferrous Metals Research Association. Its purpose is to summarize existing knowledge and to give a brief account of the various theories that have been advanced.

I. INTRODUCTION.

It has been found that ingots of alloys which solidify over a range of temperature are rarely uniform in composition. Such segregation does not necessarily imply the presence of two phases, since the composition of a solid solution may vary from point to point.

From consideration of the equilibrium diagram of a binary alloy system it is possible to visualize one type of segregation. The first crystals to separate from the molten alloy are rich in higher melting point constituent and occupy a position close to the mould face. As solidification proceeds, the crystals grow towards the centre of the ingot, pushing before them the residual liquid, which is becoming continually enriched in the lower melting point constituent. The latter might be

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expected to be found, therefore, in greatest quantity in the central, last-solidifying part of the ingot. The segregation in this case is described as "normal," and analyses show that it does occur. On the other hand, segregation in the opposite direction is frequently found, *i.e.* the lower melting point constituent is concentrated towards the outside of the ingot. This type of segregation is now usually described as "inverse." Many theories have been advanced to account for it, but so far none has been found completely satisfactory.

The phenomenon of inverse segregation was observed in copper-silver alloys as long ago as 1580,¹ and references were frequently made to it in succeeding centuries.^{2,3}

Investigation into its cause may be said to date from 1875, when Roberts-Austen⁴ began researches which extended over many years. The early work was performed chiefly on the precious metals, not only on gold and silver alloys in which the phenomenon was of considerable practical concern, but also on alloys of platinum with gold, palladium, and rhodium.^{7,8,10} Attempts to obtain uniform "trial plates" against which to compare the fineness of gold and silver coinage, are described in early Royal Mint Reports.⁵

At this period the phenomenon was always referred to as "liquation." The term "inverse segregation" was introduced only 16 years ago, but it gained rapid acceptance, being a welcome alternative to liquation which already had one well-established meaning in metallurgy. A few workers still prefer the older term, however, and both are still liable to occur in literature.

II. SOME EXPERIMENTAL DATA ON INVERSE SEGREGATION.

The first investigations were directed to the determination of variations in composition in different parts of particular ingots, and there was little attempt at correlation of the results or at the formulation of a general theory to account for liquation. Silver-copper alloys received a great deal of attention,^{2,3,4,5,9,15} and at the Mint work has been continued on them. One method of procedure, as described in the Annual Report for 1924, was to explore different parts of "fillets" or strips which had been rolled from bars cast in vertical chill moulds for coinage purposes. Assays were carried out on samples in the form of small strips $\frac{1}{8}$ in. wide, taken parallel to the direction of rolling, at positions corresponding to the top, middle, and bottom of the original ingot. The width of the fillets was such that 18-22 determinations were made across each. The results of these assays show a regular gradation of composition from edge to centre, and on the whole there is a close approximation to a symmetrical distribution on each side of the

centre line of the fillet. Table I shows figures given by Smith,⁴² which are typical of those obtained at the Mint.

TABLE I. (Smith. ⁴²)

Composition of Alloy, Silver per 1000.	Direction of Liquation of Silver.	Maximum Differences Due to Liquation, Parts of Silver per 1000.		
		Top.	Middle.	Bottom.
925	towards centre	3.5	4.8	1.5
900	" "	5.8	6.4	1.3
835	" "	4.1	6.3	1.6
800	" "	7.0	6.9	2.4
750	" "	7.0	3.7	0.6
720	uniform	0.5	0.4	0.4
700	towards outside	2.8	0.7	0.8
650	" "	4.7	11.0	1.6
500	" "	4.7	12.4	3.2

Researches on the occurrence of inverse segregation in commercial alloys, of which there have now been a great number, began in 1921, when Bauer and Arndt²² investigated 16 alloys from ten different systems in an endeavour to find some general relation between alloys which exhibit the phenomenon. In three systems (copper-nickel, copper-zinc, and mercury-lead) no segregation took place at all; in two others (gold-silver and iron-carbon) the segregation was normal, while in the remaining five systems (copper-tin, copper-manganese, aluminium-zinc, aluminium-copper, and silver-copper) it was inverse. The moulds used by Bauer and Arndt were of two sizes, machined from cast-iron cubes of 125 and 130 mm. side, respectively. In the smaller cube a hole was machined 50 mm. in diameter at the top, 30 mm. in diameter at the bottom, and 60 mm. high, and in the larger a hole 90 mm. in diameter at the top, 60 mm. in diameter at the bottom, and 100 mm. high. These moulds were used both cold, for obtaining rapid cooling, and red hot for slow cooling of the ingots. No details of casting conditions are given.

Bauer and Arndt concluded that the conditions necessary for the production of inverse segregation are a long solidification range in the alloy concerned and a considerable temperature gradient between the outside and centre of the ingot. The alloy may be of either the solid solution or the simple eutectic type, as Iokibe⁶² showed later. They also evolved a theory to account for inverse segregation, which has since aroused considerable discussion and undergone modification by later workers. The two main conditions given above, however, have never been disputed, and have, indeed, always been borne out in other researches.

Consideration of a number of results led Masing and Haase⁴⁸ to suggest that there are two distinct types of inverse segregation, probably due to separate causes. There is the type that occurs in solid solution alloys rapidly solidified in a chill mould, which is detectable only by

TABLE II. (Woronoff.⁵⁴)

Average.		Exudations.	
Iron, Per Cent.	Silicon, Per Cent.	Iron, Per Cent.	Silicon, Per Cent.
0.39	0.30	1.31	0.73
0.45	...	1.69	...
0.54	0.30	1.54	0.75
0.70	0.42	0.93	0.99

chemical analysis; and there is the type which takes the form of exudations, forced to the surface of the ingot at a late stage in the course of solidification. These exudations usually consist of a very low melting-point constituent in the alloy, and in some cases impurities are ejected in this form. Table II shows figures for the composition of exudations found on commercial aluminium ingots as given by Woronoff.⁵⁴

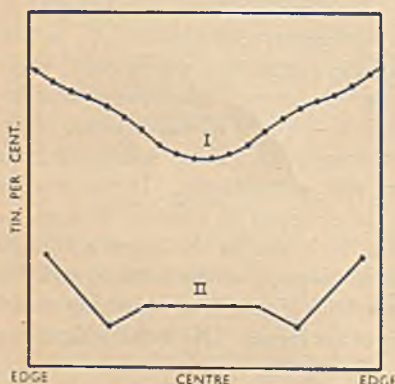


FIG. 1.—Variations in Tin Content Found in Bronze Ingots after (I) Rapid, and (II) Slow Cooling. (Masing and Haase.)

The distribution of low melting point constituent across the section of the ingot is quite different in the two types of inverse segregation, as shown in Fig. 1. Curve I shows the variation in tin content in a chill-cast bronze ingot. The increase in tin is more or less uniform from centre to outside. Curve II shows the variation in a slowly cooled ingot. Near the centre the tin content is uniform; then there is a tendency to normal segregation; and finally a sharp increase in tin occurs at the edge. The essentially

different natures of these two curves, convinced Masing and Haase that there are two quite separate phenomena here, and they proposed that the term "inverse segregation" should be applied only to the former kind (as shown in Curve I). They illustrate their contention by Fig. 2, which is purely qualitative. Bohner,⁶³ as the result of experiments in which the mould temperature could be

varied over a wide range, decided that the relation between segregation and rate of solidification could be expressed by Fig. 3. The two diagrams can presumably be reconciled on the assumption that the first will apply in cases where there is a very low melting point constituent which can be expelled at a late stage in solidification, whereas the second will apply more particularly to a single-phase solid solution.

As has been mentioned already, the segregation of many alloys has now been investigated. To the list of those which show no inverse segregation may be added aluminium bronze (Claus and Goederitz⁵⁰), Silumin, and Elektron (Bauer and Vogel⁵⁸); the latter have also confirmed that no inverse segregation occurs in brasses.

It should be noted, however, that exudations may occur if additions, such as lead, are made which lead to the formation of a low melting point constituent; for instance, Price and Phillips⁴¹ found that in an alloy of average composition—copper 70.21, tin 1.21, and lead 0.01 per cent., exudations occurred having a composition copper 66.66, tin 4.02, and lead 0.03 per cent., and containing a large amount of copper-tin eutectoid: no description was given of how the ingots were cast. Alloys at the other end of the copper-zinc system display pronounced inverse segregation, which reaches a maximum in the 15 per cent. copper alloy. Considerable research has been done on these alloys, first by Iokibe³¹ and later by Masing and Haase³⁵ and Haase,⁶¹ not because of their importance in practice, but because they also show considerable expansion on slow solidification, and

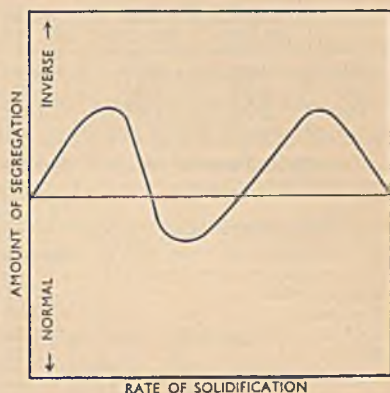


FIG. 2.—Relation Between Segregation and Rate of Solidification. (Masing.)

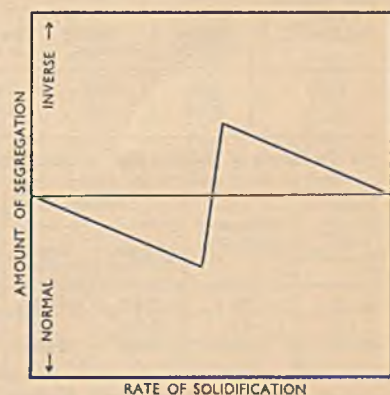


FIG. 3.—Relation Between Segregation and Rate of Solidification. (Bohner.)

TABLE III. (Woronoff.⁵⁴)(1) *Influence of Casting Temperature.* (No other details given.)

° C.	Surface.		Centre.		Difference.	
	Copper, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Iron, Per Cent.
750	3.94	1.00	3.66	0.67	0.28	0.33
730	3.98	0.95	3.61	0.72	0.37	0.23
700	3.96	0.91	3.39	0.56	0.57	0.35

(2) *Influence of Mould Temperature.* (No other details given.)

Mould Temperature.	Copper, Per Cent.		
	Exudations.	Surface Layer.	Centre.
Water-cooled	15.24	8.42	3.71
Uncooled	13.59	7.23	3.96
150° C.	11.10	4.88	3.74
200° C.	8.79	4.99	3.69

(3) *Influence of Rate of Pouring.* Weight of the Ingot 20 kg. Casting Temperature 730° C. Chill Mould.

Mean Rate of Pouring, Kg./Second.	Surface.		Centre.		Difference.	
	Copper, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Iron, Per Cent.
0.40	3.89	0.81	3.66	0.56	0.23	0.25
0.15	4.04	0.80	3.50	0.62	0.54	0.18

(4) *Influence of Relative Size of Ingot and Mould.* (No other details given.)

Mould Diameter Ingot Diameter	Thickness of Ingot, mm.	Surface.		Centre.		Difference.	
		Copper, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Iron, Per Cent.	Copper, Per Cent.	Iron, Per Cent.
4 : 1	20	3.48	0.64	3.24	0.57	0.24	0.07
2 : 1	45	4.04	...	3.66	...	0.38	...
1 : 1	90	3.68	0.68	3.14	0.50	0.54	0.18

(5) *Influence of Mould Material.* (No other details given.)

Type of Mould.	Mould Diameter, Ingot Diameter	Copper, Per Cent.		
		Surface.	Centre.	Difference.
Sand		4.09	4.08	0.01
Chill		4.29	4.21	0.08
	1 : 1	4.33	4.00	0.33
	2 : 1	4.48	3.81	0.67
	3 : 1	4.58	3.87	0.71

attempts have been made to correlate the two phenomena (see p. 50).

Apart from the precious metals, the alloys to which most attention has been devoted by investigators, are bronzes and aluminium-copper alloys. Since the size and shape of the ingots and the conditions of casting vary in every case it is difficult to attempt comparison between the data published by different workers. It cannot be too strongly emphasized that results are applicable only to the conditions under which the experimental ingots were produced, and that anything which causes change in the temperature gradient in the casting, such as casting temperature and speed, nature, size and temperature of mould, will lead to a different set of results. The influence of these factors on the extent of inverse segregation is demonstrated by results given by Woronoff⁵⁴ for Duralumin, as shown in Table III.

TABLE IV.—*Copper Content, Per Cent.* (Bohner.⁶³)

Position of Sample in Ingot.		Mould Temperature.			
		15° C.	230° C.	300° C.	500° C.
Top	Outside	5.45	5.34	5.01	4.75
	Centre	5.09	5.01	4.96	4.90
$\frac{1}{4}$ -way down	Outside	5.40	5.77	4.64	5.01
	Centre	4.65	4.38	4.80	5.91
$\frac{1}{2}$ -way down	Outside	5.65	5.95	5.03	5.14
	Centre	4.90	4.80	7.84	7.50
$\frac{3}{4}$ -way down	Outside	5.46	5.78	5.55	5.52
	Centre	4.80	4.75	7.15	7.20
Bottom	Outside	5.60	5.42	5.61	5.65
	Centre	5.58	5.25	5.51	5.65

The influence of mould temperature is further demonstrated by experiments of Bohner,⁶³ who, by sufficiently increasing the mould temperature, caused inverse segregation to be replaced by the normal kind. The percentages of copper found in different parts of ingots cast into moulds at various temperatures are given in Table IV. The alloy was cast at 720° C. into a taper mould made of welded sheet iron 6 mm. thick. The ingots were 165 mm. in diameter at the bottom, 195 mm. in diameter at the top, and 325 mm. high. To bring the mould to the different temperatures used, it was placed in a gas-heated bath containing a molten eutectic mixture of sodium and potassium nitrates, the bath being strongly agitated. When the ingots had cooled to about 500° C., they were quenched in cold water in order to minimize diffusion.

Bohner⁵⁹ also investigated the effect on inverse segregation of small additions of other elements (manganese, titanium, and silicon) to 6 per

cent. aluminium-copper alloys. Only limited amounts can be added, since excess leads to the formation of large brittle crystals in the ingot centre which have a harmful effect on further working. From the figures given in Table V, manganese appears to be the most useful addition for reducing inverse segregation. The ingots were 200 mm. in diameter and 700 mm. high. The alloys were cast at 690°–710° C. into

TABLE V. (Bohner.⁵⁹)

	Copper, Per Cent.		
	Outside.	Centre.	Difference.
(1) Alloy A : Silicon 0.26, Iron 0.28, Copper 6.23 Per Cent.			
Top	6.75	5.03	1.72
$\frac{1}{3}$ way down	6.69	5.18	1.51
$\frac{2}{3}$ "	6.56	5.56	1.00
Bottom	6.56	6.19	0.37
(2) Alloy B : Silicon 0.36, Iron 0.52, Copper 6.32, Manganese 0.73 Per Cent.			
Top	6.51	5.75	0.76
$\frac{1}{3}$ way down	6.57	5.82	0.75
$\frac{2}{3}$ "	6.41	6.03	0.38
Bottom	6.39	6.06	0.33
(3) Alloy C : Silicon 0.27, Iron 0.38, Copper 6.31, Manganese 0.27, Titanium 0.21 Per Cent.			
Top	6.79	5.63	1.16
$\frac{1}{3}$ way down	6.82	5.79	1.03
$\frac{2}{3}$ "	6.79	5.88	0.91
Bottom	6.66	6.14	0.52
(4) Alloy D : Silicon 0.28, Iron 0.37, Copper 5.42, Titanium 0.33 Per Cent.			
Top	5.94	4.65	1.29
$\frac{1}{3}$ way down	6.04	5.08	0.96
$\frac{2}{3}$ "	---	---	---
Bottom	5.78	5.21	0.57
(5) Alloy E : Silicon 1.08, Iron 0.29, Copper 5.30 Per Cent.			
Top	5.87	4.67	1.20
$\frac{1}{3}$ way down	5.85	5.01	0.84
$\frac{2}{3}$ "	5.82	5.41	0.41
Bottom	5.81	5.81	0.00

a cast-iron mould heated to 210°–230° C. The wall thickness of the mould was 55 mm. and the thickness of the bottom was 75 mm. At the end of the solidification of the alloy, the mould had a temperature of 320°–350° C. Pouring from the crucible took 150–180 seconds and feeding, which required about 2.25 kg. of metal, $3\frac{1}{2}$ –4 minutes.

The influence of various casting conditions on the segregation in bronzes has been investigated by Claus and Goeke,⁵² from whose work the following figures given in Table VI are taken. The segregation is

in all cases inverse. The experiments were carried out with round bars 400 mm. long and 40 mm. in diameter. The alloys were melted sometimes in a coke-fired crucible furnace and sometimes in an oil-fired furnace, both fuels containing some sulphur. The copper was first melted under a protective covering of wood charcoal, then phosphor-copper was added to deoxidize it; and finally the tin was added and the

TABLE VI. (Claus and Goeke.⁵²)

(1) *Influence of Composition.* All Cast in Vertical Dry-Sand Mould.

Position in Bar.	Excess Copper in Centre, Per Cent.			
	6 Per Cent. Tin.	10 Per Cent. Tin.	14 Per Cent. Tin.	20 Per Cent. Tin.
Top	0.8	1.2	1.2	0.5
Middle	0.6	0.8	0.8	0.5
Bottom	0.7	0.9	0.0	0.7

(2) *Influence of Casting Temperature in the case of 6 Per Cent. Tin Alloy.* Cast in Vertical Dry-Sand Mould.

Position in Bar.	Excess Copper in Centre, Per Cent.	
	1220° C.	1100° C.
Top	0.8	0.0
Middle	0.6	0.6
Bottom	0.7	0.1

(3) *Influence of Mould Material in the case of 10 Per Cent. Tin Alloy.* Cast at 1200° C.

Position in Bar.	Excess Copper in Centre, Per Cent.				
	Mould Vertical.			Mould Horizontal.	
	Dry Sand.	Green Sand.	Chill.	Dry Sand.	Green Sand.
Top	1.2	0.9	1.9	0.4	0.7
Middle	0.8	1.3	1.9	0.4	0.7
Bottom	0.9	0.4	2.0	0.4	0.5

whole well stirred. The charge was about 120 kg. and the melting time 45 minutes. After reaching the required temperature, the metal was taken from the furnace with a hand ladle and poured by hand. The casting temperature was in general 200° C. above the liquidus temperature of the particular alloy, and it was measured with an optical pyrometer. The sand used for the moulds contained 6-8 per cent. water. It was left in this condition for the green-sand moulds, and well dried for the dry-sand moulds. The chill mould was of cast iron

machined so that ingots cast in it had the same dimensions as those cast in sand.

Genders⁴⁷ found that the mode of pouring also influences the extent of inverse segregation. His results are summarized in Table VII, the ingots used being in slab form $12 \times 6 \times 1$ in. Analyses were carried out on shavings taken from layers $\frac{1}{16}$ in. thick. The alloy used was 5 per cent. bronze. No other particulars are given.

TABLE VII. (Genders.⁴⁷)

Position in Bar.		Tin, Per Cent.
<i>I. Chill-Cast, Top-Poured.</i>		
Bottom	Regular inverse segregation.	5.34 per cent. outside—4.91 centre.
Centre	Normal segregation changing to inverse.	4.96—5.20 (midway)—4.80.
Top	" " "	5.01—5.16 ($\frac{1}{16}$ in.)—4.88.
<i>II. Chill-Cast, Bottom-Poured.</i>		
Bottom	Regular inverse segregation.	5.18—4.94.
Centre	Irregular inverse segregation.	5.30—5.08 ($\frac{1}{8}$ in.)—5.22 ($\frac{1}{4}$ in.)—5.0
Top	Regular inverse segregation.	5.20—4.89.
<i>III. Rotary Chill-Cast Ingot (Durville).</i>		
Bottom	Regular inverse segregation.	5.88—5.28.
Centre	" " "	5.93—5.29.
Top	" " "	5.95—5.48.
<i>IV. Sand-Cast.</i>		
Segregation slight and irregular.		

The main inference to be drawn from the results set out in the foregoing tables is that the extent of inverse segregation in an ingot of an alloy of particular composition is dependent primarily on rate of cooling. This determines the time during which homogenization by diffusion can take place, which in turn decides the actual solidification interval of the alloy, as opposed to the theoretical interval indicated by the equilibrium diagram. Changes in the conditions of casting such as have been made in the experimental work described above, influence the degree of segregation only in so far as they in some way alter the rate of cooling in the ingot. For example, a high casting temperature leads to less segregation than does a low one, since the mould walls become hotter, the thermal gradients in the ingot are reduced, solidification time is prolonged and diffusion can proceed further. The same effect can be produced by the use of a sand mould, so that the rate of loss of heat is low, or by preheating the chill mould, which, as Bohner showed, if carried far enough results in a reversal of the direction of segregation. On the other hand, intensification of the chilling action by water-cooling the

mould or greatly increasing the ratio of mould thickness to ingot diameter leads to more pronounced inverse segregation, except in the case of very small ingots in which the whole of the metal solidifies practically instantaneously. A reduction in the rate of pouring appears to increase segregation by promoting cooling, and, as Genders showed, the mode of pouring also has an influence, that method which produces least turbulence in the mould causing the greatest amount of segregation.

III. THEORIES OF INVERSE SEGREGATION.

The theories which have been advanced to account for the occurrence of inverse segregation may be divided broadly into two classes :

A. In which the assumption is made that since the outside of an ingot is richer in low melting point constituent than the centre, therefore the crystals which separated first were also, for some reason, abnormally enriched in that constituent. This is accounted for by some difference in properties of the components in the liquid alloy, leading to such an adjustment of composition.

B. In which it is maintained that solidification begins quite normally in a manner predictable from the equilibrium diagram, but that at some stage prior to complete solidification, the residual liquid is forced from the centre to the outer region of the casting. The outside is thereby enriched in low melting point constituent, and the centre is impoverished. Several forces have been suggested to account for this displacement of liquid, but there is still considerable disagreement as to their relative importance in particular cases.

A.—Theories Involving the Dependence of Inverse Segregation on Conditions Set Up in the Liquid Alloy Prior to the Beginning of Solidification.

(1) *Smith's Theory* (1917).—In the course of a discussion on "Surface Tension and Cohesion in Metals and Alloys." ¹⁸ Smith put forward a "working hypothesis" by which he claimed to be able to predict the direction of segregation in a binary alloy, given a knowledge of the freezing point curve of the series, the rule being that the constituent which lowers the freezing point of any particular alloy is the constituent which tends to liquefy towards the chilling surface. From a consideration of liquation in alloys of silver-copper, gold-copper, and silver-gold, he suggested that the variation in composition in different parts of these alloys could be ascribed to differences in surface tension and intrinsic pressure of the component metals. He suggested that liquation might be an instance of the operation of Le Chatelier's principle of "mobile equilibrium," viz. that "when the state of a system is changed

the system alters so as to oppose a greater resistance to that change." In the case of molten silver-rich alloys, *e.g.* standard silver, cooling in a mould, chilling occurs which tends to change the condition of the system at the surface of the mould from liquid to solid. Unless the conduction of heat is sufficiently rapid to equalize the temperature throughout the mass, the only way in which this tendency can be opposed is by a change in the system such that the region affected may have a lower melting point and so remain liquid at the temperature prevailing. This can only be effected by a change in the relative proportions of silver and copper, the latter, in the case of the silver-rich alloys, increasing, so that an alloy of lower melting point may be formed. The suggestion was made that such a change in composition may occur because the different cohesions of copper and silver molecules result in limited miscibility. By the use of this theory, Smith successfully interpreted the results of Matthey,⁷ ¹⁰ Claudet,¹¹ and Rose.¹³ In a later paper in 1926,⁴² he extended these views to other alloys with the object of correlating the various occurrences of this form of segregation which had so far been observed. In a contribution to the discussion of Watson's paper in 1932,⁶⁵ he expressed agreement with the conclusions which had been reached and regarded his work as simplifying the problem by supplying direct evidence of the mechanism by which an unequal distribution of the constituents of these alloys is brought about.

(2) *Benedicks' Theory* (1925).—The theory propounded by Benedicks³⁴ assumed that the Ludwig-Soret effect, which had long been known to be operative in both aqueous and non-aqueous solutions of salts, could likewise occur in molten alloys, though its existence had never been directly observed at that time. The effect had not been extensively investigated because of the long period required for the attainment of equilibrium, but it was known that wherever a temperature gradient exists in a solution, a concentration gradient is also set up, the concentration being greater in the cold region than in the hot. On the basis of this theory, Benedicks accounted for the segregation of carbon and phosphorus he had observed in steel and cast iron, but he found much more convincing evidence of the truth of the theory in the extensive data on segregation in non-ferrous alloys set out in Smith's paper,⁴² to the discussion of which he contributed, than he had been able to find himself in ferrous metals. The theory has been criticized on the following grounds :

- (i) absence of experimental proof of the existence of the Ludwig-Soret effect in metals. Experiments by Hanson⁴² (discussion) and Ballay⁴⁹ on several different alloys led to negative results;

- (ii) the establishment of the concentration-gradient is known, at any rate in aqueous solutions, to be exceedingly slow ;
- (iii) to obtain the observed difference in concentration, it is necessary to assume a temperature gradient far in excess of anything possible in practice ; Desch ⁴³ (discussion) ;
- (iv) turbulence and convection currents would prevent the concentration gradient from being set up ; Vivian, Gulliver ⁴² (discussion).

(3) *The Undercooling Theory* (1922).—The theory that undercooling might be the cause of inverse segregation was first set out in extended form by Masing, ²⁷ although it had previously been suggested by Hanson ¹⁸ (discussion) and Johnson. ^{19, 20}

Masing based his argument on the fact that crystallization from a supersaturated salt solution is governed by two factors : (i) the latent heat of crystallization, and (ii) the diffusion between the crystals already separated and the surrounding liquid.

In Fig. 4, when a molten alloy containing x per cent. X is super-cooled to a temperature t below the solidus and then begins to crystallize the above two factors determine the course of solidification. If the latent

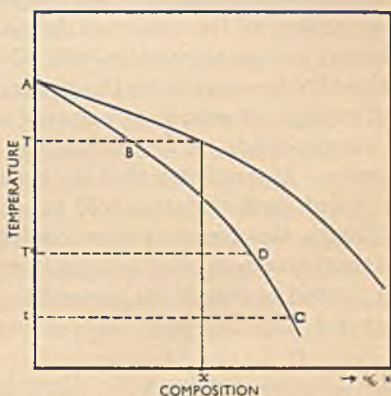


FIG. 4.—Portion of Equilibrium Diagram of Solid Solution Alloy.

heat of crystallization is the predominating factor, and a large amount of heat is evolved, the temperature will soon increase to T and crystals having a composition indicated by the point B will separate. The result is then the same as if the alloy had cooled slowly. On the other hand, when the latent heat is small and diffusion is the determining factor, the temperature of the alloy remains constant at t and it is possible for crystals having a composition C to separate, which will be richer in X than the mother liquid. The two cases just considered are extreme ones, and in general both factors will be operative. The consequence is that the temperature will increase to T' and crystals of composition D will separate, the position of T' being dependent on the relative importance of the two factors. Masing's reasoning has been criticized by some (e.g. Genders ⁴⁷), and the inadvisability of trying to apply conclusions reached from equilibrium diagrams to systems considerably out of equilibrium is clear. On the practical side, experiments by Bauer ²⁷

(discussion) and Fraenkel and Gödecke⁵³ have shown that inverse segregation can occur in alloys in which no undercooling has taken place. There is no doubt that the outer regions of some chill-cast ingots have been undercooled, as was found by Johnson^{19, 20} and by Masing and Haase⁴⁸ in the case of bronze, and by Iokibe⁶² in the case of tin-zinc alloys, but there is no evidence to show that this played an important part in leading to inverse segregation.

The above are the three main theories belonging to Class A. Certain experiments make it hard to believe that any of these theories is the correct one. For instance, Fraenkel and Gödecke⁵³ bled ingots of a copper-zinc alloy containing 12.42 per cent. copper and determined the composition of the solid shell formed. If the latter were very thin it showed normal segregation with 13.6 per cent. copper, but if it were allowed to become thicker the copper content decreased to 11.85 per cent., indicating that some transference of zinc-rich liquid must have occurred.

Experiments on Duralumin by Woronoff⁵⁴ led to the same conclusion. It was found that the residual liquid poured from a partially solidified ingot contained 6.32 per cent. copper and 1.23 per cent. iron, although the average copper content was only 4 per cent. Analysis of the central portion of an ingot in which solidification had been allowed to proceed to completion, showed that the copper had decreased to 3.60 per cent. and the iron to 0.50 per cent.

B.—Theories Involving the Dependence of Inverse Segregation on a Transfer of Liquid Metal During the Course of Solidification.

(1) *Contraction Pressure Theory* (1922).—One of the earliest investigators to suggest a force to cause displacement of the residual liquid in an ingot to the outside, was Kühnel.²⁶ His argument was that when solidification begins a crystalline envelope is formed surrounding the molten metal. Cooling causes this envelope to shrink, thereby subjecting the liquid centre to a pressure and leading to the withdrawal of the crystals from the mould walls for a short distance. When the hydrostatic pressure of the melt becomes greater than the tensile strength of the envelope—which is quite small at the high temperature—rupture takes place by intercrystalline cracking. The cracks thus formed are filled by outflowing metal, which almost instantly welds the envelope into a tight container. Their separate researches led Reader,²⁹ Bassett and Bradley,³⁷ Price and Phillips,⁴¹ and Woronoff⁵⁴ to support this theory. The observations made by Iokibe,⁶² however, on the contraction taking place in various parts of a cast ingot, cannot be reconciled at all with this theory; and Masing and Haase⁴⁸ performed a calculation,

as a result of which they concluded that the temperature gradient necessary in an ingot if contraction pressure is to be exerted is much greater than is found by experiment to exist in practice.

(2) *Interdendritic Flow Theory* (1921).—As a result of their work on sixteen different alloys from ten systems, Bauer and Arndt²² were led to formulate the interdendritic flow theory, which in a modified form is the most generally accepted theory to-day. As already stated, Bauer and Arndt found two conditions necessary to inverse segregation, *viz.* a steep temperature gradient and a long solidification interval in the alloy. They further suggested that segregation is dependent on three factors: (a) velocity of growth of the primary dendrites; (b) velocity of interdiffusion of the two constituents; and (c) the particular direction in which the dendrites show a preference to grow. If diffusion is very rapid no segregation at all occurs, but if it is slow then segregation does occur, being inverse or normal according to whether the dendrites grow very rapidly in one direction or more slowly and equally in all directions. In the case of a bronze, primary dendrites tend to grow very rapidly along the crystallographic axis, and, in the chilled outer layer of a cast ingot, these axes are largely perpendicular to the surface. Bauer and Arndt supposed that the volume of the dendrites is smaller than that of the spaces between them, and that the latter are kept filled by an influx of liquid which has been enriched in tin by the rejection of the copper-rich portion either on the already existing dendrites or by the formation of new dendrites nearer the centre of the ingot. The reason for assuming that the volume of the spaces exceeds that of the dendrites is to allow considerable influx of residual liquid and thereby to account for the big change in composition that takes place in the outer layers of the ingot during the course of solidification.

Later workers directed their efforts to finding reasons why cavities should be formed in the outer layers and to discovering forces likely to expel the liquid from the centre. Masing and Haase,³⁵ Phelps and Gulliver⁴² (discussion) independently suggested that the reason lay in the contraction in volume which accompanies the change of state of most metals. They supposed that the spaces between the arms of the primary dendrites are filled with liquid and when this solidifies and contracts more liquid flows from the centre to replace it. Since the supply of liquid is limited, its flow leads to a deficiency in the centre of the casting, with the result that the cavities so often associated with inverse segregation, are formed. Gulliver, and also Allen,⁶⁶ directed attention to the fact that the curve showing variation of composition from centre to edge of ingot is the reverse of that showing change in density and concluded the two could not be unrelated. Iokibe's work on tin-zinc alloys⁶²

led him also to accept the volume change on solidification explanation.

Masing and Scheuer ⁷⁰ made calculations from which they concluded that volume change is in many cases the chief cause of inverse segregation, but that it is not always sufficient to account for the observed amount of segregation, so that some other factor must often enter.

Reluctance to accept this theory has been centred chiefly on the uncertainty surrounding the force which causes the outward flow of liquid. Gulliver thought gravity and capillary attraction sufficient reason. Later, Ellis ⁶⁸ advanced new reasons, based on considerations of surface energy and vapour pressure.

(3) *Crystallization Pressure Theory* (1925).—The failure of contraction on solidification to account wholly for the amount of inverse segregation observed in chill-castings, has led to a search for some other cause of the outward flow of residual liquid, and it has been suggested by Masing and Haase ³⁵ that one may be found in a crystallization pressure, which, in slowly cooled ingots, manifests itself as an expansion of the solidified outer zone by the mutual pushing apart of the growing dendrites. Turner and Murray ¹⁶ had recorded the expansion that occurs on the slow solidification of zinc-copper alloys and shown that the amount of expansion is proportional to the solidification range of the alloy. The work on these alloys was extended by Iokibe ³¹ who directed attention to the remarkable similarity between the curve of expansion on slow solidification against composition and the curve showing amount of inverse segregation in chill-cast alloys against composition. The expansion depends on a strongly directional crystal growth, similar (as Desch suggested in the discussion of Iokibe's paper) to that which causes the swelling observed during the slaking of lime. The crystals formed extend to the centre of the ingot and finally push the opposite sides apart.

Masing and Haase based their theory on Iokibe's observations. They assumed that, since it is impossible in a chill-casting to have an actual expansion such as is found in the slowly-cooled specimens mentioned above, owing to the rapid formation of a solid shell, the growing dendrites therefore exert pressure on the residual liquid in the centre of the ingot and expel it towards the outside. Despite the fact that Iokibe subsequently showed that tin-zinc alloys, although liable to inverse segregation, do not expand on slow solidification, Masing and Scheuer ⁷⁰ still believed that crystallization pressure might be a factor in some cases. It may be noted that between 1925 and 1933 Masing appears to have altered his opinion of the relative importance of crystallization pressure and contraction on solidification. In 1925 he thought the influence of contraction on solidification in cases of pronounced inverse segregation

to be negligible compared with that of crystallization pressure, whereas in 1933 he regarded the latter as only supplementary to contraction on solidification. Masing and Scheuer were led by the work of Masing and Overlach⁵⁶ and of Haase,^{64, 72} on the volume and density changes which occur when cast alloys are annealed at temperatures up to the solidus, to the conclusion that crystallization pressure is best regarded as being due to an enlargement of the primary dendrites resulting from the inward diffusion of a second constituent from the residual liquid. It is well-known that in the crystallization of solid solutions the centres of the dendrites are far less concentrated than the edges and that as cooling proceeds they tend to become richer in lower melting point constituent by diffusion from the residual liquid. In doing so the crystals often become larger as a whole and not only on the side into which diffusion is taking place.

In Fig. 5, the solid solution dendrite, *A*, which is in contact with other similar dendrites, takes up a second constituent by diffusion from the residual melt, *R*, and grows out to the boundary, *b*, thereby pushing apart the adjacent dendrites which are also tending to grow in the same manner. The residual melt will



FIG. 5.—Effect of Crystallization Pressure. (Masing.)

then no longer fill the enlarged space between them; more may be drawn in from elsewhere, if available, or a cavity will be left. In certain alloys the mechanism just outlined leads, in cases of slow solidification, to an expansion of the whole ingot and, in cases of rapid solidification where a rigid shell is quickly formed, to the subjection of the residual liquid to a pressure sufficient to force it through the interdendritic channels to the periphery of the ingot, and hence cause inverse segregation.

(4) *Gas Evolution Theory* (1927).—Researches on bronzes containing 5 per cent. tin led Genders⁴⁷ to believe that gas evolution during the later stages of solidification is the primary cause of all inverse segregation. Every molten metal contains more or less dissolved gas, which, as solidification proceeds, becomes concentrated in the residual liquid until the latter becomes supersaturated at the prevailing temperature, whereupon the gas is liberated and immediately forces the liquid metal along the interdendritic passages towards the outside of the ingot, giving

rise at the same time to the central porosity which is always associated with inverse segregation. This theory has the advantage of being easy to visualize, but there has been general reluctance to accept it as the primary factor in all cases of inverse segregation, though there is agreement among most workers that evolved gas is responsible for that type which occurs on slow cooling, often accompanied by the appearance of exudations at a very late stage in solidification. Indeed, Genders was not the first to suggest the explanation in these cases; Woyski and Boeck²⁸ attributed tin-sweat to the liberation of gases absorbed from the furnace atmosphere, and Masing and Dahl⁴⁰ showed that exudation of eutectic in aluminium-iron alloys is due to a similar cause. Masing⁷⁰ has proposed that this type of segregation, which is illustrated by Curve II, Fig. 1, should be called "gas segregation." Various attempts have been made to disprove Genders' theory by bleeding ingots (Archbutt⁴⁷ (discussion); Fraenkel and Gödecke⁵³) and showing that inverse segregation begins at a very early stage in solidification, before the liquid is likely to have become supersaturated with gas; and by observing inverse segregation in ingots cast from vacuum-melted metal (Gayler⁵⁵; Bohner,⁶³ Fraenkel and Gödecke⁵³) in which the amount of gas present is very small if not entirely absent.

(5) *Watson's Theory* (1932).—The theory advanced by Watson⁶⁵ is based on experiments carried out on copper-silver alloys, which were maintained for some hours at a temperature between the solidus and liquidus. In this way large primary dendrites were grown which migrated under the influence of gravity either to the top of the crucible (if copper-rich) or to the bottom (if silver-rich). Severe chilling action was then applied at the end at which the dendrites had collected and chemical and microscopic examination was made of the resulting ingot. In all cases it was found that the large primary dendrites had receded from their former position by a short distance, and that a region of chilled metal existed between them and the ingot surface, which was now relatively impoverished in respect of the constituent which had accumulated there previously. Watson reached the conclusion that all inverse segregation phenomena could be explained on the assumption that the primary crystals which are formed at the mould surface when an ingot begins to solidify, immediately migrate towards the centre of the ingot. The particular force which occasioned the migration was not identified, but it was suggested that there were many possible ones. Such a radically unorthodox conception of the process of crystallization naturally did not go unchallenged, and it was criticized by Genders⁶⁵ (discussion) and Allen,⁶⁶ both of whom thought that the experimental observations had been misinterpreted.

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- ³² K. Iokibe and K. Matsuyama, "On Inverse Segregation in Bronze," *Tetsu-to-Hagane*, 1924, 10, 599-612 (Abstract : *J. Inst. Metals*, 1926, 36, 441). Work on similar lines to that of Iokibe,³¹ leading to the same conclusions.
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- ³⁷ W. H. Bassett and J. C. Bradley, "Exudations on Copper Castings," *Trans. Amer. Inst. Min. Met. Eng.*, 1926, 73, 700 (Abstract : *J. Inst. Metals*, 1926, 35, 466).
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- ⁴⁹ M. Ballay, "The Ludwig-Soret Effect in Metallic Alloys," *Rev. Mét.*, 1928, 25, 427-454, 509-520 (Abstract: *J. Inst. Metals*, 1929, 41, 468). An article entitled "Inverse Segregation," *Metallurgist* (Suppt. to *Engineer*), 1928, 4, 165-167, is largely devoted to Ballay's work. Experiments on lead-tin, copper-tin, zinc-tin, cadmium-tin alloys.
- ⁵⁰ W. Claus and F. Godercitz, "(Contribution) to our Knowledge of Inverse Segregation in Aluminium Bronze," *Giesserei*, 1928, 15, 398 (Abstract: *J. Inst. Metals*, 1929, 41, 445). Conclude inverse segregation does not occur in alloy containing 4.5 per cent. aluminium.
- ⁵¹ R. Law, "Segregation in Non-Ferrous Alloys," *Chem. Eng. and Min. Rev.*, 1928, 20, 135-139 (Abstracts: *J. Inst. Metals*, 1928, 40, 535; 1929, 42, 467). The principal theories are discussed.
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- ⁶⁴ C. Haase, "Volume Changes by Diffusion in Connection with Inverse Segregation.—I," *Z. Metallkunde*, 1932, 24, 258-261 (Abstract: *J. Inst. Metals*, 1932, 50, 730). Expansion attributed to diffusion causing increase in size of dendrites.
- ⁶⁵ J. H. Watson, "Liquation or Inverse Segregation in Silver-Copper Alloys," *J. Inst. Metals*, 1932, 49, 347-362. New theory advanced depending on repulsion from mould face of primary dendrites.
- ⁶⁶ N. P. Allen, "Further Observations on the Distribution of Porosity in Aluminium and Copper Ingots, with some Notes on Inverse Segregation," *J. Inst. Metals*, 1933, 52, 193-220. Detailed investigation of two ingots of 6.7 per cent. aluminium-copper alloy.
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- ⁷⁰ G. Masing and E. Scheuer, "Investigations on Segregation," *Z. Metallkunde*, 1933, 25, 173-179; complete translation in *Light Metals Research*, 1933, 2, (35), 12-29 (Abstract: *J. Inst. Metals*, 1933, 53, 698). A somewhat abridged version is found in an article by Masing: "A Few Problems in Non-Ferrous Castings," *Metals and Alloys*, 1933, 4, (7), 99-104. A very comprehensive review of previous work.
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- ⁷² C. Haase, "Volume Changes by Diffusion in Connection with Inverse Segregation.—II," *Z. Metallkunde*, 1934, 26, 181-185 (Abstracts: *Met. Abs.*, 1935, 2, 154; *Metals and Alloys*, 1935, 6, (M.A.), 119). Similar work to that in ⁶⁴ above on further alloys.
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- ⁷⁴ N. P. Allen and S. M. Puddephat, "Observations of the Porosity and Segregation of Two Bronze Ingots," *J. Inst. Metals*, 1935, 57, 79-92.

- ⁷⁵ C. Bernhoeft, "Segregation Phenomena in Cast Bolts and Bars of Brass," *Z. Metallkunde*, 1935, 27, 115-116 (Abstracts: *Met. Abs.*, 1935, 2, 463; *Metals and Alloys*, 1936, 7, (M.A.), 52). Inverse segregation observed in 58 : 40 : 2, copper-zinc-lead alloy and 64 : 36 brass.
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- ⁷⁷ G. Somigli, "Inverse Segregation and the Tin Sweat of Bronzes," *Industria meccanica*, 1936, 18, 347-355, 424-434 (Abstracts: *Met. Abs.*, 1936, 3, 511; *Chem. Abs.*, 1936, 30, 7077). Reaches same conclusion as Claus and Bauer ⁷⁶.
- ⁷⁸ J. Vero, "On the Mechanism of Segregation," *Mitt. berg- u. hüttenmänn. Abt., kgl. ung. Palatin-Joseph Univ. (Sopron, Hungary)*, 1936, 8, 194-218; (Abstract: *Light Metals Research*, 1937, 5, (10), 238).
- ⁷⁹ W. Claus, "A Remarkable Example of Inverse Segregation," *Z. Metallkunde*, 1936, 28, 391-393 (Abstract: *Met. Abs.*, 1937, 4, 183). Behaviour of a Cu-Pb-Sn-Ni alloy (72/15/10/3) is studied. This example is also dealt with by Claus in a paper: "Segregation in Tin-Bronzes," *Congrès Internat. Fonderie, Paris, Preprint*, 1937, (June); *Found. Trade J.*, 1937, 57, 343 (Abstract: *Met. Abs.*, 1937, 4, 496).
- ⁸⁰ A. Phillips and R. M. Brick, "Segregation in Single Crystals of Solid Solution Alloys," *Metals Technology*, 1937, 4, (2); *A.I.M.M.E. Tech. Publ. No. 785* (Abstract: *Met. Abs.*, 1937, 4, 186). Conclude that in single crystals inverse segregation is due to interdendritic flow caused by contraction on solidification.
- ⁸¹ H. N. Bassett, "Bearing Metals and Alloys" (Arnold, London), 1937. Pp. 255-265 contain a review of some of the theories, and there are numerous references throughout the book to the prevention of segregation in different bearing metals (Review: *Met. Abs.*, 1937, 4, 314).
- ⁸² M. P. Slavinskiy, N. I. Zedin, A. K. Konstantinov, and P. G. Kusmarzov, "The Phenomenon of Inverse Segregation in Brasses," *Trudi Leningradskogo Industriального Instituta (Trans. Leningrad Indust. Inst.)*, 1936, (4), 3-9 (Abstract: *Met. Abs.*, 1937, 4, 232).
- ⁸³ E. Longden, "Inverse Segregation in Ring Castings," *Met. Ind. (Lond.)*, 1937, 50, (23), 631 (Abstract: *Met. Abs.*, 1937, 4, 300). Addition of nickel is recommended to minimize segregation of lead and tin in large lead-bronze ring castings.
- ⁸⁴ W. Claus, "Theories of Inverse Segregation," *Metallwirtschaft*, 1937, 16, 917-926 (Abstract: *Met. Abs.*, 1937, 4, (12)). Five theories are examined and all rejected except that of gas evolution.

* Those papers marked with an asterisk should certainly be consulted by anyone wishing to pursue the subject of inverse segregation further.

CORRESPONDENCE.

MR. R. CHADWICK,† M.A. (Member): I have always felt that the literature dealing with inverse segregation describes two distinct types of phenomenon, and these the author fails to differentiate clearly in this review.

The first of these types I would typify by the kind of inverse surface structure found in chill-cast ingots of the tin bronzes and Duralumin. Here the ingot commonly has a surface layer of low melting point constituent almost sharply differentiated from the mass of the ingot. Such an ingot may be of quite fine equiaxed structure, the body of the ingot after removal of a thin surface layer showing very little variation in composition. The ingot during solidification reaches a stage at which it consists of primary crystals, wetted by,

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and embedded in, a continuous network of low melting point constituent; it has been shown that this constituent flows outwards and solidifies to form the outermost layer of the ingot; to some extent gas evolution would appear to be responsible for this, for gas cavities, resulting from the displacement of the low melting point network, may be clearly seen in the cast bronzes and Duralumin, whilst the considerable diminution in the extent of inverse segregation by reduction of the gas content of the molten alloy has been frequently described.

The second type I would describe as inversion throughout the whole ingot thickness, probably in conjunction with a columnar type of structure. Unfortunately investigators have devoted little attention to macrostructure; in many cases detailed observations on density, composition, microstructure, &c., have been made, whilst the macrostructure of ingots has not been described. In the case of Rosenhain's experiment * on a 12 per cent. copper-88 per cent. aluminium alloy, it would appear that such a columnar structure was present, as otherwise it is difficult to see how the sharp liquid-solid division occurred in the freezing mass. It would appear to be of considerable interest, therefore, to show whether primary columnar crystals themselves show an inversion in composition, the outer ends being of lower melting point than the inner ends. Watson may have been dealing with such an inversion, but one cannot deduce from the data given whether the primary dendrites formed portions of long columnar crystals. Watson attempted to explain such an inversion, but could give no scientific reason for the migration of his primaries. I have, however, previously put forward a theory † (unnoted by the author of this review) which explained the migration of primaries described by Watson, by assuming that the primary crystals grew only at the side adjacent to the mould wall, and were therefore pushed inward by the mechanical force of the growing crystals. Such a mechanism requires only the assumption of a liquid layer wetting the outside of the solidifying ingot, whilst a further characteristic would be a very small temperature gradient in the solidifying ingot. The formation of beads of low melting point constituent on the surface layer of prematurely-stripped ingots of bronze and Duralumin have been frequently described, with chill moulds one can frequently observe a liquid layer wetting the ingot surface in these and other alloys, and if the mould wall is smooth, an unbroken surface layer normally results.

The two types of inverse segregation postulated have in common the outflow of liquid during solidification. In the former, however, the outflow occurs only during the solidification of the last low melting point fraction, whilst in the latter the whole of the primary columnar growth is assumed to occur by an outflow of liquid. From a study of equiaxed and columnar structures, it should not be difficult to show whether two such types do in fact occur. It is also worth noting that an outflow of liquid would permit of a more rapid heat transfer than the conventional conduction through a solid outer shell, and some evidence might be obtained from the observation of rates of solidification and heat transfer.

Previous investigators appear to have been rather shy of the idea of a partly solidified ingot consisting of primary crystals completely separated by films of liquid alloy. One has only to think of the strong adhesion between flat plates of glass or metal separated by a liquid film, to realize the possible strength of such a structure, and the author should not therefore regard such an idea as too improbable.

Finally, I should like once again to make a plea for the examination of large ingots, for it is then possible to observe more clearly and leisurely the intermediate stages of solidification.

* *J. Inst. Metals*, 1927, 37, 275.

† *J. Inst. Metals*, 1935, 57, 89.

Mr. A. R. UBBELOHDE,* M.A., B.Sc.: Mechanical theories of inverse segregation (Class B in Mr. Vaughan's paper) assume that the composition of solid deposited at any point from the liquid agrees with the usual solidus-liquidus curves, and that any departure from normal segregation, in which the purest solid is that first deposited, is due to a mechanical transport of residual liquid to abnormal parts of the ingot. Direct evidence of such transport would be of great value. A method which does not seem to have been tried is to "mark" a layer of the liquid in the mould with minute quantities of an indicator element. Although certain experimental difficulties suggest themselves, the range of radio elements available makes it possible to add small amounts of a suitable element without seriously disturbing the physico-chemical behaviour of the layer of "marked" liquid. A radiation photograph † of sections of the solidified ingot would show what movement, if any, had taken place with the marked liquid, under different conditions of cooling.

In the absence of conclusive information on possible mechanical causes of inverse segregation, it is useful to review the thermodynamical implications of certain physico-chemical theories (Class A). These are all based in some way on the observation that inverse segregation is only marked when rapid chilling is used, so that there are large temperature gradients in the liquid, and crystallization takes place under irreversible conditions.

(a) *Types of substance which might give an appreciable Ludwig-Soret effect.* It has been suggested that when large temperature gradients are present in the liquid, a concentration gradient may be set up, as in the Soret effect in salt solutions. It may be useful to indicate in what circumstances (if ever) such gradients might become sufficiently large to account for inverse segregation. According to fairly generally accepted theory,‡ a temperature gradient dT/dx in a liquid mixture of two components *A* and *B* leads to a concentration gradient dN_A/dx , where N_A is the mol fraction of *A*, and

$$-S_A (dT/dx) = (\delta \bar{F}_A / \delta N_A)_T (dN_A/dx).$$

In this equation $-S_A$ is the "entropy of transfer" of the component *A* in solution, and $(\delta \bar{F}_A / \delta N_A)_T$ is the change in partial molal free energy of the component *A* with concentration. Owing to the fact that the magnitude and sign of the entropy of transfer can only be determined experimentally from measurements of the Soret effect, this equation is of little use in predicting the magnitude of the concentration gradients, except in one class of systems. It is clear that when $(\delta \bar{F}_A / \delta N_A)_T$ tends to become very small, even quite small values of the entropy of transfer may lead to large concentration gradients. Well-established experiment and theory show that $(\delta \bar{F}_A / \delta N_A)_T$ tends to become very small in the region of concentration and temperature where the liquid is about to separate into two liquid phases. (The system phenol + water is a well-known example.) This may possibly account for the fact that in steel ingots containing a number of impurities, the elements *C*, *S*, *P*, whose miscibility in the liquid is probably limited, show large inverse segregations in suitable circumstances, whereas elements closely similar to iron, such as nickel or chromium, show much smaller segregations. Unfortunately, it must be emphasized that the Soret effect in liquid metals has not been sufficiently investigated to warrant any firm conclusions on its practical importance in ingot casting.

(b) *Irreversible crystallization.* Solidus-liquidus curves refer to true

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† Investigations on a limited number of radio elements have been published by Tammann and co-workers: *Z. anorg. Chem.*, 1932, 205, 145; *Z. Metallkunde*, 1933, 25, 153, 207.

‡ E. Eastman, *J. Amer. Chem. Soc.*, 1928, 50, 283; 1937, 59, 1198.

C. Wagner, *Ann. Physik*, 1929, [v], 3, 629.

thermodynamic equilibrium between solid and liquid, in which each component has the same partial molal free energy in the solid and the liquid phase. This requires considerable rearrangement of the molecules on solidification, and in consequence crystallization is only thermodynamically reversible when the rate of crystallization is slow compared with the rate of rearrangement of the molecules.

Irreversible crystallization takes place when the free energy of the solid deposited is appreciably less than that of the mother liquor. This must be the case whenever crystallization is proceeding rapidly. Although the thermodynamics of irreversible processes is not completely worked out, the experimental evidence suggests that the composition of the solid separating from the liquid is that which can be most rapidly formed, with the smallest fluctuation of entropy.* For example, in the crystallization of a single substance the *least stable* form tends to separate spontaneously, whereas in thermodynamic equilibrium the *most stable* crystal form would be present. This reversal of the behaviour which might be expected from equilibrium considerations may also apply to the spontaneous formation of solid solutions. If there were no volume change on crystallization, the solid requiring the minimum entropy fluctuation would be that with the same composition as the liquid, since this involves no rearrangement of the molecules. On this basis alone, solid solutions separating under conditions where the crystallization was rapid might be expected to approximate more closely to the mother liquor in composition than if sufficient time is allowed for thermodynamic equilibrium.

Crystallization is, however, accompanied by a change in volume. A decrease in volume, for example, usually involves a decrease in entropy, and under conditions of irreversible crystallization the tendency would be for the solid to separate with the minimum volume change from the liquid. This could lead to the abnormal segregation of impurities which minimize the volume change on crystallization, into those crystals which are most rapidly formed. At present, experimental information on the volume changes occurring on crystallization is too scanty to test the possible importance of irreversible crystallization in leading to abnormal segregation. It can be stated quite definitely, however, that the composition of the solid separating under irreversible conditions is not determined solely by equilibrium considerations, and cannot be completely inferred from equilibrium phase diagrams.

The AUTHOR: I am surprised to find that Mr. Chadwick has not noticed that the two distinct types of inverse segregation that he believes to exist are clearly differentiated in the paper, and illustrated in Fig. 1. I may add that not everyone agrees that there are two types; some who have investigated the subject closely are of the opinion that the difference is one of degree only, and not of kind.

Mr. Ubbelohde's observations, from the theoretical point of view, are worthy of close attention from all who are interested in the problem of inverse segregation.

* A. R. Ubbelohde, *Trans. Faraday Soc.*, 33, 1203.

THE MECHANICAL PROPERTIES OF SOME METALS AND ALLOYS BROKEN AT ULTRA HIGH SPEEDS.* 773

By D. W. GINNS,† Wh.Sc., B.A.

SYNOPSIS.

The mechanical properties of carbon steels, copper, brasses, and aluminium alloys were investigated when broken in tension at very high speeds. The average time taken to reach the yield-point is 0.001 second, and to fracture 0.005 second. A pressure-resistance method was used for measuring stress, and a photo-cell method for strain, the two being combined to give a direct diagram on the cathode ray oscillograph.

It is shown that, compared with the ordinary commercial tensile test values: (a) the yield-point is increased very considerably, over 100 per cent. increase being recorded for some materials; (b) the maximum stress is increased by a much smaller amount; (c) the percentage elongation and the percentage reduction of area show comparatively small changes; (d) the types of fracture are almost identical with those obtained for the slow test.

INTRODUCTION.

It was observed by Hopkinson¹ in 1905 that stresses greatly exceeding the normally accepted values of ultimate strength could be applied to iron and copper wires for very short intervals of time without the occurrence of rupture. This fact is now generally accepted for all the more common engineering materials.

Much work has been carried out to find the maximum force applied and the energy absorbed during an impact fracture, and a historical survey is given in a symposium on impact testing of the American Society for Testing Materials.²

Körber and Storp³ also give a survey. They produced stress-strain diagrams by recording photographically the displacement-time curve of the pendulum of a Charpy machine, and deriving acceleration-displacement curves from the records. They used the results only to obtain the energy required to fracture their specimens.

There has been some discussion recently on the time factor in tensile testing, and some work at comparatively slow speeds has been carried out on this subject, the most recent being that by Quinney.⁴

So far as the author is aware there are no available data of the be-

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haviour and mechanical properties of the more common engineering materials during high-speed stressing, and this investigation was undertaken to meet this need.

GENERAL METHOD.

For work at very high speeds, the use of mechanical recording apparatus was out of the question, on account of inertia effects. Electrical methods, using the cathode ray oscillograph, were therefore developed. The tests were carried out on a new type of impact machine,⁵ the salient feature of which is the method of applying the load. A strong plate spring is held in rollers at either end, and deflected vertically at the centre to a known degree. One end of the specimen is held in a self-centring chuck fixed to the centre of the spring, and the other end held in a

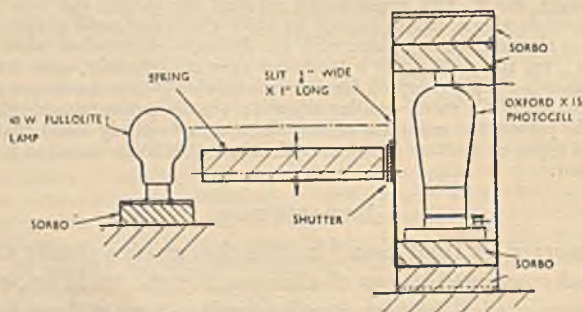


FIG. 1.—Arrangement Used to Measure Strain.

similar chuck attached rigidly from above. The spring can be released suddenly to fracture the specimen, which is thus subjected to direct tension (see Fig. C, page 78).

Measurement of Strain.

The method of obtaining the strain curve depended on the fact that the upper end of the specimen was rigidly fixed and only the lower end was allowed to move; hence the displacement of the spring at any instant was proportional to strain. A shutter connected to the centre portion of the beam was made to intercept a light shining on to a photocell, arranged in a closed box with a slit opposite the light (Fig. 1). A single-stage amplifier was used before connecting the photocell to the west plate of the oscillograph. The cell was an Oxford X15 (hard) type. Sorbo rubber pads proved most successful for damping any vibrations of the cell and light, which may have occurred owing to the sudden application of the load.

Measurement of Stress.

Stress curves could be obtained: (a) by measurement of the difference of acceleration of the spring when free to vibrate without a specimen, and when resisted by the breaking of a specimen; the difference of these would be a measure of the effective force; (b) by measurement of the force applied to the specimen by means of some rigid device between the top of the specimen and the fixed top support.

The first method was attempted by vibrating a coil, attached to the centre of the spring, in a uniform magnetic field. The resulting induced voltage was passed through a differentiating and integrating circuit to give voltages proportional to acceleration and displacement, and these voltages were applied to the north and west plates of the oscillograph. This method was discarded owing to the instability of the system, and

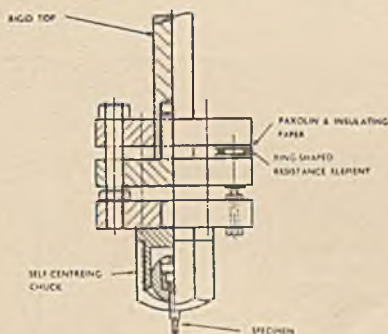


FIG. 2.—Arrangement Used to Measure Stress.

also because of the lack of purity of the free motion of the spring. A pure sinusoidal motion was required to give a straight base line in this method. The second method was therefore used.

P. Postlethwaite has developed a new material whose electrical resistance varies linearly with the pressure applied to it. This material was strong enough to withstand the load taken by a specimen, and hence method (b) for measuring stress became possible. A shackle arrangement as shown in Fig. 2 was used between the top chuck and the fixed head to bring the resistance elements into compression. Three small screws were tightened and locked whilst a static load of approximately 2.5 tons was being applied, to ensure that the elements would always be in compression during any subsequent sudden application of load. This static load was greater than any sudden load which was applied to the specimens. Three elements were equally spaced round the shackle to ensure correct alignment; they were connected in series to one arm of a Wheatstone bridge circuit arranged to allow only the unbalanced

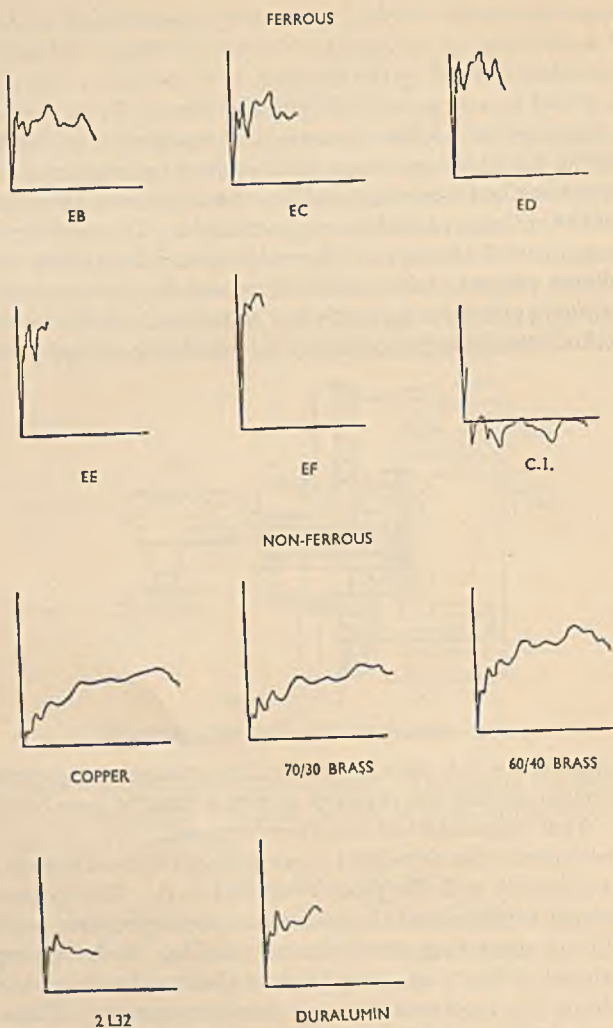


FIG. 3.—Types of Stress-Strain Diagrams.
(Not to a Fixed Scale.)

Steels: E.B. = 0.15 Per Cent. C; E.C. = 0.34 Per Cent. C; E.D. = 0.485 Per Cent. C; E.E. = 0.75 Per Cent. C; E.F. = 0.89 Per Cent. C.

Cast Iron: Figure also shows Free Vibration of Apparatus after Fracture of Specimen. Omitted from other Diagrams (see pp. 65 and 78).

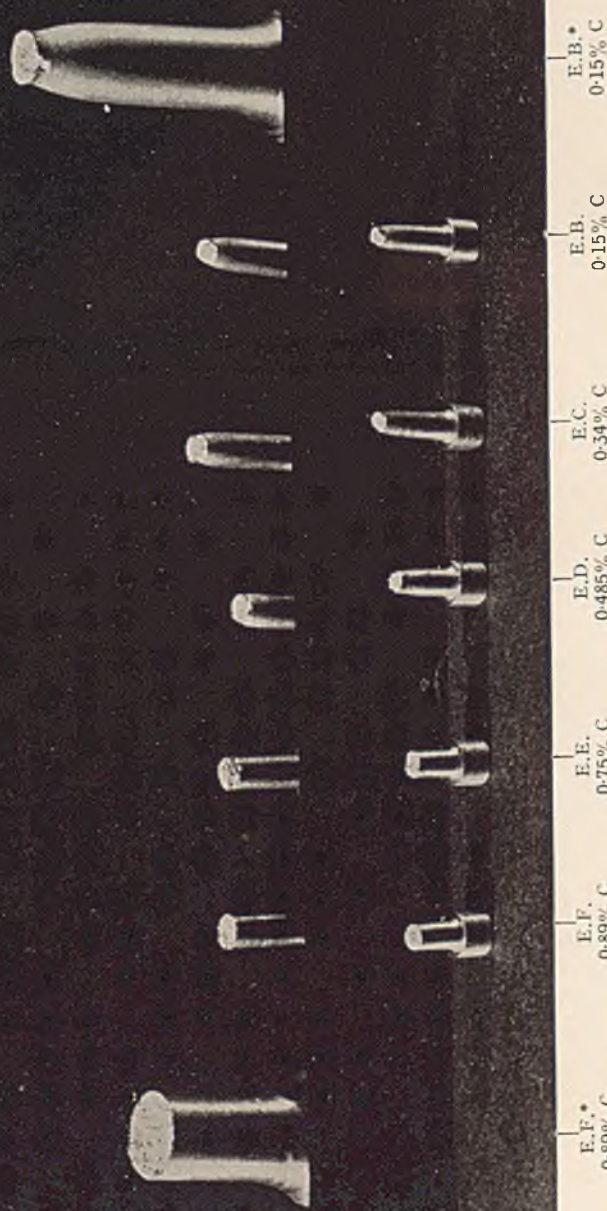


FIG. 5.—Types of Fracture. Carbon Steels.
 Top row : E.F., E.E., E.D., E.C., E.B., High-Speed Test Specimens. E.F.*, E.B.*, Avery Slow-Test Specimens.
 Bottom row : Hounsfield Slow-Test Specimens.

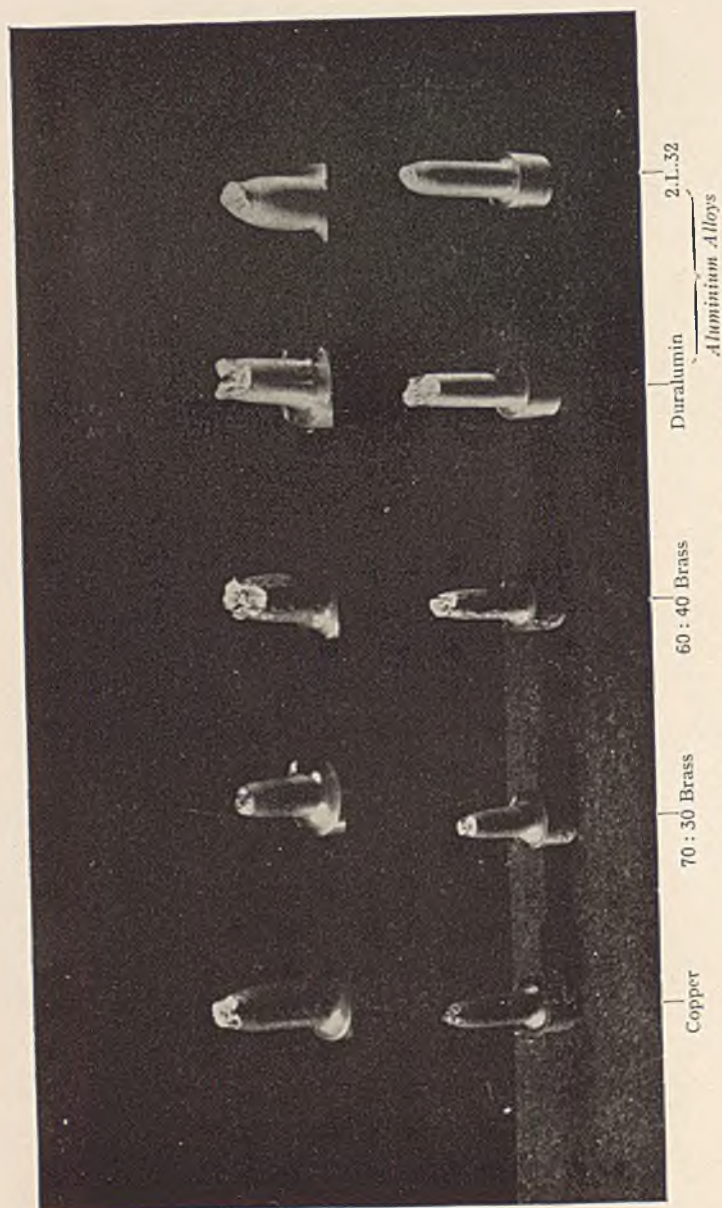


FIG. 6.—Types of Fracture. Non-Ferrous Metals.

Top row : High-Speed Test Specimens.

Bottom row : Hounsfield Slow-Test Specimens.

variations of voltage to pass to the grid of a one-stage amplifier, and hence to the north plate of the oscillograph.

Calibration.

A very great advantage was that a static calibration method could be used in each case, and the characteristics thus obtained were sensibly linear. The displacement characteristic was plotted by photographing the spot on the screen for measured deflections of the spring. The load characteristic was plotted similarly, the load for known deflections of the spring being applied to the recording apparatus through a 1-in. diameter bar which screwed into the chuck sockets. The constants of the spring were accurately determined, and gave a load coefficient of 3.70 tons per inch of deflection.

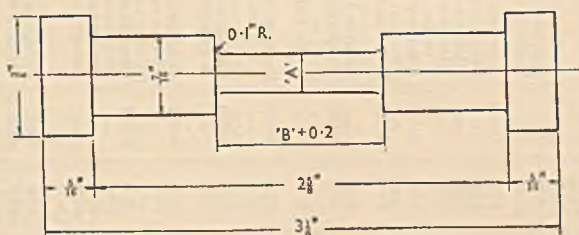


FIG. 4.—Type of Specimen Used.

Photography.

A camera with an $f1.5$ lens, which was available in the laboratory, was adapted to take single photographs. An electro-magnetic tripping device was used to trip the camera at the correct instant. An adjustable contact switch was closed by the swinging arm of the machine immediately before the spring was released, thus opening the shutter for $\frac{1}{1000}$ second, and during this period the fracture took place. Agfa isochrome film was used, and developed with Ilford special oscillograph developer.

Geometrically similar specimens were used of the form shown in Fig. 4, the diameter, and hence gauge-lengths, being varied with different materials to suit the capacity of the apparatus. In each case $B = 2\sqrt{\pi}A$. The materials used were all of commercial origin, and their analyses are given in Tables III and IV.

Measurements and Sources of Error.

The diagrams obtained showed the presence of a free vibration of the recording apparatus which distorted them (Fig. 3). That it was due to the apparatus was shown by a comparison of the vibration after the fracture of the cast-iron specimen, with the vibration after the yield-

TABLE I.—Ferrous Materials.

Material and Treatment.	Number of Specimens Fractured.	Diameter, Inch.	Elongation, Per Cent.	Reduction of Area, Per Cent.	Yield-Point, Tons/In. ²	Maximum Stress, Tons/In. ²	Time to Fracture, Second.	Type of Fracture.
<i>Carbon Steels.</i>								
E.B. 0.15% C:	6	0.252	34.6	65.2	37.0	37.0	0.006	½ cup and cone. Fibrous centre. Silky sides.
As received	1	0.179	33.0	67.0	23.3	31.0	...	Part cup and cone. Fibrous.
Machined from shank	1	0.179	39.5	71.0	29.1	29.1	...	Almost complete cup and cone. Fibrous centre. Silky sides.
As received	1	0.564	37.5*	69.0	19.1†	29.8	...	Almost complete cup and cone. Fairly shallow. Fibrous centre. Silky sides.
As received	1	0.564	37.5*	69.0	19.1†	29.8	...	½ cup and cone. Fibrous. Silky sides.
Annealed from 850° C.	3	0.252	30.3	67.8	31.0	31.0	0.006	½ cup and cone. Fibrous.
Quenched from 850° C. in cold water	1	0.252	No fracture	62.0	52.0	...	0.005	Shallow ½ cup and cone. Fibrous.
Annealed from 900° C.	1	0.236	43.2	64.3	34.0	34.0	...	½ cup and cone. Fibrous centre. Silky sides.
Machined from shank. Annealed from 900° C.	1	0.179	35.0	66.0	17.2	27.2	0.003	½ cup and cone. Steep sides. Fibrous.
Quenched from 900° C. in cold water	1	0.252	12.2	55.6	61.0	61.0	...	½ cup and cone. Fibrous. Silky sides.
Machined from shank. Quenched from 900° C. in cold water	1	0.179	20.0	50.0	31.0	47.8	...	½ cup and cone. Fibrous. Silky sides.
E.C. 0.34% C:	3	0.252	24.5	55.1	37.0	37.0	0.005	½ cup and cone. Fibrous. Silky sides.
As received	1	0.179	30.0	53.0	17.3	34.5	...	½ cup and cone. Fibrous. Silky sides.
Machined from shank	1	0.179	24.0	45.0	21.1	43.2	0.004	Rather irregular shallow cup and cone. Granular.
E.D. 0.48% C:	3	0.252	21.0	32.2	28.0	55.0	...	Jagged fracture. Fibrous.
As received	1	0.179	24.0	45.0	21.1	43.2	...	Irregular. Fine crystalline, small patches of fibrous.
Machined from shank	1	0.226	12.0	21.7	30.7	55.0	0.003	Fibrous central core. Crystalline outer ring.
E.E. 0.75% C:	2	0.226	14.0	21.7	30.7	55.0	...	Straight across. Fine crystalline. Trace of fibrous.
As received	1	0.179	11.6	11.2	68.0	72.0	0.003	Straight across. Crystalline. Trace of fibrous.
Machined from shank	1	0.179	12.0	14.0	37.5	66.8	...	Straight across. Fine crystalline.
As received	1	0.179	10.0	13.0	30.0	65.3	...	Straight across. Fine crystalline.
As received	1	0.564	9.4*	10.5	25.0†	65.2	...	Straight across. Fine crystalline.
<i>Cast Iron.</i>								
As received	3	0.292	nil	nil	18.0	18.0	0.001	Straight across. Fine grey.
Machined from shank	1	0.179	nil	nil	12.5	12.5	...	Straight across. Fine grey.

Figures in Italic = Slow-Speed Tensile Test Results.

† Fracture slightly damaged.

Figures in ordinary type = High-Speed Tensile Test Results.

* Estimated on 2 in. gauge-length.

† Measured by drop on beam.

TABLE II.—Non-Ferrous Materials.

Material and Treatment.	Number of Specimens Fractured.	Diameter, Inch.	Elongation, Per Cent.	Reduction of Area, Per Cent.	Yield-Point, Tons/In. ²	Maximum Stress, Tons/In. ²	Time to Fracture, Second.	Type of Fracture.
<i>Copper.</i>								
As received	3	0.292	25.5	67.9	22.0	22.0	0.004	Irregular cup and cone. Silky to fibrous.
Annealed from 550° C. in cold water	3	0.292	59.3	74.5	5.0	19.0	0.003	Cup and cone. Fibrous centre. Silky sides.
Machined from shank. Annealed from 550° C. in cold water	1	0.179	54.0	76.0	2.4	13.8	...	Irregular, matte.
70 : 30 Brass.								
As received	3	0.252	30.8	67.2	30.0	30.0	0.005	$\frac{1}{2}$ cup and cone. Fibrous centre. Silky sides.
Annealed from 550° C. in cold water	3	0.252	65.3	74.4	11.0	24.0	0.003	Almost complete cup and cone. Fibrous centre. Silky sides.
Machined from shank. Annealed from 550° C. in cold water	1	0.179	75.0	75.0	7.6	22.1	...	Part cup and cone. Fibrous centre. Silky sides.
60 : 40 Brass.								
As received	3	0.292	43.4	57.6	16.0	29.0	0.005	Irregular. Silky to fibrous. Gauge-length irregular, showing crystal deformation.
Annealed from 550° C. in cold water	3	0.292	43.1	61.8	14.0	23.0	0.007	Irregular 45° shear. Silky to fibrous. Gauge-length irregular showing crystal deformation.
Machined from shank. Annealed from 550° C. in cold water	1	0.179	47.0	62.0	9.8	26.4	...	Practically 45° shear. Silky edges, matte centre. Gauge-length irregular, showing crystal deformation.
<i>Aluminium Alloys.</i>								
2 L. 32.								
As received	2	0.202	21.4	67.4	15.0	16.0	0.004	$\frac{1}{2}$ cup and cone. Fibrous centre. Silky sides.
Machined from shank	1	0.179	21.0	65.0	11.3	14.6	...	Part cup and cone. Fibrous centre. Silky sides.
Duralumin.								
As received	2	0.252	30.0	40.7	23.0	30.0	0.004	Irregular 45° shear. Fibrous.
Machined from shank	1	0.179	24.0	35.0	18.2	27.0	...	45° Shear. Silky.
Annealed from 350° C.	1	0.252	15.6	49.0	13.0	20.0	0.004	$\frac{1}{2}$ cup and cone. Part fibrous. Part silky.
Quenched from 600° C. in cold water.								
Broken 2 minutes 20 seconds later.	1	0.252	24.5	52.3	11.0	17.0	0.004	$\frac{1}{2}$ cup and cone. Part fibrous. Part silky.
Age-hardened for 4½ hrs. at 150° C.	1	0.252	17.8	46.1	24.0	30.0	0.004	$\frac{1}{2}$ cup and cone. Part fibrous. Part silky.

Figures in ordinary type = High-Speed Tensile Test Results.

Figures in italic = Slow-Speed Tensile Test Results.

• Fracture slightly damaged.

TABLE III.—Analyses of Ferrous Materials.

Material	C.	Si.	Mn.	S.	P.	Ni.	Cr.
Carbon Steels:							
E.B.	0.15	0.254	0.71	0.034	0.044	0.05	0.01
E.C.	0.34	0.19	0.58	0.045	0.035	0.09	0.04
E.D.	0.485	0.221	0.75	0.025	0.034	0.15	0.08
E.E.	0.75	0.24	0.31	0.020	0.006	0.04	0.03
E.F.	0.89	0.20	0.68	0.022	0.016	0.05	0.04
Cast Iron	3.59	1.66	0.40	0.07	0.73		

TABLE IV.—Analyses of Non-Ferrous Materials.

Material	Cu.	Zn.	Sb.	Pb.	Fe.	Aln.	Ni.	Al.	Mg.	Si.	As.	Op.
Copper	99.96				0.03	<0.01	<0.01				<0.01	0.043
70 : 30 Brass	70.56	29.47	Ni1	<0.01	0.06	<0.01	0.06					
60 : 40 Brass	59.74	40.05	0.07	0.05								
Aluminium Alloys:												
2.L.32	2.42	4.77			0.53	<0.01	<0.01	91.9	0.08	0.28		
Duralumin	4.20				0.40	0.60	<0.01		0.69	0.21		

point in the other specimens. The fact that the vibration after the complete release of the load in the case of cast iron had not the datum line for its axis was accounted for in the design of the apparatus. Although a true diagram was not obtained, a mean line through the vibration could readily be drawn, and the vibration was extremely useful in showing the exact yield-point, as whilst the load was being applied uniformly no vibration could take place, since it was equivalent to steadily loading a spring system. At the yield-point a change of rate of loading took place, equivalent to a force in the opposite direction, which made the system vibrate. (The bottom of the recording apparatus showed a movement of 0.0025 in., relative to the top, under a static load of 2.44 tons.) (See further discussion, p. 78.)

In measuring the yield-stress, the point on the diagram at which the vibration first showed was taken as the yield-point.

The maximum stress was measured by means of a mean line drawn through the vibration.

The natural frequency of vibration of the spring was 35.7 per second. This was obtained by vibrating the beam by means of an electromagnet excited by a variable frequency generator.

The calculation of the time to fracture a specimen assumed no change in this frequency, owing to the presence of the specimen. A mathematical analysis showed that this assumption was justified.

The force due to the acceleration of the recording apparatus was estimated, and shown to give an error of less than 1 per cent. on the recorded load on the specimen.

The time taken to reach the yield-point was very small, and a high degree of accuracy could not be obtained in the measurement of this quantity. An average figure was 0.001 second.

Results.

The results are given in Tables I and II. The figures in italic type were obtained from tensile tests taking approximately 2 minutes in a Hounsfield Tensometer. The shanks of specimens broken in the high-speed tests were used to obtain test-pieces for this purpose. One only of each type was tested in this way. To check these results, specimens of the steels marked E.B. and E.F. were turned from bars in the "as received" condition, and broken in the Hounsfield Tensometer, and 0.564-in. diameter standard screwed end test-pieces made of these materials were pulled in the Avery testing machine. It was found that, whereas the results from the Hounsfield and Avery test-specimens in the "as received" condition agreed quite closely, using the material from the shanks of broken specimens, the tensile strengths were higher than

those obtained for the "as received" material, suggesting some work-hardening. For this reason it must be assumed that unless the slow-test specimens were annealed, the recorded yield and maximum stresses for these materials in the Tensometer test are probably high.

Ferrous Alloys.

In general, the type of diagram obtained was similar in shape to the ordinary slow-test diagram (Fig. 3), except that the yield-stress in the lower-carbon steels was the maximum stress reached. The yield-stress was increased very considerably as compared with the slow test, but the maximum stress showed a much smaller increase. The type of fracture was the same as that obtained in the slow test (see Fig. 5, Plate V). The percentage elongation and the percentage reduction in area were generally slightly decreased. The yield in mild steel (E.B.) was sudden, as shown by the sudden and irregular vibration which was introduced at that point. The suddenness of the yield decreased as the carbon content increased.

A photomicrograph was taken of a mild steel (E.B.) specimen in a direction parallel to the line of application of the load; this showed the typical distortion of the crystals in the direction of loading, and was indistinguishable in appearance from a similar section from a slow-test specimen.

Non-Ferrous Alloys.

In general, the type of diagram obtained was similar in shape to the slow-test diagram. Again, the yield-point was increased considerably, but the maximum stress showed comparatively less change. The appearance of the fracture was very similar to that obtained in the slow test (see Fig. 6, Plate VI).

The percentage elongations showed varying changes. Copper and the brasses showed a very slight decrease in percentage reduction of area, but the aluminium alloys showed a slight increase, as compared with the slow test.

An interesting result was obtained by breaking Duralumin very shortly after quenching; this showed that at that time the material was in a very soft condition, as age-hardening had not had time to start.

SUMMARY.

The results varied considerably with different materials, but, in general, when materials were broken in tension at high speeds (the average time to reach the yield-point being 0.001 second, and an average

fracture taking 0.005 second), as compared with the properties obtained in the ordinary commercial tensile test,

(a) The yield-point was increased very considerably, over 100 per cent. increase being recorded for some materials.

(b) The maximum stress was increased by a much smaller amount.

(c) The percentage elongation and the percentage reduction of area showed comparatively small changes.

(d) The types of fracture were almost identical with those obtained for the slow test.

ACKNOWLEDGMENTS.

The author's thanks are due to Professor C. E. Inglis, who suggested the need for this investigation, and who gave the facilities to undertake it, to Dr. P. Postlethwaite for his assistance with the electrical technique, to Mr. E. Colbeck, and to the many members of the staff of the Engineering Laboratories at Cambridge for their help, and especially to Mr. A. Hall, who assisted with the experiments.

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- ¹ B. Hopkinson, *Proc. Roy. Soc.*, 1905, **74**, 498.
- ² *Proc. Amer. Soc. Test. Mat.*, 1922, **22**, (II), 1-137.
- ³ F. Körber and H. A. von Storp, *Mitt. K.W. Inst. Eisenforschung*, 1925, **7**, 81; 1926, **8**, 127.
- ⁴ H. Quinney, *Engineer*, 1936, **161**, 669.
- ⁵ Brit. Pat. No. 448,130.

ADDITIONAL NOTE.

Table V (page 72) gives the values of the energy absorbed by the specimens during fracture. These were calculated from the areas under the load-elongation diagrams. In all cases the values are probably high, owing to the elongation recorded on the diagram being greater than that measured on the test-length of the specimens. This is due to the type of specimen that was used. The recorded elongation was that of the whole specimen including the shanks, together with any give under the heads of the specimen or in the apparatus,

TABLE V.—*Energy Absorption During Fracture of Specimens.*

					Diameter, Inch.	Energy to Fracture, Ft.-lb.
FERROUS MATERIALS.						
<i>Carbon Steels.</i>						
E.B.	As received	.	.	.	0.252	92
	Annealed from 850° C.	.	.	.	0.252	86
	Annealed from 900° C.	.	.	.	0.236	101
	Quenched from 900° C.	.	.	.	0.252	58
E.C.	As received	.	.	.	0.252	90
E.D.	" "	.	.	.	0.252	95
E.E.	" "	.	.	.	0.226	55
E.F.	" "	.	.	.	0.226	52
<i>Cast Iron.</i>						
	As received.	.	.	.	0.292	4
NON-FERROUS MATERIALS.						
<i>Copper.</i>						
	As received.	.	.	.	0.292	56
	Annealed from 550° C.	.	.	.	0.292	123
<i>70 : 30 Brass.</i>						
	As received.	.	.	.	0.252	78
	Annealed from 550° C.	.	.	.	0.252	118
<i>60 : 40 Brass.</i>						
	As received.	.	.	.	0.292	147
	Annealed from 550° C.	.	.	.	0.292	163
<i>Aluminium Alloy : 2.L.32.</i>						
	As received.	.	.	.	0.292	35
<i>Duralumin.</i>						
	As received.	.	.	.	0.252	55
	Annealed from 350° C.	.	.	.	0.252	26
	Quenched from 500° C.	.	.	.	0.252	32
	Age-hardened at 150° C.	.	.	.	0.252	50

DISCUSSION.

(Condensed.)

THE AUTHOR, in introducing his paper, stated that there had been a limited time at his disposal for the completion of this work, and, owing to the late development of the technique, (i) the form of specimen used; and (ii) the possible elimination of the vibration introduced by the stress-recording apparatus, had not received full attention.

He also stated that the history of the materials tested was in some cases not available. He considered, however, that a record of the method used and of the results obtained warranted the publication of the paper.

Professor F. C. THOMPSON,* M.Sc., D.Met. (Member): In view of the manner in which the author has introduced this paper, I have not much to say. In other circumstances I might have been more critical.

It is a very curious feature of many of the results which the author has obtained that the yield-point and the maximum stress in his high-speed tests coincide exactly, although that does not apply to all the materials. Normally, one would have expected that to occur, at any rate at ordinary temperatures, only in material of a relatively brittle character, and yet both the elongation and the reduction of area are quite high. Is the author really satisfied that the method which he has adopted does justify the conclusion that the yield-point and the tensile strength may, at any rate in some cases, be the same, even if the material is quite ductile?

Dr. W. H. HATFIELD,† F.R.S. (Member): The question of the mechanical properties of metals broken at ultra-high speeds is of very great interest and importance in many directions. I therefore read this paper and then had it read by several members of our research organization. It may be of interest to learn what we think on several of the points.

In the first place, there is some uncertainty regarding the interpretation of the results, owing to the superposition in the stress-strain curve of an oscillatory motion resulting from the natural frequency of vibration of the stress-recording system. This may not seriously affect the yield-point estimation, but it renders somewhat uncertain the estimation of the maximum stress. There is a possibility, however, that the special material which is used to measure the load may not give the true load under dynamic conditions of loading. It is possible, for example, that on account of the adiabatic changes of temperature in the material under rapid loading the electrical characteristics of the substance will not be the same as if the loading was carried out isothermally. This feature must be looked into before the results are accepted as they stand. As regards the influence on the elongation and reduction of area, the author's findings are in agreement with our own tests, in which specimens were broken in a Charpy impact machine and by the ordinary method. It is very strange that these characteristics are independent of the speed of loading, if there is such a big difference in the yield-point as the author indicates.

That is intended to be a constructive contribution to the discussion, but I should like to add that we must know very much more on this subject; much more work must be done. We hope that the author will continue his studies in this field.

Dr. S. F. DOREY, Wh.Ex. (Member of Council), made some brief remarks on the paper, which are incorporated in a written contribution to the discussion (see p. 75).

Mr. T. H. TURNER,‡ M.Sc. (Member): This paper is given to us from the point of view of the engineer; two of the author's conclusions can be compared with the results of macroscopic examination in the case of mild steels. The author has dealt with many materials, so that what I have to say does not

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† Director, Brown-Firth Research Laboratory, Sheffield.

‡ Chief Chemist and Metallurgist, London and North-Eastern Railway, Doncaster.

necessarily apply to them all. In the Summary (*d*) on p. 71, it is stated that: "The types of fracture were almost identical with those obtained for the slow test." In making an ordinary tensile test of mild steel, you know that it will start to fail with a wedge of deformation—Lüders line or whatever you like to call it—which starts from the concentration of the stress, and generally, because the test-piece cannot be pulled truly axially, it will start as shown



FIG. A.



(a)

FIG. B(a).—Fast Bullet Hole: Little Deformation of Mild Steel Plate.



(b)

FIG. B(b).—Slow Bullet Indentation: Deformation Lines Spread Wider.

in Fig. A, and then there will be others and a criss-cross appearance is obtained on the surface, though finally the test-piece will break in the centre. Those Lüders lines occur as curves when a bullet is fired at a mild steel plate. By firing bullets at different velocities—this was done many years ago, and we repeated it not many years ago—two pictures are obtained, as shown in Fig. B (*a*) and (*b*). In (*a*) the bullet has gone right through; it has made a hole right through the plate, and the deformation lines are short. A slower bullet, which merely dents the plate, produces the same shape of deformation, the same Lüders lines, but, as in (*b*), they extend further; the slower speed has allowed a greater absorption of energy in deforming the material, whereas the faster has used itself up in punching a hole through the centre, and the yielding or straining of the surrounding metal is less.

The other conclusion is "The yield-point was increased very considerably." That is only another way of saying that the yielding has decreased, and it is said that with the high speed the amount of yielding before rupture which has taken place in the metal is very much less than with the low speed. Fig. B (*a*) with the high-speed bullet shows smaller Lüders line curves, *i.e.* less yielding, *i.e.* a higher yield-point than Fig. B (*b*), in which a slower speed bullet has produced more yielding, *i.e.* longer Lüders lines, although stressing the metal below the point of rupture. That is something which anyone can repeat on a piece of mild steel by using Fry etching after firing bullets at different speeds, and that is an easy way of obtaining very rapid failure.

The AUTHOR (*in reply*): Regarding Professor Thompson's remarks as to the yield-point and maximum stress being the same for some materials, I would point out that work, which has been done at slower speeds on the effect of the rate of loading on tensile test results, tends to show that for some materials the yield-point is increased at a greater rate than the maximum stress, and this result would appear to be the final outcome of this tendency.

Dr. Hatfield referred to the pressure material which was used. This material is used commercially in a high-speed pressure recording device, and its properties have been carefully investigated.

The fact that the percentage elongation, percentage reduction of the area,

and the type of fracture are the same as for the slow test is confirmed by Mann, to whose work Dr. Hoyt refers in his discussion on this paper. Below the "transition velocity" of Mann these properties are unaffected.

The acceptance of the mean line drawn through the vibration for measurement of the maximum stress is doubtless open to criticism, but as I had only a limited time at my disposal for this work, the late development of the technique gave me no time to try to eliminate this obvious defect. I hope that at some future date the method will be refined and diagrams will be obtained giving a load elongation diagram free from any distortion.

CORRESPONDENCE.

PROFESSOR DONALD S. CLARK *: It should be pointed out that the speeds employed in this work can scarcely be classified as "ultra-high speeds," since they correspond approximately to the speeds that are used on our present-day impact testing machines, which are in the region of 15-20 ft. per second. Attention is directed to work being carried out at Watertown (Mass., U.S.A.) Arsenal at velocities up to 300 ft. per second.†

It has been my opinion for some time that a thorough understanding of the fundamentals of impact loading under tension could be obtained only through an investigation of the stress-strain relations which exist during the application of loads of short duration. Mr. Ginns has made an excellent start, and has developed a method which seems to have possibilities. It would seem very desirable to have a continued and more thorough investigation of this work. Additional work should include an improvement of the force-measuring system in order to decrease the oscillations in the diagrams. It is my opinion that the oscillations which appear in the force deformation diagrams could be reduced by a simple redesign of the equipment. These oscillations tend to give some uncertainty to the exact nature of the diagrams.

It would have been of particular interest to have compared the energies represented by the area under these force deformation diagrams with determinations made with the standard tension impact machine. Further, in view of the work of H. C. Mann of the Watertown Arsenal, it would be interesting to see how the energy absorption determined by Mr. Ginns' method compared with the energy required to cause failure under static conditions.

It is indeed interesting to note that Mr. Ginns reports that the yield-points of the materials tested under impact are considerably higher than when tested under static conditions. I am a little doubtful of the accuracy of the determinations of these values, because of the oscillations which exist in the diagrams. Some work which has been done under my direction would seem to substantiate the order of magnitude of Mr. Ginns' findings.

Dr. S. F. DOREY,‡ Wh.Ex. (Member of Council): The experimental results given in this paper are an indication of what is to be expected in high-speed stressing, such as occurs in ship collisions, and at the firing point in internal combustion engines.

I feel that a more detailed description of the apparatus used would be welcome, particularly an explanation of why the vibration diagram, after complete release of the load on the cast iron specimen, has not the datum line as its axis. Further, it is stated that the natural frequency of vibration

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† *Proc. Amer. Soc. Test. Mat.*, 1936, 36, 85-109.

‡ Chief Engineer Surveyor, Lloyd's Register of Shipping, London.

of the spring was 35.7 per second, and that a mathematical investigation showed that the assumption that the presence of the specimen made no change in this frequency was justified. It is also stated that the time to fracture a specimen was calculated on this basis, but as it appears that the average time to fracture a specimen was 0.005 seconds, and the stress-strain diagrams show several complete vibrations, it is assumed that the vibration was of a higher order than the fundamental. It is also difficult to see how this order and frequency were ascertained.

If the design of the apparatus could be altered to give different rates of stressing, by some such method as connecting the centre of the plate spring to an oil cylinder with a small orifice, the size of the orifice being adjusted to give different rates of stressing, a very useful field of research could be developed, and the variation of yield-point and maximum stress with speed of stressing fully investigated.

Dr. E. W. FELL * (Member): Knowledge of the behaviour of metals when subjected to stresses varying in magnitude at high rates is of especial value in itself, and also in supplementing existing data about their behaviour at stresses much less rapidly applied. The author's conclusion that the yield-point at ultra-high speeds was very considerably increased in value, over 100 per cent. increase being recorded for some materials whilst the other properties show no unfavourable change, implies a much extended elastic range, and is therefore of great importance.

The ordinary yielding phenomena in soft steel and annealed Duralumin, under stresses varying in the elastic range at speeds used in general testing to-day, require time to reach completion. When the rate of loading is great, such as about 0.005 second to reach fracture, it would appear that there is no time for yielding to occur, and so it seems that a much higher stress is necessary to permit yielding in the shorter time available. It is possible that there is a quite simple relation between the elevation of the yield-point and the rate of loading—perhaps a linear one.

At slow rates of loading the distortion at the remarkable yield-points in these materials for tensile bars is found to be propagated along the bar. It would be of interest to ascertain any changes in the distortion, such as in propagation, due to the high rates of loading. Bullet and impact tests on soft steel plates suggest that a marked change occurs in the distribution of the distortion occurring at the yield-point, for the distortion (lines of Hartmann) extends to a greater distance from the centre of the disturbance than it would do if the penetration were very much slower, e.g. in the case of a hole made by a stamp slowly pressed. In carrying out such tests, it seems as well to remark that the mode of support of the plate of material should receive attention, otherwise misleading results may occur as a result of reactions set up at various points at the back of the plate.

As explained in the text, the curve *EB* of Fig. 3 for a type of stress-strain curve found for soft steel is very erratic beyond the stage at which yielding starts, and similar remarks apply to the other curves. Still further investigation of testing methods might result in stress-strain curves being produced more representative of the properties of the material beyond the yield-point at these high speeds.

Dr. S. L. HOYT † (Member): Experimental data on the behaviour of metals when strained and broken at high speeds are very welcome. Mr. Ginns describes a most ingenious device for recording stress-strain diagrams,

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† Director of Metallurgical Research, A. O. Smith Corporation, Milwaukee, Wis., U.S.A.

or load-strain diagrams, and has added materially to the literature on impact testing.

I wish particularly to refer to the work of Mr. Mann of the Watertown Arsenal, of whose papers, presented to the American Society for Testing Materials in recent years, Mr. Ginns appeared not to be aware. Mann reported that above a certain velocity, termed by him the "transition velocity," the energy absorbed by straining and fracturing the test-bar decreased as the velocity continued to increase. In one case it was reported that the energy absorption decreased practically to nil. Mann further reported that the elongation, reduction of area, and work-hardening continued to increase, even though the energy absorption decreased. I sought to compare Mann's results with those of the present paper, for the necessity of securing an independent check is obvious, but a simple calculation shows the velocity of deformation to be well below the "transition velocity" of Mann.

Mr. Ginns' method has the distinct virtue of producing a load-strain diagram, and I hope that arrangements can be made very materially to increase the speed of deformation. Considère, an early student of impact testing, reported, somewhat similarly to Mann, that steel breaks at high velocities with practically no energy absorption, but with the very significant difference that the rupture was not preceded by plastic deformation. It would appear that a method which records the actual diagram should yield results of real significance in this important and interesting study of metallic behaviour.

The AUTHOR (*in reply*): Dr. Dorey has raised a number of interesting points. Some confusion, resulting in a wrong assumption, has arisen between the plate spring, used to apply the load to the specimens, and the stress-recording apparatus (Fig. 2), which was supposedly a rigid device, but which, in effect, acted as a spring system owing to the presence of the non-elastic insulating materials.

The load was applied by means of a plate spring (see Fig. C), of approximate dimensions 48 in. \times 6 in. \times 1 in., supported in roller bearings at the ends. It could be deflected vertically 0.7 in. at the centre, and the specimen was then fixed in the chucks so that it was just in tension. The sudden release of the spring afforded the means of applying the load to the specimen. The natural frequency of the spring was 35.7 per second. The assumption that the introduction of a specimen did not alter this frequency was readily justified by consideration of the equations of motion of a spring freely supported at the ends, released from a known deflected position, with a constant force resisting its motion. The term introduced by the force on the specimen was negligible compared with that due to the spring.

Since the natural frequency of the loading spring was known, the time taken to reach any position in its motion was readily calculable from a sine law, and since the elongation of the specimen was identical with the amount of travel of the spring from its initial deflected position, the time to fracture could be determined by this relationship.

The stress-recording apparatus (Fig. 2) was designed to be effectively a rigid body. The presence of the non-elastic insulating materials and resistance elements, however, made it possible for it to vibrate effectively as a spring system, with a natural frequency of the order of 400 per second. This vibration occurred after any sudden change of load or change of rate of loading applied to the recording apparatus. It is this vibration, i.e. the natural frequency of the stress-recording apparatus (see Fig. C), and *not* a harmonic of the natural frequency of the loading spring (as Dr. Dorey assumes) that is shown in the diagrams.

After the fracture of a specimen, with a corresponding sudden complete

release of load from the stress-recording apparatus, the stress-recording apparatus vibrates at its own natural frequency, and this is recorded on the diagram, since the displacement of the loading spring is still being recorded by the strain-recording apparatus. This part of the curve has only been shown for the *CI* diagram in Fig. 3, but is actually present on every record. It can be seen that it has the same frequency as the vibration which occurs after the yield-point in the more ductile specimens. The fact that it has not the datum for its axis after the complete release of load is due to the non-elastic nature of the insulating materials, which are sluggish in returning to normal as compared with steel. The fact that, owing to a change in rate of

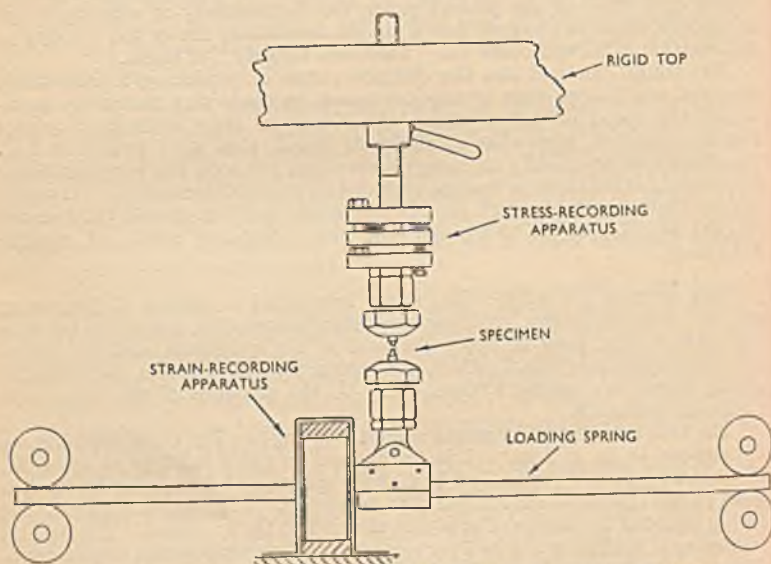


FIG. C.—Diagrammatic Arrangement of Recording Apparatus on Machine.

loading, this same vibration can be introduced before the fracture of a specimen, but not before the yield-point is reached, is argued on p. 69.

Since the vibration is due to an internal effect in the stress-recording apparatus only, it is assumed that a true load-elongation curve will be obtained with a vibration superposed upon it. The mean line drawn through the vibration should give an accurate diagram in the case of the non-ferrous materials where the yield is not sudden, but higher harmonics are introduced in the case of the ferrous materials where the yield is sudden with a consequent doubt as to the exact shape of the curve immediately after the yield-point. The redesign of the stress-recording apparatus should eliminate this defect.

Unfortunately, the present design of the loading device affords very little flexibility in the time to fracture a specimen, but the method of recording could be readily applied to any other apparatus, such as the standard forms of impact-testing machines, and I hope that this work will be undertaken at some future date.

NOTE ON THE EFFECT OF SILICON ON 786 THE MECHANICAL PROPERTIES OF 7 PER CENT. COPPER-ALUMINIUM ALLOY (L11).*

By T. H. SCHOFIELD,† M.Sc., MEMBER, C. E. PHILLIPS,‡ A.C.G.I., D.I.C.,
and S. L. ARCHBUTT,§ F.I.C., MEMBER.

SYNOPSIS.

A summary is given of an investigation of the effect of silicon on the mechanical properties of 7 per cent. copper-aluminium alloy (L11). In general, there is a slight improvement, except in the Izod impact value, with the addition of silicon up to 1 per cent. With more than 1 per cent. silicon the effect is less definite, although the proof stress continues to increase with increase of silicon to 2 per cent.

THE work described has been carried out at the National Physical Laboratory for the Metallurgy Research Board of the Department of Scientific and Industrial Research.

Addition of silicon up to 1.5, or even 2 per cent., has been found in industry to improve very considerably the casting properties of most aluminium casting alloys (excluding "Y"-alloy and the modified silicon-aluminium alloys), particularly when the iron content is high, so that the general soundness and reliability of castings is definitely improved. Moreover, this addition has been found not to affect the tensile strength and elongation determined in the normal routine tests. It was not known, however, what was the effect, if any, on fatigue strength, shock resistance, and elastic properties, and it was desired that this should be determined on casting alloys covered by British Standard Specifications.

This note gives a summary of an investigation of the effects of 0.35, 1.0, and 2.0 per cent. silicon in each case with a normal (0.35 per cent.) and a high (0.8 per cent.) iron content, respectively, on a 7 per cent. copper-aluminium alloy (L11). The alloys, six in all,

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were prepared from notched-bar aluminium containing iron 0.16-0.17, silicon 0.13-0.17 per cent., and hardener alloys containing copper 45-50, iron 9-10, silicon 10-12 per cent., respectively. In one or two alloys of high iron content, aluminium containing iron 0.56, and silicon 0.18 per cent., was used.

The tests were made on bars 1 in. diameter, chill-cast and sand-cast, respectively.

The chill-cast bars were cast in cylindrical open-ended, machined cast-iron moulds $7\frac{1}{4}$ in. long, with a wall thickness tapering from $\frac{1}{2}$ in. at the top to $\frac{5}{8}$ in. at the bottom, dressed with a mixture of china clay and silicate of soda, preheated to 150°-160° C. and inclined at 30° to the vertical on a dry sand base. Sand-cast bars were prepared under the conditions laid down in British Standard Aircraft Specifications for 3L11 and other aluminium casting alloys.

Melting was carried out in an electric (metal resistor) furnace in a cast-iron crucible protected with a dressing of china clay and silicate of soda. Melts were treated to remove gas either by one of the methods developed at the National Physical Laboratory, in which a mixture of purified dry nitrogen and carbon tetrachloride is bubbled through the molten alloy, or by a method similar to that developed by the British Non-Ferrous Metals Research Association, in which the melt is covered with a flux and stirred in an atmosphere of dry nitrogen.

Pouring was carried out by means of an iron hand ladle dressed with a mixture of china clay and silicate of soda, filled from the crucible of molten alloy held at 750° C. for chill-castings and 695° C. for sand-castings.

The uniformity and suitability of the bars for complete mechanical tests was judged by density determinations, preliminary tensile tests, and macroscopical examination of specimen bars from each batch, after which tensile, standard notched-bar (Izod) impact, and rotating bending fatigue tests on an endurance basis of 20 million cycles were carried out on alloys in the "sand-cast, as cast" and "chill-cast, as cast" conditions. The results are shown graphically in Fig. 1.

In general, the mechanical properties of alloys containing 0.35 per cent. and 0.8 per cent. iron, respectively, are similarly affected by increasing silicon content. Owing to individual differences between bars of the same cast, there is insufficient evidence on which to reach definite conclusions as to the influence of composition on the ultimate tensile stress.

Increase of silicon causes a pronounced increase in 0.1 per cent. proof stress and a less marked improvement in limit of proportionality.

Increase of silicon from 1 to 2 per cent. causes a decrease in elonga-

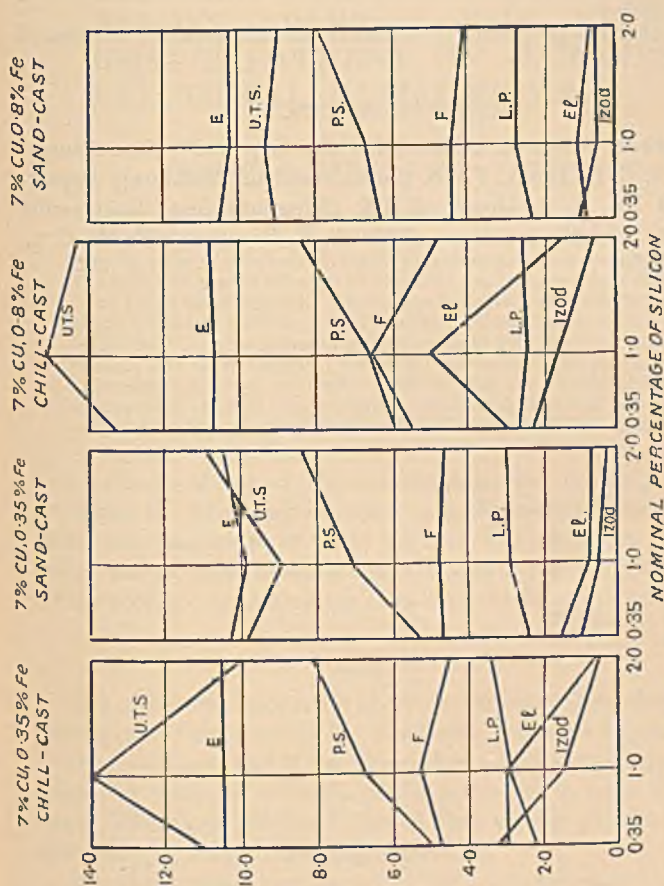


FIG. 1.—Variation of Mechanical Properties with Composition.

UTS = Ultimate Tensile Stress, tons/in.²; E = Modulus of Elasticity, 10⁶ lb./in.²; P.S. = 0.1 Per Cent. Proof Stress, tons/in.²; F = Limit of Proportionality, tons/in.²; L.P. = Endurance Fatigue Limit (20 × 10⁶ cycles), ± tons/in.²; El. = Elongation, Per Cent. on 2 in. Gauge Length; Izod = Izod Impact Value, ft.-lb. (Energy Absorbed).

tion, but the effect up to 1 per cent. is not definite. In all alloys the Izod impact value decreases with increase in silicon content.

The endurance fatigue limit (20×10^8 cycles) of chill-cast alloys is greater with 1 per cent. silicon than with either 0.35 or 2.0 per cent. silicon; in sand-cast alloys little change is observed with increasing silicon content.

The mechanical properties of chill-cast bars are superior to those of sand-cast.

ACKNOWLEDGEMENTS.

The authors desire to acknowledge the help and encouragement given by Dr. C. H. Desch, F.R.S. (Superintendent, Metallurgy Department), and Dr. H. J. Gough, F.R.S. (Superintendent, Engineering Department), and the assistance of Mr. A. E. Bacon and Mr. R. C. A. Thurston, B.Sc.

COPPER-RICH NICKEL-ALUMINIUM-COPPER 774 ALLOYS. PART I.—THE EFFECT OF HEAT-TREATMENT ON HARDNESS AND ELECTRICAL RESISTIVITY.*

By W. O. ALEXANDER,† B.Sc., Ph.D., MEMBER, and
PROFESSOR D. HANSON,‡ D.Sc., VICE-PRESIDENT.

SYNOPSIS.

Some 56 copper alloys, containing quantities of nickel and aluminium varying up to 10 per cent. by weight of each metal, were cast and extruded. The effect of heat-treatment on the hardness and electrical resistivity of these alloys was observed. The results indicate that above 800° C. all the alloys consist of uniform α solid solution. When heated at temperatures below 800° C. after quenching in water from 900° C., most of the alloys harden, and their electrical resistivity decreases. The results reveal the approximate limits of the α solid solution, while the manner of the changes in properties at lower temperatures implies precipitation of new phases, the origin of one lying in the direction of the nickel-aluminium binary system.

THE primary object of the investigation was to study the factors governing the hardening in copper-rich alloys containing quantities of nickel and aluminium up to 10 per cent. of each metal. A secondary object was to examine the scope of electrical resistivity measurements for the accurate determination of solid phase limits in a ternary system.

PREVIOUS WORK.

The mechanical properties of certain ranges of these alloys after slow cooling were investigated by Read and Greaves^{1, 2}; more recently Brownsdon, Cook, and Miller³ have shown that suitable quenching and tempering produces valuable tensile properties in some of the alloys. Jones, Pfeil, and Griffiths⁴ showed that similar phenomena occur in nickel-copper alloys containing aluminium.

For the constitutional aspect of this work, reference has been made to the copper-aluminium diagram as determined by Stockdale,⁵ the copper-nickel diagram as given in the International Critical Tables, the nickel-aluminium diagram as advanced by Gwyer⁶ in 1908, and the liquidus surface as determined by Austin and Murphy.⁸

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PREPARATION OF ALLOYS.

The alloys prepared were of the nominal and actual compositions given in Table I. They were cast by a Durville machine into 3-in. diameter round billets and subsequently extruded to $\frac{3}{4}$ in. rod, sections of which were drawn to wire of 0.064 in. diameter. Messrs I.C.I. Metals, Ltd., Witton, kindly melted, extruded, drew into wire, and analyzed these alloys.

TABLE I.—Code Numbers and Nominal and Actual Percentage Compositions of the Alloys.

Series No.	Chemical		By Difference, Al.	Series No.	Chemical		By Difference, Al.
	Cu.	Ni.			Cu.	Ni.	
N0A0				N5A2.5	92.53	5.00	2.4
" A2	97.99		1.9	" A3	91.95	4.94	3.0
" A4	95.76		4.1	" A4	90.94	4.92	4.05
" A6	93.81		6.1	" A6	88.73	5.00	6.2
" A8	91.97		7.9	N6A0	93.89	6.01	...
" A10	90.32		9.6	" A0.5	93.53	6.09	0.3
N2A2	95.77	2.04	2.1	" A1	92.91	5.96	1.0
" A4	93.84	2.01	4.0	" A1.5	92.66	6.01	1.2
" A6	91.90	2.01	6.0	" A2	91.91	5.98	2.0
" A8	89.89	2.05	8.0	" A2.5	91.37	6.05	2.5
" A10	88.06	2.04	9.8	" A3	91.03	5.95	2.9
N3A1	95.93	3.01	1.0	" A4	90.03	5.82	4.0
" A2	95.06	3.00	1.8	" A6	87.82	6.05	6.0
" A3	93.92	3.01	3.0	N8A0	92.10	7.88	...
" A4	93.10	3.01	3.8	" A0.5	91.35	8.02	0.5
" A6	90.90	3.03	6.0	" A1	91.02	8.02	0.9
" A8	89.04	3.01	7.9	" A1.5	90.41	7.94	1.5
N4A0	96.07	3.89	...	" A2	89.95	8.00	1.9
" A0.5	95.42	4.05	0.4	" A2.5	89.39	7.94	2.6
" A1	94.93	3.99	1.0	" A3	88.93	8.07	2.9
" A1.5	94.47	4.02	1.4	" A4	87.82	8.05	4.0
" A2	94.04	4.03	1.8	" A6	85.82	7.99	6.1
" A3	92.86	4.01	3.0	N10A0	90.08	9.78	...
" A4	91.81	4.04	4.0	" A0.5	89.45	9.90	0.5
" A6	89.87	4.00	6.0	" A1	89.12	9.94	0.85
N5A0.5	94.60	5.08	0.2	" A1.5	88.52	10.00	1.4
" A1	93.88	4.96	1.1	" A2	88.13	9.98	1.8
" A1.5	93.37	5.07	1.5	" A3	86.61	10.23	3.1
" A2	92.92	5.06	1.9	" A4	85.92	9.97	4.0

All the alloys were analyzed spectrographically for estimation of the following impurities: Zn < 0.05; Sn < 0.05 (not detected); Pb < 0.02 (not detected); Fe < 0.1 per cent.; Si trace. Estimated total impurities < 0.1 per cent.

METHOD OF HARDNESS TESTING.

Hardness tests were carried out on discs about $\frac{1}{4}$ in. thick cut from the extruded rod. The specimens were heat-treated in a tube furnace with a nitrogen atmosphere; some of the nickel-rich specimens were

slightly discoloured after this treatment, but the surfaces of all the specimens were lightly ground by hand on a "0" emery paper before testing. A Vickers machine was used with the Diamond Pyramid Indenter under a load of 20 kg. Three impressions were made on each specimen, and the mean hardness figure expressed as a Vickers Pyramid numeral (V.P.N.).

TABLE II.—*Details of Heat-Treatments for Alloys for Hardness and Microstructures.*

Code.	Details of Treatment.				Specimens Treated.
	Initial Condition.	Temperature, ° C.	Time.	Cooling	
A	Extruded bar	900	18h	W.Q.	All
B	A	410	8d	W.Q.	"
D	A	497	11d	W.Q.	"
E	A	598	7d	W.Q.	"
F	A	689	7d	F.C. to	"
		681	2d	W.Q.	"
G	A	800	3d	W.Q.	"
H	A	917	2d	W.Q.	"
I	F.C. from H to	710	3d	W.Q.	{ N4A1, N4A1·5, N5A1 N6A0·5, N6A1, N6A1·5 N8A0·5, N8A1, N8A2
J	F.C. " I to	600	3d	W.Q.	
K	F.C. " J to	500	11d	W.Q.	
Q	A	500	1d	F.C. to	All
		730	5d	F.C. to	"
		675	4d	F.C. to	"
		660	4d	W.Q.	{ N8A1, N10A0, N10A0·5 N10A1, N10A2, N10A3, N10A4 N8-A0·5, 1·5, 2, 2·5, 3, 4, 6 N6-A0·5, 1, 1·5, 2, 2·5, 3, 4, 6 N5-A0·5, 1, 2, 2·5, 3 N4-A0, 0·5, 1, 2, 3, 6 N3-A1, 2, 3 N2-A2, 6, 8, 10, N0A10
R	A and heated as in Q then F.C. to	620	5d	W.Q.	
S	A and heated as in R then F.C. to	610	5d	W.Q.	
U	After R	640	5d	W.Q.	Kunial brasses " "
	Sheet	875	2h	W.Q.	
	Cooled after above to	520	18h	W.Q.	

W.Q. = water quenched. F.C. = furnace cooled.
Time given in hrs. = h or days = d.

RESULTS OF HARDNESS TESTS.

Table II refers to the heat-treatments of the alloys; their initial treatment in every case was 18 hrs. at 900° C. followed by quenching in water. Table IV* (deposited in the Archives of the Institute) incorporates the hardness obtained on annealing specimens at 400°.

* This Table may be consulted in the Library, on application.

500°, 600°, 700°, and 800° C. after quenching from 900° C. Some of these are analyzed graphically in Figs. 1-4 by drawing hardness contour lines on a ternary composition base.

Fig. 1 shows the hardness of the alloys in the "as quenched" condition. No great variation exists over most of the range of composition, although the alloys containing 10 per cent. of aluminium were very hard; weight for weight, aluminium had a slightly greater hardening influence on the α solid solution than nickel.

Fig. 2 refers to the hardness of alloys water-quenched after a further heat-treatment for 8 days at 410° C. The most important feature is the very marked general hardening amounting in many cases to well

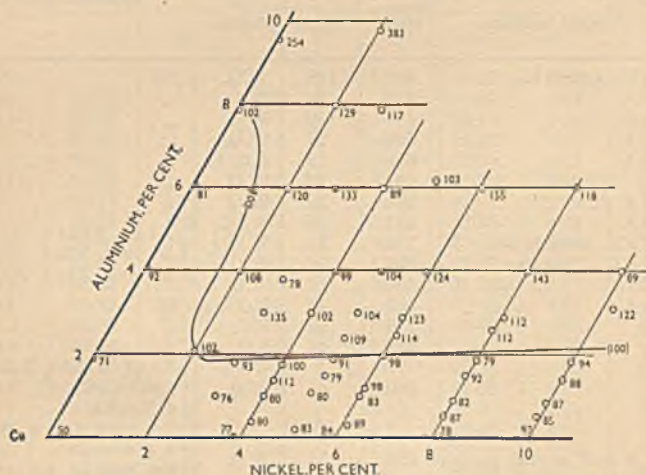


FIG. 1.—Hardness of Nickel-Aluminium-Copper Alloys (Vickers Pyramid Numerals). Treatment "A," 18 Hrs. at 900° C., W.Q.

over 100 V.P.N. above that for the quenched condition. The greatest increase occurs with alloys whose compositions lie on the line XY , while other alloys showing a large increase lie near the line VW and contain about 3 per cent. of aluminium with varying nickel contents. Between these two lines representing maximum hardness lie alloys which only increase in hardness by approximately 30 V.P.N. from the "as quenched" condition. Alloys containing about 4 per cent. of aluminium and varying nickel are relatively soft, their increase in hardness being between 30 and 50 V.P.N. but when the aluminium content is increased to about 6 per cent. or more the capacity for hardening is restored.

The stable hardnesses obtainable in these alloys by long-time treatment at 497° C. are given in Fig. 3. The hardness relations throughout this series are roughly the same as in those obtained by heating at 400° C.,

the only marked modification being the elimination of that field of relatively soft alloys containing 2-2.5 per cent of aluminium and 4-6 per

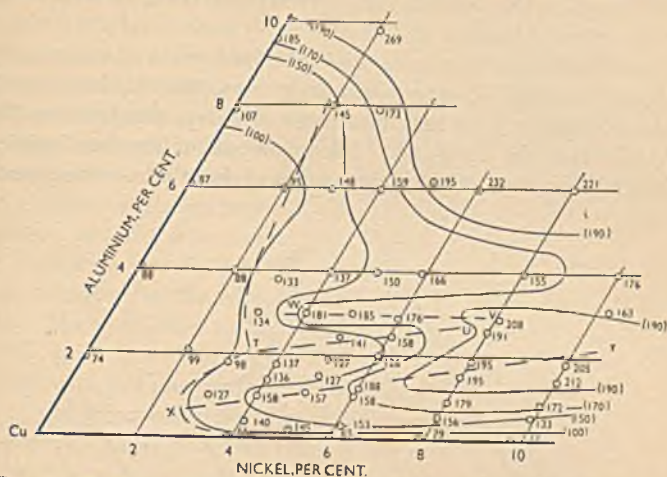


FIG. 2.—Hardness of Nickel-Aluminium-Copper Alloys (Vickers Pyramid Numerals). Treatment "B," 18 Hrs. at 900° C., W.Q., 8 Days at 410° C., W.Q.

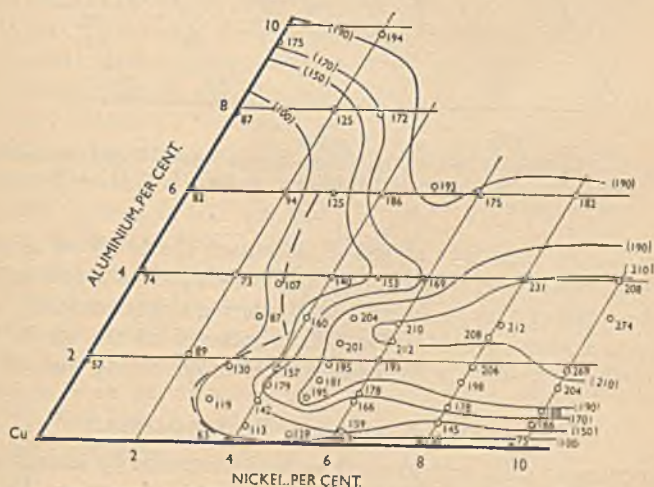


FIG. 3.—Hardness of Nickel-Aluminium-Copper Alloys (Vickers Pyramid Numerals). Treatment "D," 18 Hrs. at 900° C., W.Q., 11 Days at 497° C., W.Q.

cent. of nickel. All the alloys containing 3 per cent. or less of aluminium and more than 3 per cent. of nickel were harder when tempered at 500° C.

than at 400° C., the average increase over their initial condition being 100 V.P.N. The 6 per cent. aluminium, on the other hand, did not respond so well to this temperature of treatment, being about 30 V.P.N. softer than after treatment at 400° C.

Substantially similar results were obtained when the same alloys were heated at 600° C. after quenching from 900° C., but the final hardness obtainable by a long treatment of 7 days was less (see Table VI in Archives of the Institute). Alloys containing less than 3 per cent. of nickel and 3 per cent. of aluminium softened slightly from the quenched condition.

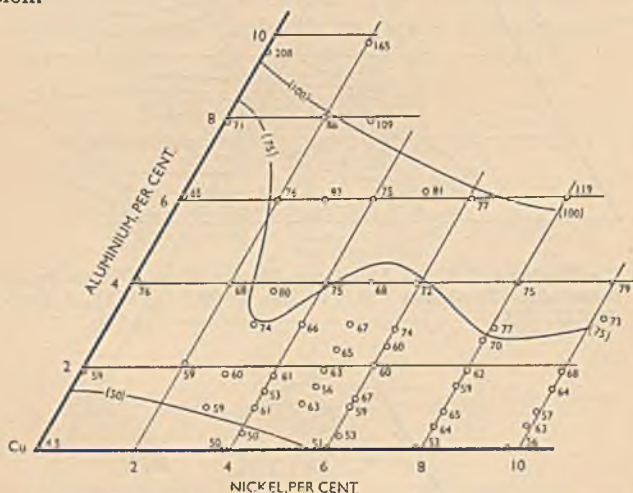


FIG. 4.—Hardness of Nickel-Aluminium-Copper Alloys (Vickers Pyramid Numerals). Treatment "G," 18 Hrs. at 900° C., W.Q., 5 Days at 810° C., W.Q.

The 10-day treatment at 685° C. increased the hardness of alloys containing 8 and 10 per cent. of nickel and 4 and 6 per cent. of aluminium. All the remaining alloys softened slightly during this treatment.

The treatment at 810° C. for 5 days softened all the alloys, their hardness being 30–40 V.P.N. lower than after quenching from 900° C.

ELECTRICAL RESISTANCE MEASUREMENTS.

The wires in coils were given their final treatment by annealing for 3 hrs. at 900° C. under charcoal, and then quenching in water. Lengths of wire 14 in. long were cut from the coils, straightened, and examined for surface blemishes. Wires of 35 compositions, covering the whole range of alloys, were prepared in this way and arranged in several batches for treatment at differing temperatures.

A furnace was constructed to enable uniform heat-treatment to be given to these wires. It was free from temperature gradient within $\pm 2^{\circ}$ C. over 25 cm. and $\pm 6^{\circ}$ C. over 40 cm. at 750° C., which was considered satisfactory, since the middle 25 cm. was the length over which the measurements of resistivity were made. The bright surface was retained by heat-treating in a dry hydrogen atmosphere.

The measurements of electrical resistance were made at 25° C. on an apparatus designed for accurate determinations and rapid exchange of wire specimens. The comparative potential drop method was used, a steady current of 1 amp. being maintained through a calibrated constant resistance and the wire under test. The decrease of potential along each resistance was determined with a Carpenter-Stansfield potentiometer, contacts for the wire specimens being knife edges fixed 25 cm. apart. The resistances and wires were kept at a constant temperature of 25° C. prior to and during measurement, by immersion in an oil-bath supplied with suitable electric heating and stirrers. The cross-sectional area of the wires was determined with a micrometer. The mean diameter was obtained from nine readings over the 25 cm. length. Most of the wires were uniform in section, but those showing some variations were again measured and the mean of fifteen readings obtained.

The determination of the cross-section of the wires contributed the largest error to the values of specific resistance at 25° C., the error being ± 1 in 500. Numerous observations of the resistivity of the wires were made in the course of treatment at each temperature, partly to study the rate of attainment of equilibrium and partly to ensure that equilibrium was finally obtained. The results are tabulated in Tables VII and VIII (deposited in the Archives of the Institute), and some examples plotted on a time basis in the case of the 6 per cent. nickel alloys with varying aluminium content at 500° and 600° C. (Figs. 12 and 13) and the 8 per cent. nickel alloys at 400° C. (Fig. 14).

To facilitate interpretation of the results *iso*-electrical resistivity lines plotted on the ternary base were derived from vertical sections drawn at the following constant compositions of one added metal: 0, 1, 2, 3, 4, and 6 per cent. of aluminium, of which Fig. 9 at 1 per cent. of aluminium is an example, and at 0, 2, 3, 4, 5, 6, 8, and 10 per cent. nickel of which Figs. 10 and 11 at 6 and 10 per cent. nickel, respectively, are further examples.

RESULTS OF RESISTIVITY MEASUREMENTS; EQUILIBRIUM CONDITIONS AT VARIOUS TEMPERATURES.

One batch of wires was treated at 900° C. for a total of 6 hrs. and water-quenched. The results are incorporated in Fig. 5 and in part in

Figs. 9, 10, and 11. Any of the figures referred to and particularly Fig. 5 show that in alloys quenched from 900°C. , uniform increases in resistance

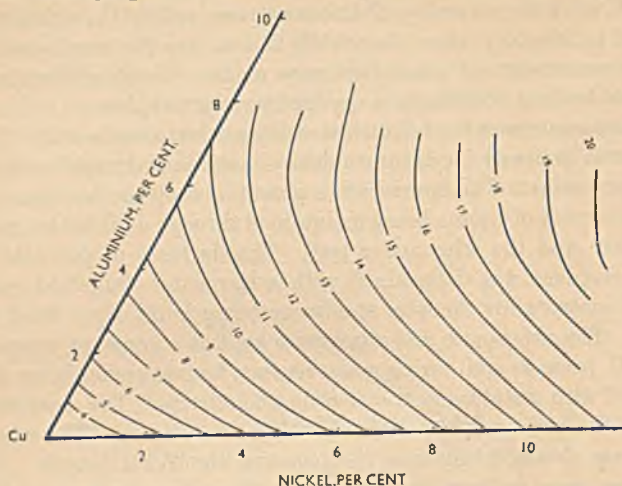


FIG. 5.—Electrical Resistances of Nickel-Aluminum-Copper Alloys (Microhms/cm.³). Treatment "A," 6 Hrs. at 900°C. , W.Q.

of copper alloys occur with additions of aluminium, nickel, or aluminium and nickel combined.

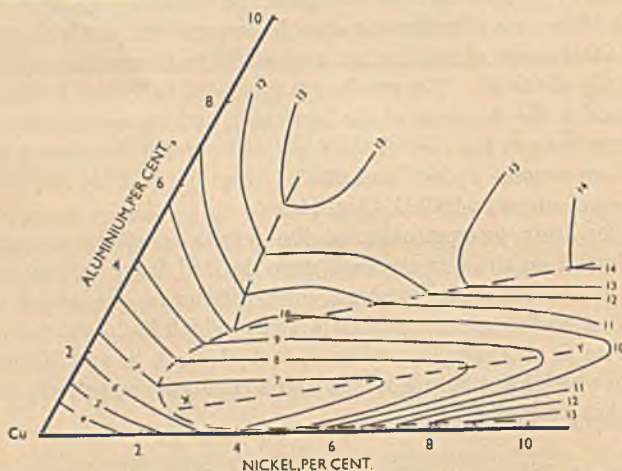


FIG. 6.—Electrical Resistances of Nickel-Aluminum-Copper Alloys (Microhms/cm.³). Treatment "B," 10 Days at 400°C. , W.Q.

Fig. 6 shows the electrical resistivities obtained by a 10-day treatment at 400°C. Comparison of Figs. 5 and 6 reveals large decreases

in electrical resistance in the majority of alloys, giving some abrupt changes in the continuity of the electrical resistance contour lines. One such change lies parallel to the copper-aluminium axis at approximately 2 per cent. nickel, and curves round to the second very abrupt change parallel to the copper-nickel axis at less than 0.5 per cent. aluminium. The major decreases in resistivity occurred with alloys whose compositions lie along the line *X Y*. Figs. 10 and 11 are examples of the minimum resistivities obtained with alloys of certain concentrations.

After 6½ days at 500° C., similar and slightly lower values were obtained for electrical resistivity than at 400° C.

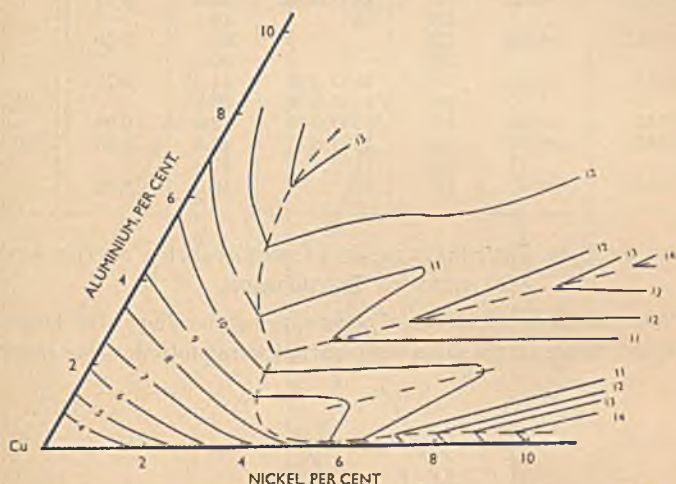


FIG. 7.—Electrical Resistances of Nickel-Aluminium-Copper Alloys (Microhms/cm.³). Treatment "E," 3 Hrs. at 900° C., W.Q., 30 Hrs. at 600° C., W.Q.

Treatment at 600° C. for 30 hrs. was sufficient to ensure equilibrium, the results of which are represented graphically in Fig 7. The values of resistivity were higher than those of alloys heated at 400° C. though lower than in those quenched from 900° C. The discontinuity lying parallel to the copper-aluminium axis receded slightly. Alloys whose compositions varied linearly between 5 per cent. nickel, 2 per cent. aluminium, and 10 per cent. nickel, 4.5 per cent. aluminium possessed resistances relatively greater than neighbouring alloys of higher or lower aluminium content (see also Fig. 7).

The resistances of the majority of the alloys quenched from 900° C. were not altered by annealing at 700° C. Alloys of high nickel and aluminium content alone decreased in resistance, the disposition of the changes being similar to those at lower temperatures.

A few tensile tests were made on certain of the wires, the results together with their resistivity values are given in Table III.

TABLE III.—*Tensile and Electrical Resistivity Properties of Some Wires.*

Nominal Composition.	Diameter, Inch.	Load, Kg.	Elongation on 2 in., Per Cent.	Ultimate Stress, Tons/in.	Electrical Resistivity, Microhms/c.c.	Treatment.
N4A1	0.0646	105.5		31.6	6.39	7 D at 400° C.
		110	11	33.0		
N6A1	0.0644	141	16	42.6	6.58	
		143	15	43.2		
N6A2	0.0647	143	18 O.G.M.	42.8	8.71	6½ D at 500° C.
		137	23	42.8		
N10A2	0.0648	172		53	9.29	
		169		50.5		
N4A1	0.0644	105.5	10 O.G.M.	31.8	6.79	6½ D at 500° C.
		100	10 O.G.M.	30.2		
N6A1	0.0645	133	10 O.G.M.	42.0	6.98	
N6A2	0.0645	145	12 O.G.M.	43.5	8.55	
		146	14	43.8		
N10A2	0.065	177	10	52.5	8.85	

EFFECT OF TIME, TEMPERATURE, AND CONCENTRATION OF THE ATTAINMENT OF EQUILIBRIUM.

Observations on the electrical resistivities of the alloys after annealing for various times at the same temperature were plotted, using electrical

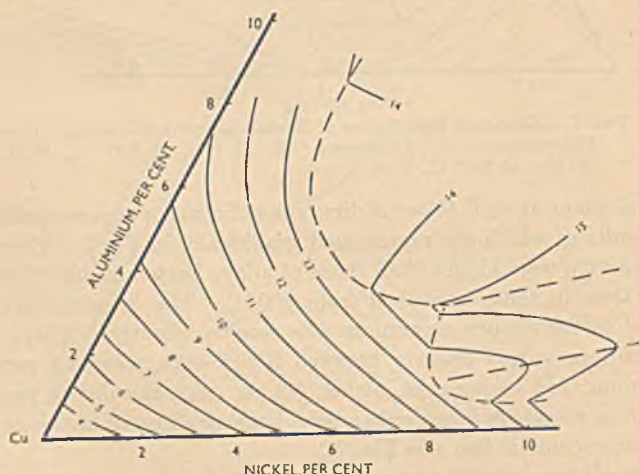
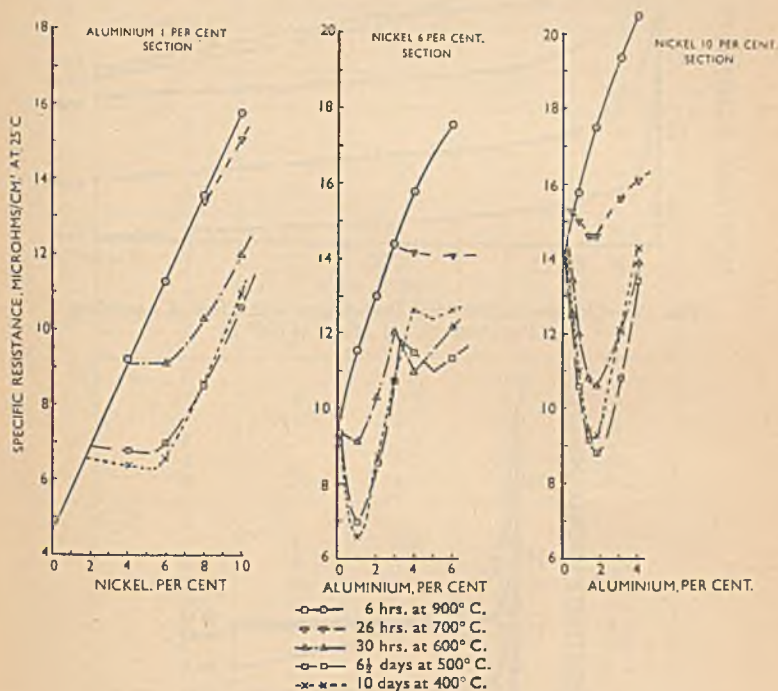


FIG. 8.—Electrical Resistances of Nickel-Aluminum-Copper Alloys (Microhms/cm.²). Treatment for 26 Hrs. at 700° C., W.Q.

resistivity as ordinate and time as abscissa. Four sets of graphs corresponding to the four temperatures of annealing 400°, 500°, 600°, and 700° C. were plotted.

and 700° C. and relating to the effect of time on the electrical resistivity of every alloy were plotted.

For any given alloy the initial and final values of electrical resistivity at one temperature were known, and from the graphs mentioned above the time required to reach the mean of these two values was readily obtained. Such an arbitrary standard of intermediate value was necessary, since the time required to reach complete equilibrium could not be accurately determined.



FIGS. 9-11.—Electrical Resistances, Vertical Sections.

The majority of the electrical resistance observations when plotted on a time basis as in Figs. 12-14 showed continuous decreases from the initial condition, the curves being of the usual form. The chief exceptions to this general observation were the changes produced by annealing at 400° C. after quenching from 900° C. Fig. 14, for alloys containing 8 per cent of nickel, shows that initial increases in resistance were obtained with these alloys rich in aluminium (*i.e.* exceeding 2.5 per cent.). This phenomenon, of which examples have previously been observed during

the gradual hardening of quenched alloys, seemed prevalent in these alloys, and further examples of increases prior to large decreases in

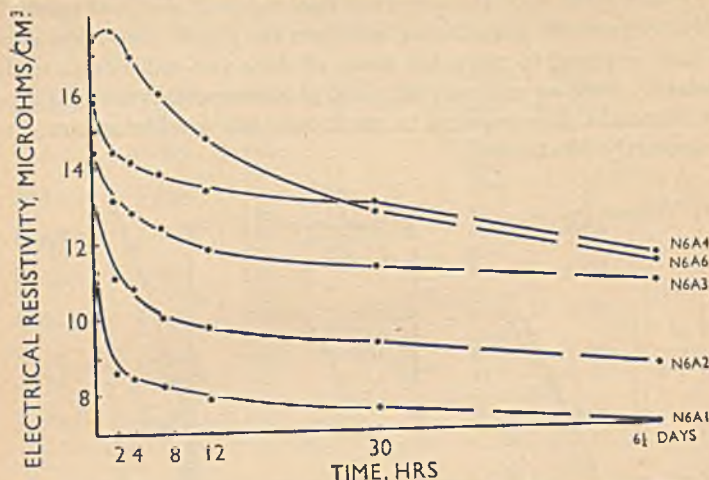


FIG. 12.—Changes in Electrical Resistances with Time of Annealing 6 Per Cent. Nickel Alloys at 500° C.

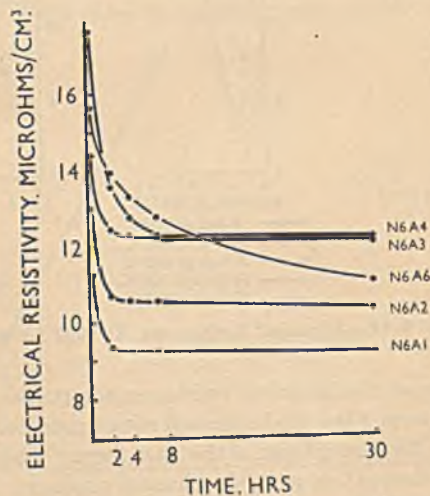


FIG. 13.—Changes in Electrical Resistances with Time of Annealing 6 Per Cent. Nickel Alloys at 600° C.

resistance were produced at 500° C. in the nickel 6, aluminium 6 per cent. and nickel 4, aluminium 6 per cent. alloys.

Table IV (a-d) contains all the observations made on the wires annealed at the various temperatures together with the derived mean value of the resistance and the time required in hours to reach this intermediate value. The latter results have been retabulated in Table IV.

TABLE IV.—*Time to Complete Half of the Total Change in Resistance on Annealing at a Lower Temperature after Quenching from 900° C.*

Nominal Composition.		Time taken in Hrs., with Temperature of Annealing.			
		a.	b.	c.	d.
N.	A.	400° C.	500° C.	600° C.	700° C.
2	2
	4
	6
	8	100	70
3	8	a 50	31	2	0.4
4	0
	1	a 50	5	7	...
	2	"	2.5	6	...
	4	"	18	10	...
	6	"	36	3	0.4
6	0	0.4	...
	1	8	0.8	0.4	...
	2	50-100	3.7	0.5	...
	3	"	5.5	1.0	...
	4	"	8.2	3.5	2
	6	"	14	1.2	0.3
8	0
	1	7	0.9	0.6	...
	1.5	8	1.1	0.7	0.4
	2	5	1.3	1.0	0.3
	2.5	a 50	5.5	3.7	0.2
	3	"	4	3.0	0.1
	4	"	7	1.3	2.5
	6	"	17	1.0	0.4
10	0
	0.5	40	...	0.5	...
	1	2	1	0.8	0.2
	1.5	14	1.1	1.0	0.2
	2	13	1.5	0.5	0.1
	3	a 50	4	0.8	0.2
	4	a 50	6	1.0	0.6

a = approximation.

The effect of nickel on the copper-base alloys containing constant aluminium contents is well marked. These alloys vary in the times to reach half equilibrium, and the variation is such that the richer the alloy

in nickel the shorter the time to reach equilibrium. The alloys containing 4 per cent. of aluminium illustrate this well. A selection of results from Table IV recast in Table V, show this.

This effect is not so evident at the lower aluminium contents,

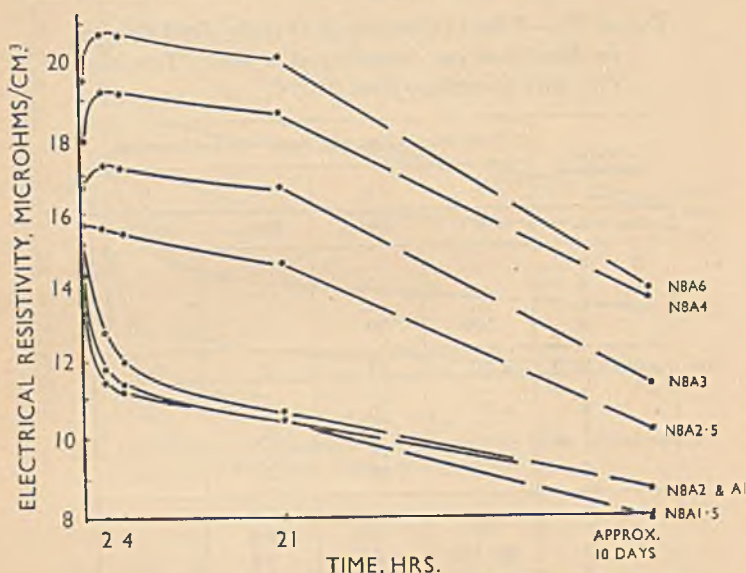


FIG. 14.—Changes in Electrical Resistance with Times of Annealing 8 Per Cent. Nickel Alloys at 400° C.

TABLE V.—Alloys of Aluminium 1 Per Cent. at 400° C.

Alloys of:	Nickel Content, Per Cent.	Time to Acquire Half Equilibrium, Hrs.
Aluminium 1% at 400° C.	4	50
" "	6	8
" "	8	7
" "	10	2
Aluminium 4% at 500° C.	4	18
" "	6	8.2
" "	8	7
" "	10	6
Aluminium 6% at 600° C.	4	3
" "	6	1.2
" "	8	1

probably owing to the slightly decreased accuracy of interpolation arising from the rapid changes of resistance in these alloys.

The results as set out, *e.g.* in Table IV, column *b* (nickel 6, 8, and 10 per cent. series at 500° C.), show that alloys constant in nickel content

need longer soaking to reach "half equilibrium" the greater the aluminium content. This observation is contrary to the effect of increasing nickel while the aluminium remains constant.

As would be expected, the general effect of an increase in temperature is to increase the rate of attaining equilibrium. A selection of results for certain alloys has been plotted. The vertical ordinate is the reciprocal of the temperature in degrees absolute, and the horizontal ordinate the logarithm of the time required for the resistivity to decrease by one-half towards its final value. The linear relationship suggested by Jenkins and Bucknall ⁷ as applicable to all age-hardening systems was found to be a suitable first approximation.

DISCUSSION OF RESULTS.

Hardness Tests.

The longer annealing at 800° C., coupled with the more effective quench due to smaller specimen sizes, rendered the alloys softer than the initial treatment for 18 hrs. at 900° C. The gradual change in hardness throughout the whole range of alloys when quenched from 800° or 900° C. suggests that they all consist of α solid solution.

The hardness values obtained from the specimens quenched from 800° C. were accepted as characteristic of annealed α solid solution. In Figs. 1-4 broken lines have been drawn, one on each diagram. All alloys showing no increase in hardness on annealing at 400°, 500°, 600°, or 700° C. were included between the broken line and the concentration axes of the diagrams; by this means an estimate of the variation of the α solid solubility limit with temperature and concentration was derived. In Fig. 2 (alloys re-heated at 400° C.) additional dotted lines are included representing zones of maximum or minimum hardness.

It is also noteworthy that alloys containing not greater than 2.5 per cent. aluminium and 5-10 per cent. of nickel hardened to 200 V.P.N. and this hardness was stable at 500° C.

Electrical Resistivity Measurements.

The changes in electrical resistivity which accompany hardening were similar in every respect to age-hardening phenomena occurring in other alloy systems.

Attention has been directed to the influence of concentration on the attainment of equilibrium. Increase of aluminium in alloys of given nickel composition increases the time necessary to ensure equilibrium, whereas increase of nickel in alloys of given aluminium content diminishes that time. An explanation may be advanced based on fundamental grounds. The atomic volume of aluminium is 9.98,

that of copper 7.14 and of nickel 6.6. It seems reasonable that the most important factor governing the diffusion of the atoms is their relative size. The aluminium atom, being larger than copper, does not diffuse in the copper matrix so readily as the nickel atom, which is smaller; hence increase in the quantity of aluminium atoms would necessitate a proportionately longer time to reach equilibrium.

The uniform nature of the changes in electrical resistance of the alloys as quenched from 900° C. leaves no doubt that a solid solution exists over the whole range at this temperature.

The changes in resistivity caused by the heat-treatment are systematic, and can be related to a definite system of "boundary lines," which are shown dotted in the diagram. These lines may be compared with a similar series in the hardness-composition diagram (Fig. 2). The most remarkable feature in each case is the change in properties in the region of the line *X Y*.

The abrupt discontinuities reproduced in the *iso*-resistivity lines on Figs. 5-8 and vertical sections Figs. 9-11 enable the single-phase field of α solid solution to be followed with decrease in temperature. The electrical resistivity results give slightly lower limits to the α solid solution than those obtained from hardness measurements. This is to be expected, since accurate interpolation of the electrical resistance results may be performed. Consequently, the areas representing alloys which remain supersaturated and therefore unchanged in hardness and resistivity are eliminated.

The significance of the variation in relative values obtained in alloys whose resistances have decreased on annealing, cannot be readily interpolated on the evidence given here. The most conspicuous feature is the coincidence in composition of alloys exhibiting maximum hardening, optimum tensile properties, and minimum electrical resistivity (see line *X Y*, Figs. 2-6). The effect is explained on the assumption that maximum precipitation of the separating phase or phases has occurred with alloys of these compositions. It will be recalled that Brownsdon, Cook, and Miller³ advocated the addition of nickel and aluminium to copper in the ratio of 4:1 in order to develop the optimum properties of the alloys on heat-treatment. This ratio gives compositions lying coincident with the line *X Y*.

GENERAL CONCLUSIONS.

The limit of α solid solubility is shown to decrease with decrease of temperature. Up to 8.5 per cent. of aluminium and 10 per cent. of nickel, which was the field of alloys investigated, α solid solution exists throughout the whole range at 800° C. and above. The greatest decrease

in α solid solubility occurs over the temperature range 750° to 550° C. The limit of α solid solution at 400° C. and below is of the order of 1.5 per cent. nickel and 0.2 per cent. of aluminium.

The disposition of alloys showing maximum hardening capacity together with minimum electrical resistivity agrees with the optimum ratio 4:1 nickel to aluminium suggested elsewhere. The origin of a separating phase lies in the direction of the nickel-aluminium binary system.

The changes in electrical resistivity and hardness on annealing at lower temperatures of alloys quenched from 900° C. are similar to those occurring in other age-hardening systems.

ACKNOWLEDGMENTS.

The authors' thanks are due to Messrs. I.C.I. Metals, Ltd., for monetary aid and other facilities afforded during this investigation, which was carried out in the Metallurgical Department of the University of Birmingham.

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DISCUSSION.

(Condensed.)

DR. C. H. DESCH,* F.R.S. (Vice-President): This paper describes a very interesting empirical series of experiments on this ternary system, but I think that we should be in a position now to go very much further than this. I notice, for example, that the figures are all given in percentages by weight, which rather obscures the meaning of the results that are obtained. If the results are expressed in the form of atomic percentages, ratios are obtained which really mean something. A ratio of so much nickel to so much aluminium by weight is of practical importance only, but when the atomic ratio is given one begins to see what causes these changes in the ternary alloys. It is probably well known that, by the X-ray method, Dr. Bradley, at Manchester, has been studying the various ternary systems making up the quaternary system iron-nickel-aluminium-copper. By the method used, he finds extremely important atomic relations between the constituents which separate, and the effects on both mechanical hardness and on the electrical and magnetic properties which are produced by

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those ratios. It is found that the electron-atom ratio in the several phases can be used to explain many of these phenomena, and then we have something more than an empirical record of hardness; we have a means of understanding what is happening. I think that in a short time, with information of that kind, we shall be able to predict accurately what will be the properties of a given ternary combination.

I would commend a study of the very important papers which Dr. Bradley and others have been publishing, largely under the inspiration of Professor W. L. Bragg. They really do lay a new foundation for the study of complex alloys of this kind. The subject of metallography is undergoing a change which will enable it to progress much more rapidly in the next few years, and material of the kind given in this paper will then be re-interpreted with, I think, very valuable results. That is not, of course, in the least to depreciate the value of the authors' results; I merely suggest that they will have to be translated into a somewhat different form before they can have the general value which we should like them to have.

Dr. H. W. BROWNSDON * (Vice-President): After the investigations that we carried out several years ago on the effect of adding nickel and copper in definite proportions to copper and copper-rich alloys, we realized that a more detailed study of the copper-nickel-aluminium system than was then possible in our laboratory would be of general interest, and we were fortunate in finding the authors willing to undertake this further work.

It is gratifying to note that one of our more important early observations relating to the nickel aluminium ratio giving optimum temper hardening properties, has been confirmed, and agrees with that indicated by the line XY in Fig. 2.

It may not be generally realized how very considerable was the amount of work involved in preparing, in wire form, the alloys listed in Table I, and I should like to thank those of my colleagues who helped in their preparation and analysis.

Although primarily of scientific interest, this contribution has a very definite bearing on the development of new alloys of commercial value.

Professor D. HANSON,† D.Sc. (Vice-President): Dr. Alexander is fully competent to deal with the technical discussion, but I should like to thank Messrs. I.C.I. Metals, Ltd., for making this investigation possible. I believe that it arose from a remark which I made in the discussion on a paper from their laboratories, when the practical results of the heat-treatment of these alloys were first presented to us. Arising out of those remarks, Dr. Brownsdon suggested that we should undertake the investigation of some of the scientific problems connected with those alloys. We have been very interested to do this, and I believe that the firm has benefited from this joint effort. It has been a joint effort; although the paper is published in our names, a very great amount of preliminary work was carried out by I.C.I. Metals, Ltd., in providing the materials and in helping us at various stages. I hope that further opportunities will arise for this kind of co-operative effort between an industrial firm and a scientific laboratory and that advantage will be taken of these opportunities, because this is a research which Universities would have the very greatest difficulty in carrying out unaided, even if they could do it at all, because the preparation of the materials in a suitable form would be beyond their resources.

Dr. ALEXANDER (*in reply*): At first I thought that Dr. Desch referred simply to plotting the properties of the α solid solution in atomic percentages; we did

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† Professor of Metallurgy, The University, Birmingham.

that, and did not obtain any linear relationships in the properties with composition. From his subsequent remarks, however, I gather that Dr. Desch was referring to the electron-atom ratios of the compounds concerned. We also thought of that and tested it on a number of ternary alloys, and obtained interesting results.

CORRESPONDENCE.

DR. A. J. BRADLEY * (Member) and Mr. H. LIPSON,* M.Sc.: This paper is of special interest to us as we have been working on the copper-nickel-aluminium system by X-rays. Our powder photographs of slowly-cooled alloys give a general survey of the phases throughout the system. From this, we can interpret some of the results given by the present authors.

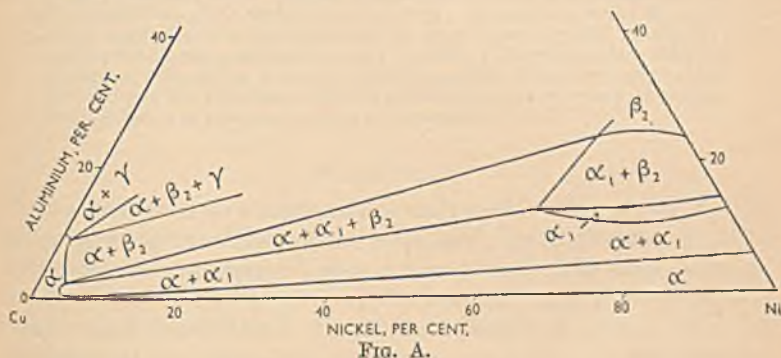


Fig. A shows the following phases :

- α —face-centred cubic.
- α_1 —face-centred cube with superlattice.
- α_2 —body-centred cube with superlattice.

The boundary of the α -phase in the neighbourhood of copper follows the trend of the dotted lines in Figs. 6 and 7. The resistivity measurements show beautifully the cusp of the α -phase, where it comes into contact with the three-phase area ($\alpha + \alpha_1 + \beta_2$). The dotted lines from the cusp to number 14 in Figs. 6 and 7 probably lie within the three-phase areas at 400° and 600° C., respectively. It would be interesting if a closer examination of the resistivity data should show the boundaries of the three-phase area separately.

The lower dotted line (XY in Fig. 6) is not a phase boundary, but probably corresponds to a tie-line in the two-phase area $\alpha + \alpha_1$. An alloy on this line breaks up as follows: the α constituent has a composition given by the point X ; the α_1 constituent has a composition about midway between Ni_3Al and $CuNi_2Al$, which are at the extremities of the α_1 phase. It is probable that the conductivity is chiefly due to the α constituent. This has the lowest resistivity at the point X . Consequently, all alloys on the tie-line XY will have a minimum resistivity.

* National Physical Laboratory, Teddington.

The AUTHORS (*in reply*): The results of Dr. Bradley and Mr. Lipson's X-ray observations on these slowly-cooled ternary alloys are known to us, and confirm what we had already determined microscopically. We hope shortly to communicate to the Institute a paper dealing with the constitution of these alloys at all temperatures. We also agree with the interpretation of the line XY (of alloys having minimum resistivity) as a tie-line between α and Ni_3Al solid solution.

PRECISION EXTENSOMETER MEASUREMENTS ON TIN.*

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By BRUCE CHALMERS,† B.Sc., Ph.D.

SYNOPSIS.

A precision extensometer, reading by means of optical interference fringes to strains of 10^{-7} cm./cm., is used for creep experiments on tin. The results are given under three headings: (a) single crystals; (b) specimens consisting of a few crystals with longitudinal crystal boundaries; and (c) specimens consisting of small crystals. The results show that the change of orientation across a crystal boundary affects the mechanical properties of the boundary, and the relation between recovery and creep, and the forms of the creep curves are discussed.

INTRODUCTION.

MECHANICAL tests on a metal may be designed for either of two objects; (1) to test the suitability of the metal for a given purpose, or (2) to investigate its fundamental physical properties. The same tests are rarely suitable for both purposes, because the engineer's type of test usually deals collectively with a number of simple properties, while the fundamental test must deal with one property only. For example, when a tensile strength is determined, the test-piece is changed progressively after its elastic limit is passed, and the tension is determined that will break a material that results from the original material as modified by the continued application of the tension.

A test suitable for fundamental investigations should detect and measure the properties of the original material, i.e. it should deal with material that has not undergone any permanent change, and detect the first permanent change rather than the last of a series of permanent changes. For a tensile test, suitable properties are the elastic properties and the effects of stresses that cause little or no permanent set.

The present paper deals with a fundamental investigation of the mechanical properties of tin. A piece of metal normally consists of crystals between which are crystal boundaries; hence a complete explanation of the mechanical properties of a metal would require a

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knowledge of the properties of the crystals, together with an examination of the way in which these properties are modified by the crystal boundaries.

The problem is approached by first studying single crystal specimens, then specimens consisting of a few crystals and their boundaries, and finally specimens consisting of many crystals of a size comparable with those met with in practice. It thus becomes possible to determine the effect of the boundaries and so to reach a more precise appreciation of the nature of the boundary region.

In order to apply this procedure, there are several desiderata to be observed in the choice of a metal: the metal should be obtainable in a state of high purity; its grain-size should be easily controllable, and its crystals should be fairly isotropic with respect to the properties to be investigated. These conditions are satisfied by tin.

The choice of a mechanical test must also be considered; in order to satisfy the requirements stipulated above, the measurement of strain must be as sensitive as possible, while the stress must be uniform, such as tension, rather than torsion or flexure. The technique described below satisfies these conditions.

Although it is impossible from *a priori* considerations to decide which of the properties determined in the tensile tests are to be regarded as fundamental, a study of the results will show that a feature of great importance is the smallest stress that will cause creep to occur. This is not necessarily the same as the limit of proportionality or the elastic limit, because completely recoverable creep can occur. The smallest stress that causes creep will be referred to in this paper as the *creep limit*. A second fundamental stress is that which will just cause permanent extension, and will be referred to as the *permanent set limit*. Such a stress cannot be measured experimentally, but its existence and value can be deduced from the experiments to be described.

The paper deals with the determination of the creep limit, and its variation with the size and arrangement of the crystals. It also describes an investigation of the effect of stresses close to the creep limit, *i.e.* the border line between elastic and plastic phenomena.

PREVIOUS WORK.

Although there have been several investigations of the creep properties of tin, notably those of Andrade,¹ Andrade and Chalmers,² and Hanson and Sandford,³ there is no previous work that is particularly applicable to the problem from the present point of view.

The investigations of Andrade, to the results of which reference will be made later, were concerned with the effects of stresses well above the

elastic limit, and with amounts of creep large enough to render high sensitivity unnecessary. The smallest extension that could be observed was of the order of 0.05 per cent. The creep was observed during the application of a stress that was maintained constant, the diminishing cross-section of the test-piece being compensated for by a reduction of tension. The experiments of Hanson and Sandford also did not require a high order of precision, since the tests were of the long period type. In this case no provision was made for maintaining a constant stress. Hence in neither case were the properties of the unaltered original material under investigation.

EXPERIMENTAL TECHNIQUE.

The experimental work under consideration consisted mainly of a precision investigation of changes of length of a cylindrical specimen during and after the application of tensile stresses.

The extensometer used for this purpose has previously been described,⁴ but a brief description may not be out of place here. The specimen *S* (Fig. 1) consists of a cylinder 2.5 mm. in diameter, and 7 cm. in length, of which the central 3 cm. form the gauge-length. The apparatus consisted of two parts, of which the functions are to apply the stress and to measure the strain. The main frame of the instrument consists of two vertical brass plates each about 25 cm. square, held parallel to each other at a distance apart of about 8 cm. by horizontal brass bars screwed to the plates. The disposition of the cross-bars is shown in section in Fig. 1 (*A, F, Z, Z*).

The specimen (*S*, Fig. 1*a*) is fixed in chucks to the cross-bar *A* and to the tension rod *B*, so that *S* and *B* are collinear. The upper end of *B* is pivoted on the cross-bar *C*, which in turn is pivoted on the two parallel bars *D*. Each of these pivots consists of two gramophone needles held vertically and resting in punch holes, the result being that no couple is applied to *B*. The bars *D* are fixed together by means of cross-bars, and pivot on the points of two gramophone needles *E* carried by screws passing through the cross-bar *F* of the main frame. A cross-bar at *G*, connecting the two bars *D* supports a glass tube *H* 25 cm. long, and 6 cm. in diameter, closed at its lower end and open at the top. Water can be introduced into or removed from the tube *H* by means of a two-way syphon (not shown in the diagram). The stress applied depends on the water level in the tube *H*, the stress being zero when the weight of water in *H* is just sufficient to balance the counterpoise weight at *J*. The water level in the tube *H* is determined by means of a pointer which is moved vertically so as just to touch the water surface. The pointer is supported by a glass rod that moves

from the screws and resting on a piece of steel. The distance and angle between the glass plates *Q* and *M* can be adjusted by means of the screws *T*.

The frames *L* and *P* are each counterbalanced by adjustable weights at *U* and *V* so that no stress is applied to *S* through *R* or *N*. The interferometer is illuminated from above by means of light from a mercury arc passing through a water cell and a mono-chromatic green filter, and reflected downwards from the glass slip *X*. The fringes produced by the interference between the light reflected upwards from the lower surface of *Q* and from the upper surface of *M* are viewed through a microscope at *W*. The direction and spacing of the fringes, which are lines of equal separation of *M* and *Q*, can be adjusted by means of the screws *T*. This adjustment is made so that the fringes form a series of parallel lines whose direction is parallel to the axis about which the interferometer unit turns. When the distance *RN* alters, the fringes move in a direction perpendicular to their length. Good fringes are obtained with no silvering on *Q* or *M*, which were pieces of good plate glass.

The apparatus was supported in a thermostatic water-bath of which the temperature variations were less than 0.05°C . Vibration was obviated by placing the whole apparatus on a pier with a foundation independent of the rest of the building, a heavy slate top being supported on the pier by 12 rubber-sponge balls. No vibration that could be detected was transmitted through this arrangement, although the pier itself underwent considerable vibration.

The syphon apparatus, the device for measuring the water level, the stirring motor and the mercury arc were supported on a second bench to avoid any disturbance originating from them.

The length of the specimen between *R* and *N* was about 3 cm. and the change of this length which will cause a displacement of the fringe system by one fringe space is 3.68×10^{-5} cm., so that $\Delta l/l$, the extension per unit length per fringe is 1.23×10^{-5} , approximately. The microscope used for observing the fringes contained an eye-piece scale. By adjusting the fringes to be about ten scale divisions apart, and reading the positions of the fringes to one-tenth of a scale division, movements of the fringes could be determined to 0.01 fringe. This represents a value of $\Delta l/l$ of 1.23×10^{-7} . The accuracy of reading the water level was comparable, a change of water level of 0.1 mm. corresponding roughly to a change of length of 10^{-7} .

When observations of $\Delta l/l$ are made to an accuracy of the order of 10^{-7} cm./cm., the temperature of the specimen assumes considerable importance. The coefficient of expansion of tin is about $2 \times 10^{-5}/^{\circ}\text{C}$.,

so an increase of length of 10^{-7} cm./cm. is produced by an increase of temperature of about 0.005°C . The thermostat fluctuated within 0.05°C ., giving periodic changes of length of the order of 10^{-6} cm./cm. which were corrected for in the results.

PREPARATION OF THE SPECIMENS.

The specimens consisted of cylinders about 3 mm. in diameter and 7 cm. long, and were prepared by casting in glass tubes. The material used in all these experiments except where otherwise specified was Chempur tin (tin 99.987, copper 0.00132, antimony 0.00118, lead 0.00585, iron 0.00055, bismuth 0.00352, arsenic 0.00005, nickel 0.00003, silver 0.00018 per cent., zinc, cobalt and sulphur nil).

The method of preparing the single crystal specimens was as previously described,⁵ and was that of gradually raising a glass tube filled with tin by suction from a crucible of molten tin.

The crystal size could be reduced by increasing the rate of withdrawal of the glass tube, giving quite satisfactory control of the grain-size.

EXAMINATION OF THE SPECIMENS.

The size and disposition of the crystallites which formed the surface of a specimen could be examined visually after etching in ferric chloride solution. When the crystal size was such that there were a number of crystals in the cross-section, the method described below, analogous to the method used by Desch⁶ with brass, allowed a fuller examination to be made.

When a specimen of tin is dipped in mercury, the grain boundaries are rapidly softened by the diffusion of mercury along them, and it becomes possible after a few minutes to pull the specimen to pieces, each piece being one crystal. Thus, when the crystal size is not too small for easy manipulation, it can be readily studied. It may be mentioned in this connection that such softening by diffusion does not take place along twin boundaries prepared by a method described elsewhere.⁵

With single and large crystal specimens, a knowledge of the orientation of the crystal axes relatively to the length of the specimens becomes desirable, and for this purpose the optical reflection method⁷ was used.

EXPERIMENTAL RESULTS.

In the experiments under discussion, the crystal size was varied from that in which one crystal occupied the whole gauge-length of the specimen to that in which the number of crystals in the cross-section

was about 20. Of these experiments, those on single crystals have already been described,⁸ but for completeness the conclusions will be briefly recapitulated here and included with the other results.

In the experiments on any given specimen, results may be obtained for; (a) the extent to which Hooke's Law is obeyed; (b) the elastic modulus; (c) the limit of proportionality; (d) the variation of initial rate of creep with stress; (e) the creep limit; (f) the form of creep and recovery curves; (g) the relation between recovery and creep; and (h) the permanent set point. It may be remarked here that corrections have been made, where necessary in the present work, for the spurious "thermal" creep and recovery effect, considered in detail elsewhere.⁸

The observations show that the experiments form three distinct

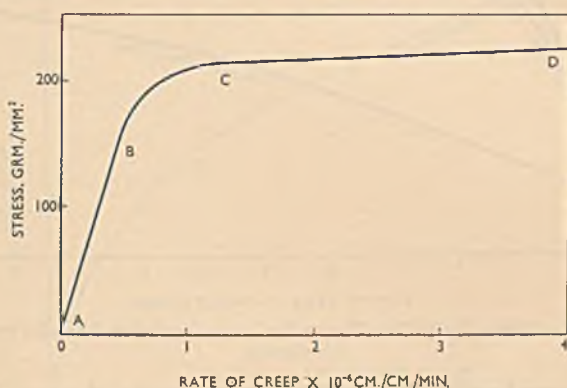


FIG. 2.—Stress-Initial Creep Rate Curve for Single Crystals.

groups: (a) the single crystals, (b) the large crystals, and (c) the small crystals; these three groups will first be considered separately.

(a) *Single Crystals.*

The general result for single crystals is that there is no creep limit, and that the initial rate of creep plotted against stress is as shown in Fig. 2. The curve consists of a region of micro-creep *AB* and of macro-creep *CD*. In the micro-creep range of stresses, the rate of creep under constant stress decreases exponentially, while in the macro-creep region it is constant. In both cases the recovery on removal of the stress is too small to be detected.

(b) *Specimens Consisting of a Few Crystals with Longitudinal Boundaries.*

With specimens of this type the stress-strain curve was straight or nearly so, up to the creep limit, which coincides with the limit of

proportionality. The initial and final creep rates varied with stress in the manner shown in Fig. 3, giving a fairly well defined creep limit for any one specimen.

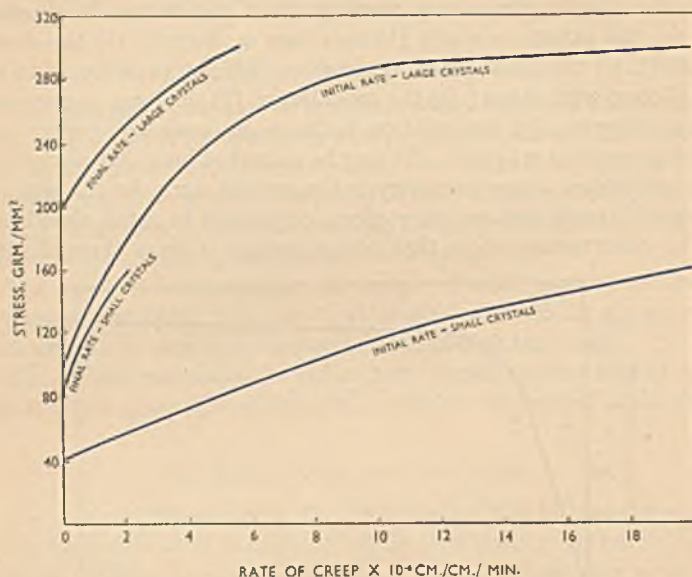


FIG. 3.—Stress-Creep Rate Curves for Large Crystal and Small Crystal Specimens.

This creep limit varied over a very wide range of stress, *i.e.* from 112 to 264 grm./mm.². For a series of typical specimens the number of crystals was counted and the total area of crystal boundaries within the gauge-length was estimated; Table I shows that there is no relation between the area of the crystal boundary and the creep limit.

TABLE I.

Creep Limit, Grm./mm. ² .	Number of Crystals.	Area of Boundaries.
A 264	3	2 cm. ²
B 238	5	6 cm. ²
C 124	5	4 cm. ²
D 112	4	3 cm. ²
E 120	3	2 cm. ²

An examination of the orientations of the crystallites was made by the optical reflection method, with the large crystal specimens. In some cases the arrangement of the reflection spots did not differ greatly

from that of a single crystal; in other cases the reflections from one of the crystallites was very different from the arrangement to be anticipated if the crystallite concerned shared the orientation of the remainder. In the former cases the differences of orientations of the crystals were small, and those were the specimens with low creep limits, *e.g.* specimens C, D, and E; the specimens with large differences of orientation were the ones which showed a high creep limit such as A and B.

The conclusion is that the creep limit is influenced to a far greater extent by the differences in orientation of the crystals than by the extent of the boundaries.

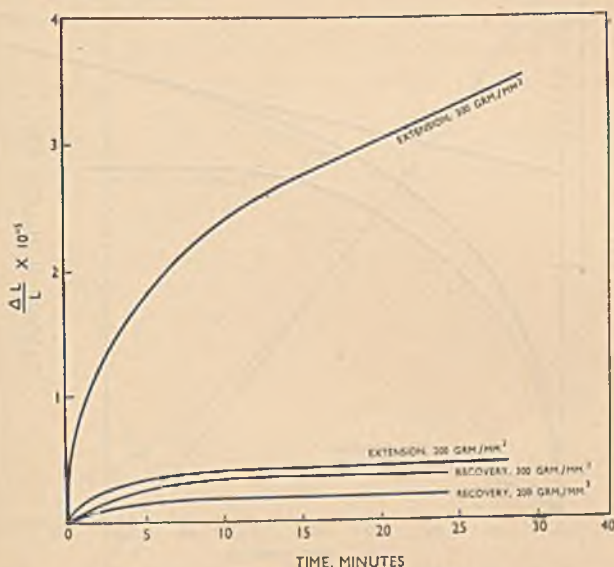


FIG. 4.—Creep and Recovery Curves for Large Crystal Specimens.

It may be noted that the creep-stress curves obtained from single crystals do not vary appreciably with the orientation.

The forms of the creep and recovery curves obtained with such specimens are shown in Fig. 4, in which two pairs of curves are given. It may be observed that the recovery depends on the creep; the curves refer only to gradual changes of length, the much larger instantaneous changes not being represented in the diagram.

(c) Specimens Consisting of Small Crystals.

There were no marked differences in behaviour between the various specimens of this type, although the crystal size varied from about 60 to about 1000 to the cubic centimeter.

Except in the conditions described below, the stress-strain line showed no deviation from linearity until the creep limit was reached. If correction for creep is made the stress-strain line retains its linearity well beyond the creep limit.

The initial creep-stress curve follows its usual form (Fig. 3), giving a fairly well marked creep limit which is rather below the stress at the bend of the corresponding curve for single crystals. The creep curves (Fig. 5) show several features of interest, the creep either becoming linear or ceasing after a fairly short time, corresponding to the β and

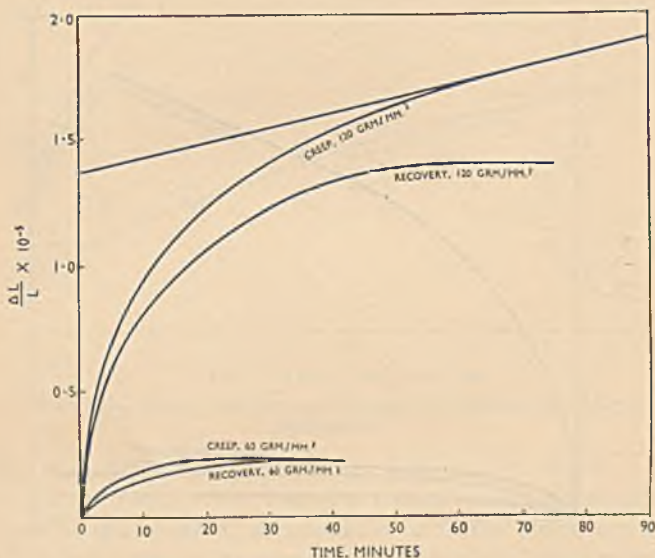


FIG. 5.—Creep and Recovery Curves for Small Crystal Specimens.

γ stages of Andrade.¹ It is found that the recovery follows a curve identical with the β curve of the creep, whether the γ part has a finite or a zero slope.

If the stress-strain data are taken when the recovery from previous strains is complete, it is linear; if, however, the readings are taken before the recovery is complete, the curve is not linear near the origin, but takes the form shown in Fig. 6, *BCD*, the point *A* of the intercept of the straight line part of the curve corresponding to a shorter length than the length *B* of the material when under zero stress by the amount of recovery that has not yet taken place.

The distance *AB* is a measure of the residual recoverable strain of

the material, and decreases with time until the curve finally becomes linear.

DISCUSSION.

The advantages of the present technique over those more often used for tensile tests will first be discussed. The necessity for thermostatic temperature control has already been indicated, and this in turn

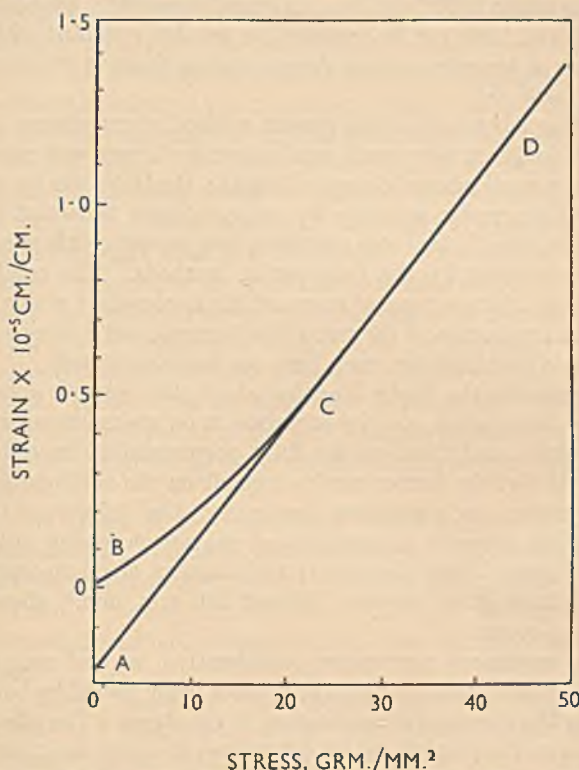


FIG. 6.—Stress-Strain Curves for Partially Recovered Polycrystalline Specimens.

demands a small specimen; a small specimen requires the detection and measurement of a very small absolute extension, for which purpose the interference method is the most convenient, and, since it requires no calibration, probably the most accurate.

In an investigation such as the present one, in which control of crystal size and shape are of importance, the small size of the specimen is also advantageous, as such control can be more easily applied to a small specimen. Further, if a particularly pure material is to be used,

as is the tendency in fundamental investigations, the small quantity of material required is another advantage. Another consideration is that the value of the stress applied is independent of the strain which results, in which particular the instrument is superior to instruments in which the stress decreases as the strain increases.

The maximum elongation that can be measured without resetting the extensometer is 10^{-3} cm./cm., *i.e.* one thousandth; hence the stress under a given force can be regarded as sensibly constant without the application of a constant stress device such as those to which reference has been made.^{1,2}

A further advantage of the present method of experiment is that it is possible to detect very small total amounts of creep and recovery, as well as very small rates of change of length; the latter can be measured with equal or greater accuracy by using a longer time unit (*e.g.* day instead of minute) if the creep continues long enough; otherwise it may remain undetected by the long period methods. The results show that there is often a type of creep which is complete within a short time of the application of the stress (the β creep), and it is by a study of creep of this kind that the creep limit can be investigated.

In considering the results described above, two features in particular yield new information, *i.e.* the experiments on specimens consisting of a few crystals, and those on the fully polycrystalline material. The interpretation of the former results depends on the data obtained with single crystals; as mentioned previously, the behaviour of single crystals of tin is nearly independent of orientation (owing to the large variety of possible slip directions) and consists of micro-creep up to a fairly definite stress between 100 and 140 grm./mm.², above which macro-creep occurs.

In the specimens now under consideration, several such crystals side by side form the specimen, the crystals being joined by boundaries parallel to the direction of application of the stress. The effect of the boundaries on the property which determines the creep limit is considerable. In the first place, such boundaries always inhibit micro-creep, and secondly the lower limit of creep varies from 110 to 264 grm./mm.². Thus the effect of the boundaries varies considerably from specimen to specimen, and, as shown above, is related to the difference of orientation between the crystals. This fact presents new evidence as to the nature of the crystal boundary, and it will first be shown that it is inconsistent with an amorphous cement theory.

If the intercrystalline material were truly amorphous, it would have an atomic arrangement independent of the structure or orientation of its surroundings, and so would always be the same in a given material;

hence, its mechanical effects would not depend on the orientations of the crystals. Further, it has previously been pointed out ⁸ that if the surface of a single crystal is polished, thus giving it a surface of amorphous material, the phenomenon of micro-creep still occurs; the presence of a boundary, however, at once prevents it, and a boundary therefore appears not to consist of amorphous cement.

The results tend to support the point of view that the boundary region consists of a few atoms each acted upon by forces arising from both lattices, and so occupying definite positions, forming a transitional region between one lattice and the other. That this view is consistent with the known properties of crystal boundaries has been shown by Hargreaves and Hills.⁹ It may be pointed out that a lattice transition of this type may contain atoms at distances considerably in excess of their spacing in the normal lattice, and so would be expected to have a lower tensile strength than the true lattice. The rupture of the true lattice across a crystal, however, is known to take place at a stress very much below the stress calculated from the total work done in separating the two parts, and is therefore an action of the tearing type in which stress concentrations cause local stresses much greater than the applied mean stress. Hence, it is probable that although the strength of the transitional lattice is less than the true strength of the ordinary lattice, it may appear greater owing to the absence of planes along which rupture can progress.

Since the atoms of the transitional lattice are not in their most stable arrangement, it follows that their energy is higher than that of the atoms on the undistorted lattice; hence, less extra energy is required to allow them to escape from each other, as when the material melts. Thus the transitional lattice must have a lower melting point than the true lattice.

Any property, therefore, which depends on the distance from the melting point will vary more quickly with temperature for the transitional lattice material than for the other, hence, the real strength of the transitional lattice may fall below the apparent strength of the true lattice at some point well below the melting point. This explains the properties associated with the equi-cohesive temperature.

It was pointed out by Hargreaves and Hills, and ignored in the discussion on their paper, that the fact that crystal boundaries can move favours the transitional lattice theory rather than the amorphous cement theory. The phenomena of recrystallization and crystal growth seem to add further support of the same kind; for example, recrystallization after cold-work; in cold-working, the lattice is distorted, and the atoms no longer occupy their true positions, and cannot readily

reoccupy them except by violent changes involving the reversion of most of the atoms to the true lattice, in many small crystals, with the remaining atoms rearranged to fill the gaps between the inclined sections of lattice so as to have the minimum potential energy. Subsequent grain-growth may be due to the fact that some of the crystallites produced in the recrystallization process did not actually reach the true lattice but only did so approximately. Such crystals will have an excessive potential energy and the boundaries will tend to move across such crystals giving growth of some at the expense of the others, the process being that in which atoms on one side of the boundary fall on to the true lattice, while atoms on the other side are pulled off their less stable lattice by the forces exerted by the atoms in the boundary regions.

A further consideration is as follows: the boundary, if it is regarded as consisting of amorphous material, must resemble a highly supercooled liquid in its properties. It should therefore possess a definite viscosity, *i.e.* a rate of shear proportional to the shear stress applied to it. That this is so follows from the properties of the Beilby layer, which, when being polished, must have a fairly low viscosity. This is also confirmed by the fact that a polished surface does not inhibit micro-creep. It is evident, however, that the boundary layer behaves plastically rather than viscously, *i.e.* below a definite stress no permanent deformation occurs, while above it, the rate of deformation increases much more rapidly than the stress (plastic) whereas for a viscous effect the rate would be proportional to the stress down to zero.

The results on specimens of small crystal size are also of interest, since they yield considerable information about the mechanism of creep. In the first place, the results show that there is a definite creep limit, of about 40 grm./mm.², below which there is no creep in excess of 10^{-8} cm./cm./second or of total amount more than 2×10^{-7} . This is well below the lower limit of macro-creep for single crystals. This must mean that the elastic anisotropy of the tin crystallites causes stress concentrations, and so local stresses are set up which are sufficient to cause macro-creep. Micro-creep has been shown to be suppressed by the presence of boundaries. Secondly, the permanent set point, as deduced from Fig. 3, is considerably above the creep limit, and is in fact about twice the stress, 80 grm./mm.².

The shape of the creep and recovery curves must now be considered; the creep curve (see Fig. 4) can be taken to consist of two superposed effects, the variable or β rate and the final γ rate. The β curve, with signs changed, also represents the recovery after removal of the stress. Hence the β curve can be taken to represent a definite physical process, on which the constant (final) rate of extension may be superposed.

In order to investigate the β curve, it is more convenient to consider the recovery curve, since it is not confused by the γ or constant flow. The process of recovery is clearly due to the fact that some of the crystallites are stretched elastically, while others are behaving plastically. The elastic ones tend to return to their original length while the plastic ones offer a retarding force. To express this mathematically, consider a number of elastic crystallites that have been stretched by a length l above their length under no stress; a force proportional to l will tend to restore them to their unstressed length, hence the force acting $F = Al$.

The mean rate of contraction $\frac{dl}{dt}$ will depend on the force and on the amount of plastic material that is affected by the elastic part, which may be assumed to be proportional to the force, *i.e.*

$$\begin{aligned}\frac{dl}{dt} &= BA^2l^2 = cl^2 \\ \text{or } \frac{1}{l} &= c(t + \text{const.}) \\ \therefore l &= \frac{l_0}{1 + bt}\end{aligned}$$

where $l = l_0$ at $t = 0$, and b is a constant. Then $L = l_0 - l$, where L is the actual decrease of length after the time t . This expression is found to agree closely with the recovery curves, and an example is given in Table II.

TABLE II.

Time.	L Calculated from $t^{\frac{1}{2}}$.	L Calculated from $l = \frac{l_0}{1 + bt}$	L Observed.
0	0	0	0
2	3.8	2.3	2.8
4	4.9	3.9	4.3
6	5.5	5.0	5.2
8	6.1	5.9	5.9
10	6.5	6.5	6.5
15	7.4	7.6	7.5
20	8.2	8.6	8.4
25	8.8	9.0	9.0
30	9.4	9.5	9.6
40	10.1	10.1	10.4
50	11.1	10.6	11.0
60	11.8	10.8	11.1

It is also shown that the $t^{\frac{1}{2}}$ law given by Andrade,¹ does not agree with the experimental curves as closely as the expression derived above. It is interesting that Andrade's formula, originally obtained with much

larger stresses and rates of flow, should still agree moderately well at these small rates.

The process of recovery is then due to the elastic contraction retarded by the plastic flow, and the creep process is the inverse of the recovery, being the process of plastic flow of a material containing elastic inclusions, where the same reasoning holds for the diminishing rate part of the length-time curve. In the conditions of zero final rate, the stress is such that the matrix is elastic, containing plastic inclusions.

The above treatment is necessarily approximate, as the parabolic relation of rate with stress for a single crystal does not agree with the single crystal data. The form of the expression, however, would probably not be altered seriously by substituting a more complicated expression.

It must be realized that the present experiments are carried out in a material that does not work-harden under the slow extensions concerned (this is proved by the constancy of rate in the single crystal experiments), the apparent work-hardening being due to the completion of the elastic part of the extension.

The form of the stress-strain line for strained specimens (see Fig. 6) adds further evidence that the explanation of creep and recovery given above is true. The constant or γ flow, which is regarded as taking place during the whole of the creep time, is to be considered as the sum of the macro-creep effects in all the crystals which behave plastically and are unaffected by elastic portions. After the β creep has finished, the material as a whole is in this condition, the elastic parts having reached a condition of equilibrium with the plastic parts.

ACKNOWLEDGMENTS.

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DISCUSSION.

(Condensed.)

DR. C. SYKES * (Member): The mechanical properties of single crystals are quite different from those of the polycrystalline material, and in particular the range of extension which is elastic, *i.e.* obeys Hooke's law, is usually very much smaller in the case of single crystals than in polycrystalline material. In the case of tin, as the author has shown, strains, less than 10^{-6} cm./cm., overstep the elastic range, assuming that there is any elastic range at all.

Debye, in his work on the specific heat, was able to calculate the C_v/T curve of all elements from a knowledge of their elastic properties. The general agreement between the experimental results and those obtained theoretically is very satisfactory, and is scarcely likely to be a coincidence. The elastic constants chosen have usually been obtained from polycrystalline material.

It would appear then that the presence of grain boundaries does not alter the elasticity of a metal, but only the range over which it is elastic, and, further, that even single crystal tin must be elastic for very small displacements. Moreover, it seems desirable to determine experimentally if: (a) there is any connection between the grain-size of a specimen and the range over which it is elastic, and (b) if the modulus of elasticity is independent of the magnitude of the elastic range.

The author has found experimentally that specimens containing more than one crystal have a definite creep limit, and that the magnitude of the creep limit and therefore the elastic range, is a function of the orientation of the crystals with respect to the grain boundaries. From this result it is concluded that the properties of the grain boundaries are affected by the orientation of the crystals. The mechanism involved is not very clear. A grain boundary can scarcely be considered as a plane, since it has considerable thickness on the atomic scale, and its orientation with respect to any given axis will vary considerably from point to point.

In the specimens examined, the grain boundaries were parallel to the direction of stress. Further experiments, using specimens in which the grain boundaries have different directions with respect to the stress, seem desirable before any definite conclusion is reached as to the mechanism of the effect of crystal orientation on the strength of the boundaries.

The author has developed a precision instrument which, judging from the results already obtained, will prove to be of great value for the investigation of the mechanical properties of metals. He should also be complimented for the marked ingenuity displayed in producing specimens having grains of controlled size and orientation.

The combination of single crystal technique and precision measurement cannot fail to produce results of first-rate significance for the development of the theory of the metallic state.

Professor D. HANSON,† D.Sc. (Vice-President): The author's testing instrument makes possible the measurement, in a relatively simple manner, of changes which we have not been able to study before, and, in consequence, his paper is a little difficult to discuss, as it deals virtually with virgin territory.

I have investigated creep phenomena, but by the more commonly used long-time tests under greater loads. While the author's conclusions do not bear directly on my results, there are certain facts which seem to have an important

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bearing on the behaviour of metals under the ordinary longer time test. If I have understood him aright, Dr. Chalmers shows that the presence of a boundary does influence the behaviour of the metallic test-piece; without necessarily having great strength itself, it interferes with the slip mechanism in its neighbourhood. That is consistent with Gough's work on the influence of boundaries in fatigue testing. In other words, it does have an effect which, mildly at any rate, is a strengthening effect in the neighbourhood of the boundary. In regard to these creep phenomena, if that is the case, it would be expected that when the number of boundaries was large, the material would become stronger and more resistant to flow. In the case of relatively small crystal sizes that does not appear to be the case, either under low stresses or under the higher stresses used in the commoner form of creep testing; and with very small grain-sizes, as in cold-worked and slightly recrystallized metal or eutectic mixtures, the flow under load takes place much more readily than when the grain-size is large. This is an apparent anomaly, and I see no clear explanation of it. If the author could explain this weakness of fine-grained material, he would make an important contribution to the understanding of the behaviour of metals under creep conditions.

Is it connected with the heterogeneous distribution of stress which undoubtedly occurs in the material when the areas enclosed by the boundaries are small? The author gives it as the cause of recovery, and it may be that in materials tested near their recrystallization range, severe local differences in flow or differences in stress would enable recrystallization to occur more readily at the testing temperature, or in some such way produce a redistribution inside the material which will allow the flow to proceed. It would give a sort of annealing effect at a lower temperature. I mention that as a possible explanation, because it is anomalous that the presence of so many apparently strengthening boundaries should produce a material which flows very readily under low loads when the grain-size is very small.

The author's explanation of recovery is similar to that given some years ago by Gough and myself, in studying fatigue phenomena. Recovery on removal of stress occurs not only in creep testing but also in repeated stress testing, such as fatigue testing. If, for example, a specimen is loaded to a sufficient stress less than the maximum stress, and the load is then completely removed, and this process is repeated, the material quickly assumes the cyclic state, in which the behaviour can be represented by a symmetrical loop, and the shapes of the loading and unloading curves are identical; in other words, the behaviour of the material is exactly the same when the load is taken off and when it is put on. That indicates that the process of quick recovery during fatigue testing is the same as the process of loading. Muir showed many years ago, when working on the effect of overstrain on iron, that in tensile testing the unloading curve has the same form as the loading curve. Gough and I concluded that it was due to the locked up elastic stresses pulling the material back into its initial form, and that it was being resisted by the plasticity of the crystals.

The author's conclusions regarding the nature of the crystal boundary are interesting, especially as they are derived from experiments in which the amount of deformation was trivial. I have come to the conclusion also that the crystal boundary is inherently weak, and the author might be interested in a paper by Wheeler and myself* on the flow of aluminium. We concluded that the boundary was a region where the material hung together at a few points, and quite a few of those points of contact would give a sufficient strength, by virtue of the cohesion of the metal, to enable one to put on a sufficient stress to make the crystals themselves flow plastically to a great extent. Under certain conditions, however, it is possible to develop the weakness of the crystal boundary, as by

* *J. Inst. Metals*, 1931, 45, 229.

maintaining a load for a long time, because under such a unidirectional stress any movements at the boundary are all in one direction, and they all tend to disrupt the metal, whereas the slip mechanism reconstitutes the crystal as the flow takes place.

The PRESIDENT asked the author to reply to the discussion in writing.

CORRESPONDENCE.

DR. U. R. EVANS,* M.A. (Member): Apart from the special interest of Dr. Chalmers' work to users of tin, the discussion of crystal-boundary conditions should appeal to a larger audience. It raises a point which I ventured to discuss 16 years ago,† in connection with the interesting work of Carpenter and Elam.‡ These authors had observed that, after mild deformation, some grains grew at the expense of others, and had seemed to suggest that it was the *more deformed* grains which grew. I expressed the opinion that the *less deformed* grains would invade their more deformed neighbours, since in any system the more stable phase will always grow at the expense of the less stable phase; for instance, an ice crystal placed in water below 0° C. will grow at the expense of the water, whereas above 0° C. the water would extend at the expense of the ice. I am glad that Dr. Chalmers takes the same view, and supplies what is, at least approximately, a true picture of the change.

I have always regretted that this exceptionally interesting work by Carpenter and Elam was discontinued—largely owing to the magic of big crystals. No one will deny the wonderful experimental impetus given to many branches of metallurgy and physics by their method of producing big crystals; nevertheless, viewed dispassionately, a large crystal only differs from a small crystal in size, whereas the work on boundary migration seemed capable of supplying answers to many very fundamental questions, which were otherwise likely to remain unanswered. In 1921, one wished to know why, when a certain number of atoms were already aligned in a straight row, other atoms tended to place themselves in the same alignment; one wished to know how many atoms in a row were needed to exert this orientating force, and over what distance the orientating force could exert itself. In 1921, the answers to these fascinating questions seemed to be just about to be obtained, but, although in the interval, mathematicians may have given us the answers in certain specially simple cases, we are still waiting for detailed experimental work on this matter, such as might have been expected from a detailed study of boundary migration. An attempt by Cook and myself § to continue the same sort of work by statistical counts of grains in tin, lead, and cadmium, was left unfinished in its early stages. Some interesting work has, however, been published by Eastwood, Bonsu, and Eddy,|| whilst the work of Straumanis ¶ on metallic crystals grown from vapour is of great importance.

Since tin has proved a suitable metal for study, I hope that Dr. Chalmers will continue work on these and correlated problems. He would not only receive the thanks of those concerned with tin and other soft metals, but he would do

* Cambridge University.

† U. R. Evans, *J. Inst. Metals*, 1921, 25, 298.

‡ H. C. H. Carpenter and C. F. Elam, *J. Inst. Metals*, 1920, 24, 83; 1921, 25, 239.

§ M. Cook and U. R. Evans, *Trans. Amer. Inst. Min. Met. Eng.*, 1925, 71, 627.

|| L. W. Eastwood, A. E. Bonsu, and C. T. Eddy, *Trans. Amer. Min. Met. Eng.*, 1935, 117, 246.

¶ M. Straumanis, *Z. Krist.*, 1934, 89, 487.

much to revive scientific interest in metallurgical research; there are many who feel that metallurgy should comprise something more than the cartography of equilibrium diagrams.

The AUTHOR (*in reply*): Dr. Sykes raises a very interesting point regarding the theory of specific heats. It would appear that a rather fundamental distinction must be made between properties, such as specific heat, that are characteristic of the material as a whole, and other properties, among which is plastic flow, that depend on some kind of local singularity affecting only a small proportion of the material. The latter are generally referred to as structure-sensitive properties, and the former as structure non-sensitive. Small quantities of impurity often have a relatively large effect on structure-sensitive properties, and a quite small effect on non-sensitive ones. Applying this distinction to the present case, the greater part of the material does not flow under very small stresses, the actual flow being due to translation along glide planes spaced, atomically, a long way apart. The bulk of the material is, then, elastic, and so Debye's theory of specific heats can be applied, although the crystal, as a whole, is plastic. The mechanism suggested to account for micro-plasticity has been discussed in a previous paper,* and reference to this will explain this point of view more fully.

With regard to the nature of the boundary material, to which Dr. Sykes, Professor Hanson, and Dr. Evans refer, I have carried out, since the completion of the paper under discussion, a fuller investigation of the effects of longitudinal boundaries on the creep limit. The experiments, an account of which has been published,† consisted of the preparation, by a "seeding" method, of cylindrical specimens consisting of two crystals with one longitudinal boundary. The yield-point was measured for each specimen, and it was found that a definite relation exists between the angle between the crystal axes of the two crystals and the yield-point. This is shown to constitute strong evidence for a transitional lattice boundary theory, and against an amorphous layer theory.

In connection with Professor Hanson's interesting comments on the creep properties of materials with small grain-size, I can only suggest that the explanation may be that the effect of a boundary in preventing glide may not be so marked when the extent of a boundary is small, perhaps disappearing altogether if the size of the boundary is reduced until it is comparable with the distance between two glide planes.

Finally, I can assure Dr. Evans that I am working on various problems, among which I include the very important problem of recrystallization and grain-growth, to which the present technique is applicable.

* *Proc. Roy. Soc.*, 1936, [A], 156, 427-443.

† *Proc. Roy. Soc.*, 1937, [A], 162, 120-127.

A STUDY OF THE MECHANICAL PROPERTIES 784 OF TIN-RICH ANTIMONY-CADMIUM-TIN ALLOYS.*

By PROFESSOR D. HANSON,† D.Sc., VICE-PRESIDENT, and W. T. PELL-
WALPOLE,‡ B.Sc., Ph.D., MEMBER.

SYNOPSIS.

The tensile strength and Brinell hardness of alloys containing up to 43 per cent. of cadmium and 14 per cent. of antimony have been determined on annealed chill-cast specimens. The results are correlated with the constitution of the alloys. Maximum stable values obtained are tensile strength 7.0 tons/in.² and Brinell hardness 36.

Tin-rich alloys containing 3 per cent. to 8 per cent. of cadmium with 1 per cent. to 9 per cent. of antimony have been tested as rolled and after various heat-treatments.

Two forms of hardening are obtained by quenching from suitable temperatures. One form is due to the solubility change of antimony in tin or in β ; the other, which produces much more intense hardening, is analogous to the hardening of binary cadmium-tin alloys by quenching and depends on the suppression of the eutectoid decomposition of the β phase. Permanent improvement results in the first case, but the second type of hardening is only temporary, since complete self-annealing occurs at normal temperature (18° C.) within 18 months.

Tempering experiments have been carried out to obtain permanently stable properties by short-time heat-treatments.

INTRODUCTION AND PREVIOUS WORK.

THE beneficial effect of antimony on the mechanical properties of tin is well known, antimony-tin alloys forming the basis of most of the commercial tin-base alloys. The effect of cadmium on tin has been studied by the present authors,¹ who have shown that the tin-rich cadmium-tin alloys can be permanently improved by heat-treatment.

There has been no previous systematic investigation of the mechanical properties of ternary alloys of antimony and cadmium with tin, but it has been shown that the addition of 1 per cent. of cadmium to tin-base bearing metals greatly improves the fatigue strength,² indentation hardness,³ tensile strength,⁴ and resistance to pounding.⁵

The present paper describes the results of a research on the

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mechanical properties of antimony-cadmium-tin alloys containing up to 43 per cent. of cadmium and 14 per cent. of antimony. The results are correlated with the constitution and microstructures of the alloys, which have been described previously by the authors.⁶

EXPERIMENTAL.

Tensile tests and indentation hardness tests have been carried out on (a) the whole series of alloys as chill-cast and annealed; and (b) alloys containing 3 to 8 per cent. of cadmium with 1 to 9 per cent. of antimony, in the form of rolled strip, after various heat-treatments. Alloys for tests (a) were prepared as ingots $6 \times 1 \times 0.2$ in., and for tests (b) as ingots $10 \times 2 \times 0.5$ in.; all were cast at 300° C. into chill moulds heated to 100° C. The strip ingots were cold-rolled to 0.1 in. thickness; all compositions rolled satisfactorily, but some blistered slightly on standing.

Tensile tests were carried out on a 5-ton vertical testing machine at a constant rate of straining of 0.1 in./in./minute, since the more rapid rate, 0.4 in./in./minute (1.6 in./minute) used for the previous work was found to be unsatisfactory for these alloys. In order to relate the results of the two different rates, a series of alloys having tensile strengths from 1 to 7 tons/in.² was tested at both rates. An approximate linear relation was obtained, as follows: Tensile strength at 0.1 in./in./minute = $0.86 \times$ tensile strength at 0.4 in./in./minute.

Hardness tests were carried out on a Vickers machine, using a 2 mm. ball and a load of 10 kg. applied for 15 seconds.

Tests on Chill-cast Material.

The chill-cast ingots were machined to test-pieces 0.5 in. wide over the parallel portion, and a gauge-length of 2 in. was marked for the measurement of the extension. The test-pieces were annealed for 7 days at 170° C. and cooled in the furnace.

The results of tensile and hardness tests are given in Appendix I and are shown graphically in Figs. 1 and 2 (Plate VII). The relation between mechanical properties and the constitution of the alloys is very marked in both diagrams. The alloys may be classified into two well-defined groups:

(1) Those in which the compounds δ and ϵ are present only as secondary separations or as separations in the solid state, *i.e.* in the state of fine dispersion;

(2) Those in which either δ or ϵ occur as primary separations. In this case the compounds are able to grow to relatively large crystals of definite form, *viz.* δ is cubic; ϵ forms in large needles.

The first group exists within the area $ABCDEFGF$ in Figs. 1 and 2, the second group in the area $BG'HFEDC$. Within the area $ABCDEFGF$, which will be considered first, the mechanical properties are closely related to the phase diagram of alloys in equilibrium at room temperature,⁶ and for convenience in comparing, the phase boundaries of this horizontal section through the constitutional model are shown as broken lines in the diagrams of hardness and of tensile strength.

The α phase field $AIJKL$ has such a limited extent that none of the alloys tested consists entirely of α , but, from the form of the contour lines and the known values for the binary alloys antimony-tin and cadmium-tin, it is clear that cadmium in solution in tin has a much greater hardening and strengthening effect than has an equal amount of antimony. This effect is also noticeable in the case of alloys which lie within the $\alpha + \delta$ phase field $LBMK$: the contour lines both of hardness and of tensile strength are almost parallel to the antimony-tin face, and are very close together, indicating a very rapid improvement with increasing cadmium content, and a very slight improvement with increasing antimony content.

In the phase fields $\alpha + \delta + \epsilon$ (KMN) and $\alpha + \epsilon$ ($NOJK$), the directions of the contours indicate a continuous steady increase of strength and hardness with increasing amounts of the ϵ phase, until the contours of 6 tons/in.² and 30 Brinell, respectively, are reached. These contours practically coincide with the limit of existence of ϵ as a solid solubility separation only; within the quadrilateral $MCDQ$, ϵ is also present as a secondary separation ($\alpha + L + \epsilon$). Beyond the line MQ the increase of strength and hardness is again in the same direction, but becomes more gradual until a flat maximum is reached in each diagram, near to the line NO , which lies on the lower limit of primary separation of the δ phase.

The remaining alloys within the first group ($JOCDEF$) are all in the phase field $\alpha + \gamma + \epsilon$, but with respect to mechanical properties, the eutectoid ($\alpha + \gamma$) behaves as an independent phase; the position of the eutectoid valley is shown at RSS' in Figs. 1 and 2. Along the line JPO , which represents the limit of existence of the eutectoid, there is a very sudden inflexion of all the contour lines, and within the area $JPSR$ ($\alpha + \epsilon + \text{eutectoid}$) both tensile strength and hardness are again proportional to the amount of the ϵ phase which is present up to line PS . In the area $PSDCO$, where ϵ is present as a secondary separation ($\alpha + L + \epsilon$), the increase in tensile strength and hardness become more gradual until the flat maxima, which have been mentioned previously, are reached.

The eutectoid line RSS' constitutes a ridge of high strength and

hardness, the contour lines running parallel to it on either side. The decrease of both properties in alloys immediately to the right of this line indicates that the appearance of secondary γ (binary complex $\beta + \gamma$) has a distinct weakening effect. This has been noted by the authors in the case of binary cadmium-tin alloys, but the effect is much more pronounced when antimony is present. A flat depression occurs between 10 and 16 per cent. of cadmium, but further increase of cadmium content has scarcely any effect on hardness or tensile strength. The closeness of the contours in the latter region show that increasing proportions of the ϵ phase have a considerable strengthening effect, whether it is present only as a solid solubility separation (area *RTEUG*) or also as a secondary separation (complex $\epsilon + \gamma$) (area *TCDEFU*). The antimony-rich limit of this area (*CDEF*) corresponds approximately to a maximum in tensile strength, and to a sudden widening of the contour lines in the hardness diagram.

All alloys within the first group (*ABCDEFGF*) have a reasonable extension (10–50 per cent. on 2 in.) in a tensile test, and break with the "ductile" type of fracture associated with considerable reduction of area of the test-piece (see Fig. 3, Plate VIII).

The alloys of the second group (area *BG'HFEDC*) contain either δ or ϵ or both as primary separations. The brittleness of these phases, and the relatively massive forms in which they grow from the liquid, exert a much greater control of the mechanical properties than do the normal phase relations. The valleys of the primary and secondary surfaces are shown, therefore, in the diagrams of hardness and tensile strength.

In the area *BG'VM* the primary separation is the δ cuboid phase, and no ϵ is present in any form. The contours in this area (Figs. 1 and 2) indicate that an increasing quantity of the cuboids has no appreciable effect on either tensile strength or hardness, whereas increasing cadmium content causes a very rapid increase of both, illustrating the great benefit of the addition of small amounts of cadmium to antimony-tin alloys.

In the area *MVWC* the alloys separate primary δ cuboids on cooling from the liquid state; the δ should react with liquid at 227°C . to produce $\epsilon + \alpha$, but it has been shown previously⁶ that this reaction is suppressed during cooling, and that ϵ is only formed after annealing. This suppression has an important effect on the size and distribution of the ϵ , which appears as small rounded masses often closely associated with the residual δ . The contours in this area indicate that increasing amounts of the ϵ cause a gradual decrease in hardness and tensile strength from the maxima mentioned previously. In alloys containing

more than 12 per cent. of cadmium, the tensile strength decreases much more rapidly than the hardness. The triangle *WCY* encloses those alloys in which either cubic crystals of δ , or elongated crystals of ϵ occur as the primary separation with the complex ($\delta + \epsilon$). In this region the hardness decreases very slowly as the quantity of ϵ increases, but the tensile strength decreases extremely rapidly, especially in alloys containing more than 12 per cent. of cadmium.

The remainder of the diagram (*S'CDEF*) consists of alloys in which ϵ "needles" are the primary separation. In these alloys the relation between tensile strength and hardness breaks down completely; hardness increases very slowly with increasing proportion of the primary ϵ , whilst the tensile strength decreases steadily with increasing antimony content, from the maximum which occurs at 5.5 tons/in.² along the boundary of primary ϵ separation (*DEF*) to a constant value of 2.0 tons/in.² along the section containing 13 per cent. of antimony. In both diagrams there is a slight change in direction of the contours, corresponding approximately to the lines *DY'*, *EZ*, which represent valleys between the surfaces of secondary separation $L + \epsilon + \alpha \rightarrow L + \epsilon + \beta$, and $L + \beta + \epsilon \rightarrow L + \gamma + \epsilon$, respectively. All alloys of the second group give "brittle" types of fracture in the tensile test, i.e. there is very little extension and no appreciable local reduction of area.

If δ is the primary separation in the alloy the fractured surface is extremely fine-grained, whilst the presence of primary ϵ produces an extremely coarse structure in the fractured surface (Fig. 3, Plate VIII).

In the case of alloys with the higher antimony and cadmium contents, it is rather difficult to obtain perfectly sound castings; several of the test-pieces fractured at blow-holes, but, since at least two specimens of each alloy were tested, a reliable result was obtained in most cases.

Tests on Rolled Material.

Specimens for tensile tests were machined to a width of 0.5 in. (the thickness being 0.1 in.) over the parallel portion. The gauge-length was 2 in. The following series of tests have been carried out:

- 1 (a) Periodical hardness measurements on specimens as rolled.
(b) Tensile tests 6 weeks after rolling.
- 2 (a) Hardness and tensile tests on specimens annealed for 7 days at 170° C., and furnace-cooled.
(b) Hardness and tensile tests on specimens quenched from 170° C.
(c) Periodical hardness measurements on specimens quenched from 170° C.

- 3 (a) Hardness and tensile tests on specimens annealed for 4 hrs. at 170° C., then for 2 hrs. at 190° C., and quenched.
 (b) Specimens treated as 3 (a) and aged at room temperature—periodical hardness tests, and tensile tests 2 months after rolling.
 (c) As 3 (a), then tempered at 100° C.

The results of a great number of tests show that there is a definite relationship between tensile strength and Brinell hardness for these alloys. For all heat-treated specimens a linear relation is obtained:

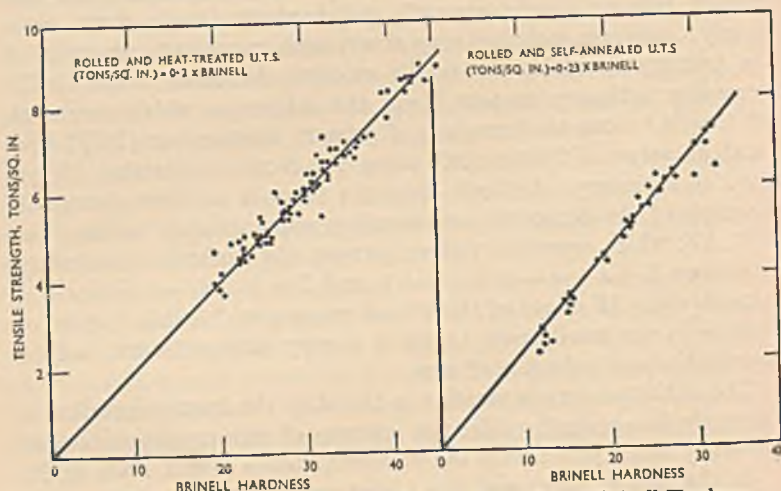


FIG. 4.—Relation Between Ultimate Tensile Strength and Brinell Hardness.
N.B. Each Point Represents Results on a Different Alloy.

Tensile strength in tons/in.² = $0.2 \times$ Brinell number. The results for alloys in the rolled and self-annealed condition do not lie in the same straight line as the former, but give a second relation: tensile strength in tons/in.² = $0.23 \times$ Brinell number. The graphs are shown in Fig. 4.

Periodical hardness tests show that during the period from 1 week until 12 weeks after rolling a gradual reduction in hardness occurs in all alloys, but the extent of softening decreases with increasing antimony content. This softening is analogous to that which occurs with the tin-rich cadmium-tin alloys after rolling,¹ and is probably due to the gradual completion of the eutectoid transition, which is partially suppressed by chill-casting.

The results of hardness and tensile strength are given in Table I,

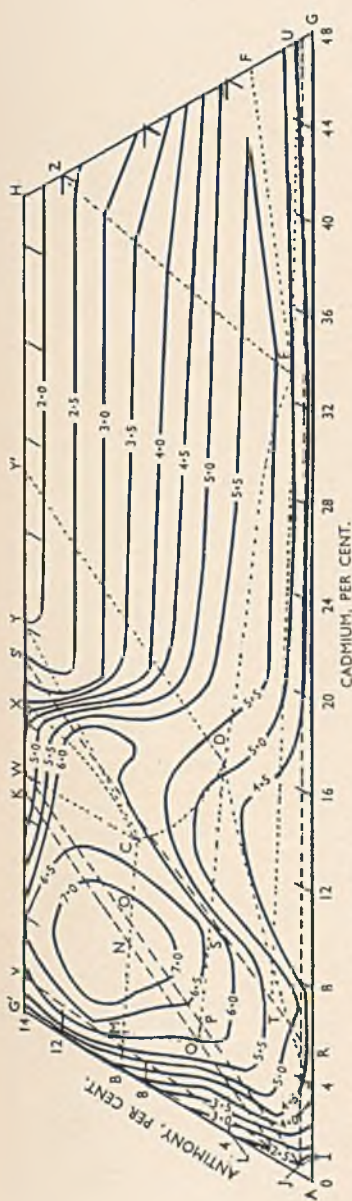


FIG. 1.—Tensile Strength of Chill-Cast Alloys, Annealed for 1 Week at 170° C., and Cooled in the Furnace. Contours at Intervals of 0.5 Ton/In.².

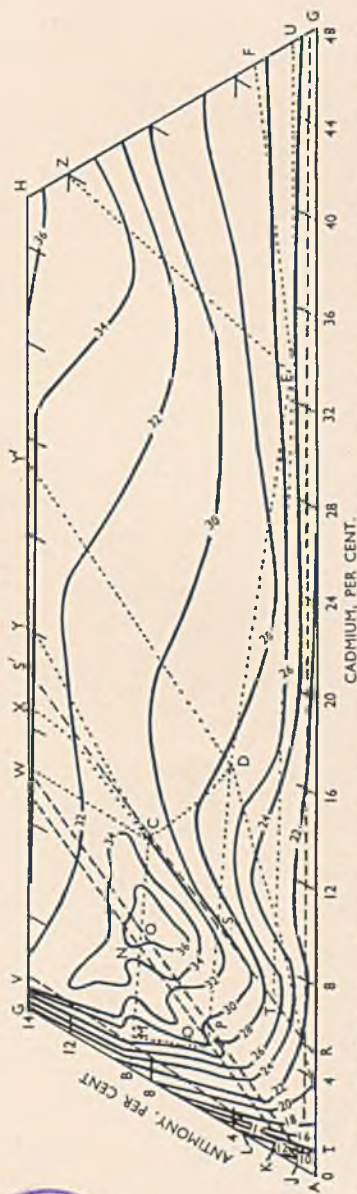


FIG. 2.—Brinell Hardness of Chill-Cast Alloys, Annealed for 1 Week at 170° C., and Cooled in the Furnace. Contours at Intervals of "2" Brinell Numbers.

Note.—The contour 32 continues from C along valley CX to meet the other branch of the same contour.



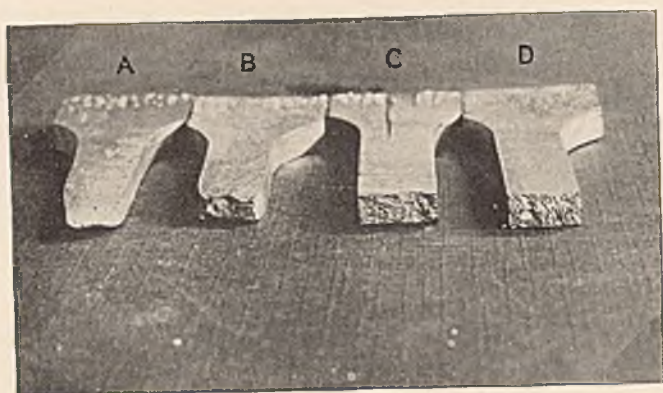


FIG. 3.—The Four Types of Fractures Obtained in the Tensile Tests. (A) Ductile; with Great Reduction of Area; (B) Fibrous, Fair Ductility, and Reduction of Area; (C) Fine Brittle Fracture Associated with the Presence of Primary δ ; (D) Very Coarse Brittle Fracture, Caused by Primary "Needles" of ϵ .

and show that in rolled alloys these properties are controlled chiefly by the antimony content, and vary only slightly with the cadmium content. The maximum values are obtained in the series of alloys which contain 7 per cent. of antimony; these are approximately constant for all cadmium contents from 3 to 8 per cent. cadmium, at 7 tons/in.² with 45 per cent. elongation and hardness of 31.

TABLE I.—*Mechanical Properties of Rolled and Self-Annealed Antimony-Cadmium-Tin Alloys.*

Alloy No.	Cadmium, Per Cent.	Antimony, Per Cent.	Brinell Hardness.			Ultimate Tensile Strength, Tons/in. ² 6 Weeks after Rolling.	Elongation, Per Cent. on 2 in. 6 Weeks after Rolling.
			1 Week after Rolling.	6 Weeks after Rolling.	12 Weeks after Rolling.		
C3.S1	3	1	13.0	11.6	12.0	2.12	78
C3.S2		2	15.8	13.0	15.6	2.98	64
C3.S3		3	19.5	18.5	19.5	3.96	52
C3.S4		4	22.1	22.5	22.9	5.0	42
C3.S5		5	25.0	24.7	26.6	5.95	37
C3.S7	4	7	31.8	31.8	27.2	7.14	47
C3.S9		9	31.0	31.0	27.8	6.91	42
C4.S1		1	15.8	12.1	12.3	2.26	60
C4.S2		2	16.2	15.4	15.9	3.18	58
C4.S3		3	19.1	18.9	19.9	4.18	28
C4.S4	5	4	22.9	22.7	23.6	5.1	50
C4.S5		5	24.3	24.1	26.1	5.48	42
C5.S1		1	15.5	13.0	12.8	2.36	76
C5.S2		2	16.9	15.7	16.4	3.26	57
C5.S3		3	20.6	19.9	20.4	4.28	46
C5.S4	6	4	22.9	22.9	24.5	5.18	41
C5.S5		5	24.5	23.7	25.6	5.64	44
C5.S7		7	31.8	32.1	30.0	6.74	35
C5.S9		9	36.3	36.3	36.3	7.14	32
C6.S1		1	16.4	14.9	11.2	3.35	62
C6.S3	7	3	20.8	19.9	18.3	4.37	49
C6.S5		5	26.3	25.9	24.1	6.2	47
C6.S7		7	31.0	31.3	29.0	7.15	44
C7.S1		1	17.0	15.3	13.5	3.41	42
C7.S3		3	23.4	21.9	19.0	4.78	47
C7.S5	8	5	27.5	27.8	24.7	6.24	42
C7.S7		7	31.4	31.8	29.0	6.95	48
C8.S5		5	23.5	26.6	24.5	6.05	51
C8.S7		7	31.8	32.1	29.8	7.31	54

The tests on rolled alloys annealed at 170° C. and furnace cooled give results very similar to those obtained for chill-cast alloys subjected to the same heat-treatment, but the latter have slightly higher values for tensile strength and hardness, and correspondingly lower elongations (Table II).

Annealing at 170° C. causes the cadmium-rich γ phase of the eutectic, which is present in the alloys when chill-cast, to be taken

quenched. Considerably improved properties were obtained by this treatment, but many alloys showed signs of having been above their respective solidus temperatures. Further experiments showed that annealing for 4 hrs. at 170° C., and then for 2 hrs. at 190° C., followed by quenching, was the most satisfactory treatment, and only 5 alloys gave no result due to the presence of the liquid phase. For all other compositions, tensile and hardness tests were carried out and the results show a very marked improvement in properties compared with those obtained with previous heat-treatments, but the strongest alloys have rather low elongations.

TABLE III.—*Mechanical Properties of Quenched Sb-Cd-Sn Alloys.*

Alloy No.	Composition.		Quenched from 190° C. Tested Immediately.			Quenched. Aged for 8 Weeks at 18° C.		
	Cad- mium, Per Cent.	Anti- mony, Per Cent.	Ultimate Tensile Strength, Tons/in. ²	Elonga- tion, Per Cent. on 2 in.	Brinell Number.	Ultimate Tensile Strength, Tons/in. ²	Elonga- tion, Per Cent. on 2 in.	Brinell Number.
C3.S1	3	1	5.32	40	29.0	3.86	42	25.0
C3.S2		2	5.53	39	29.3	4.48	39	25.0
C3.S3		3	5.80	36	29.5	5.26	37	27.0
C3.S4		4	6.00	44	30.3	5.87	39	29.3
C3.S5		5	6.48	33	33.8	6.18	30	33.8
C3.S7	4	7	6.82	31	36.0	6.77	29	34.5
C3.S9		9	6.34	39	32.0	6.27	30	31.8
C4.S1		1	8.3	12	38.8	4.65	14	28.5
C4.S2		2	6.85	30	37.8	4.85	37	29.5
C4.S3		3	6.87	30	35.0	5.39	37	30.5
C4.S4	5	4	6.88	31	35.0	6.04	32	31.5
C4.S5		5	7.19	30	35.0	6.75	37	31.5
C5.S1		1	6.60	5	40.5	5.36	26	29.0
C5.S2		2	8.59	10	41.8	5.44	15	31.5
C5.S3		3	8.48	25	44.5	6.02	24	34.5
C5.S4	6	4	8.26	27	42.0	6.50	33	36.8
C5.S5		5	8.60	30	42.8	6.68	37	37.5
C5.S7		7	7.20	10	37.0	7.03	23	35.5
C5.S9		9	6.72	29	36.0	6.64	28	34.0
C6.S5		5	10.42	3	45.8	7.73	28	39.3
C6.S7	7	7	8.45	20	42.8	6.96	25	36.3
C7.S5		5	10.50	5	48.0	6.82	22	36.5
C7.S7		7	9.70	14	45.0	7.43	12	37.0
C8.S7	8	7	8.92	2	43.8	7.04	19	35.3

The tensile strengths are shown graphically in Fig. 5 (corresponding elongations and Brinell numbers are shown in Table III). This diagram bears a close relation to the horizontal section through the ternary model at 190° C., and, in contradistinction to the results of all previous tests, the tensile strengths are greatly improved with increasing cadmium content and vary only slightly with antimony content.

The extent of the improvement over the results for slowly-cooled alloys is proportional to the amount of the β phase present, and the maximum values correspond closely to the phase field (β plus ϵ), whilst alloys which gave no results are at this temperature in the phase fields (β plus liquid) or (β plus ϵ plus liquid). Thus, the improvement obtained by quenching from 190° C. is due chiefly to the suppression of the β decomposition, but is also affected to some extent by the prevention of the separation of the δ and ϵ precipitates from both α and β , since some alloys which contain no β show a considerable increase in hardness and tensile strength after this treatment.

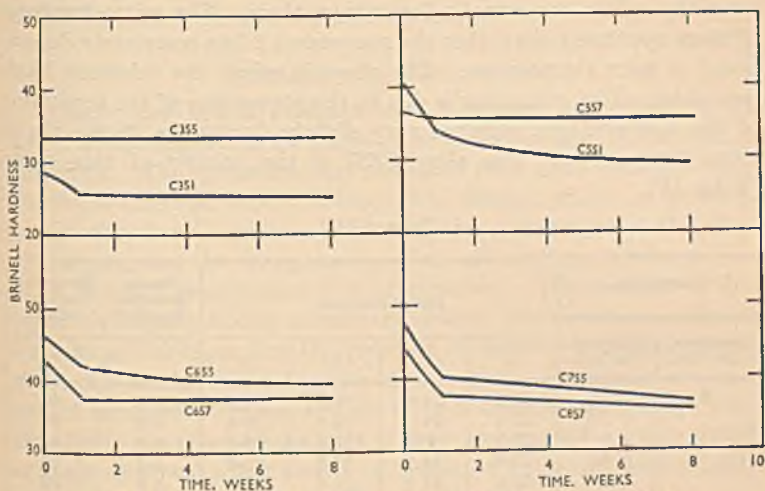


FIG. 6.—Hardness of Sb-Sn-Cd Alloys Quenched from 190° C.

Periodical hardness tests on specimens quenched from 190° C. and aged at room temperature (Fig. 6) show that most of the alloys undergo considerable softening during the first week after quenching, but that after this period the rate of softening decreases very rapidly in all cases, whilst some alloys become quite stable. The softening is most marked in those alloys which consist chiefly of the β phase as quenched. The results of tensile tests carried out on specimens which had been quenched from 190° C. and aged for 8 weeks at room temperature (18° C.) are given in Table III. For most of the alloys tested, the ultimate strength is lower than in the quenched condition, but those alloys which gave the highest tensile values with very low elongation figures when tested immediately after quenching are much more ductile after the tempering effect of ageing at 18° C. The best combination of these properties occurs with the alloy C6S5, which has a

tensile strength of 7.73 tons/in.² with 28 per cent. elongation and a Brinell hardness of 39.

Some of the alloys which, as slowly-cooled, contain no eutectoid but a considerable amount of the δ or ϵ precipitates, were improved by quenching from 190° C., and these alloys undergo only a very slight lowering of tensile strength on ageing at room temperature.

Hardness tests on quenched alloys were repeated at intervals until 18 months after quenching. After this time all alloys which (as quenched) contained the β phase have softened to the values obtained in specimens which were furnace-cooled from 170° C., and in some cases the values are actually lower than these. The microstructures of these specimens show that the suppressed β has completely decomposed at room temperature. The alloys in which the enhanced hardness obtained on quenching is due to the prevention of the separation of the δ or ϵ phases, softened very slightly during the 18 months at room temperature. The alloy C3S7 is the hardest of this group (Table IV).

TABLE IV.

Composition.		Brinell Hardness.				Tensile Strength, Tons/in. ²	Elongation, Per Cent. on 2 in.
Cadmium. Per Cent.	Antimony. Per Cent.	A.	B.	C.	D.	E.	
3	1	20.5	24.0	21.3	21.0	4.0	40
	2	21.5	24.0	23.6	22.4	4.3	35
	3	23.2	25.2	24.8	24.8	4.8	45
	4	27.5	28.3	27.8	25.8	5.3	45
	5	32.0	31.8	31.0	30.8	5.9	37
	7	33.0	35.0	35.0	34.2	6.6	25
	9	31.0	32.0	32.0	31.5	6.0	18
	1	21.5	27.3	24.4	23.4	4.4	40
	2	23.0	28.8	24.8	24.8	4.7	44
4	3	25.5	29.8	27.3	26.0	5.0	40
	4	28.0	29.8	29.0	27.1	5.1	45
	5	29.0	30.0	30.0	29.5	5.8	40
	1	22.0	30.0	24.0	22.0	5.0	30
	2	23.0	31.3	27.1	25.0	5.4	22
5	3	26.0	33.3	29.0	28.0	5.7	25
	4	29.0	29.3	29.3	29.5	5.8	38
	5	30.5	35.0	32.0	31.0	6.1	25
	7	32.0	33.5	33.5	32.5	6.0	20
	9	30.5	35.0	35.0	34.0	6.2	18
	7	30.0	35.2	32.2	31.2	6.3	25
	7	30.0	36.5	31.5	30.8	6.5	20

- A. Quenched 190° C. Aged 18 months at 20° C.
 B. Quenched 190° C. Tempered for 4 hrs. at 100° C.
 C. Quenched 190° C. Tempered for 12 hrs. at 100° C.
 D. Quenched 190° C. Tempered for 24 hrs. at 100° C.
 E. Quenched 190° C. Tempered for 24 hrs. at 100° C.

Tempering experiments have been carried out to determine the most rapid heat-treatment which will produce stable properties in these alloys. A series of alloys was quenched from 190° C. and tempered for various periods at 100° C. The results (Table IV) show that the softening is very rapid during the first hour, but subsequently it proceeds very slowly. After 24 hrs. at 100° C. the values are approximately the same as those obtained by "tempering" for 18 months at room temperature. Tensile tests were carried out after the same heat-treatment. The best results were obtained with the alloy C3S7, which has a tensile strength of 6.5 tons/in.², an elongation of 25 per cent. on 2 in., and a Brinell hardness of 34.

SUMMARY AND CONCLUSIONS.

Tensile and Brinell hardness tests have been carried out on 112 alloys containing up to 43 per cent. of cadmium and 14 per cent. of antimony. The specimens were machined from small chill-cast ingots, and were annealed before testing. The results, which are presented graphically, have been correlated with the constitution of the alloys. It is shown that the strengthening effect of cadmium in solid solution in tin is much greater than that of antimony. The presence of the δ phase (principally SbSn) as primary cuboids has no adverse effect on strength or hardness, but the presence of primary ϵ (CdSb) destroys the useful mechanical properties of the alloys. Maximum combination of hardness, strength, and ductility is obtained with alloys which have finely-dispersed precipitates of the δ and ϵ phases in an α matrix, or finely-dispersed ϵ in a matrix consisting of α (tin-rich solid solution) with a eutectoid of α plus γ (cadmium-rich solid solution).

The maximum stable values obtained are of the order of 7 tons/in.², with 15 per cent. elongation on 2 in., and a Brinell hardness of 35, in alloys containing 7-9 per cent. of antimony with 5-7 per cent. of cadmium.

Tin-rich alloys containing 3 per cent. to 8 per cent. of cadmium with 1 per cent. to 9 per cent. of antimony have been tested as rolled and after various heat-treatments. All alloys in this group will withstand 80 per cent. reduction by cold-rolling.

Periodical hardness tests on rolled alloys stored at 20° C. show that slight softening occurs during 12 weeks at this temperature. Tensile tests, carried out 6 weeks after rolling, show that maximum values of the order of 7 tons/in.², 40 per cent. elongation on 2 in. and a Brinell hardness of 35 are obtained in alloys containing 7 per cent. of antimony with 3-8 per cent. of cadmium.

Annealing at 170° C. produces considerable improvement in alloys

containing less than 5 per cent. of antimony, but there is very little change with higher antimony contents.

Quenching from 170° C. effects no improvement in these alloys, but on quenching from 185° to 200° C. two forms of hardening are obtained, due to :

(1) The change of solubility with temperature of antimony in the α and β phases. This gives permanent improvement over the annealed condition.

(2) The suppression of the eutectoid decomposition of the β phase, analogous to the hardening of binary cadmium-tin alloys by quenching.¹ Maximum values of 10.5 tons/in.², with 5 per cent. elongation on 2 in., and a Brinell hardness of 45 are obtained in the alloy containing 7 per cent. of cadmium with 5 per cent. of antimony, but these improvements cannot be maintained, and complete self-annealing occurs within 18 months at ordinary temperatures.

Tempering experiments show that permanently stable values can be obtained by short-time heat-treatments. The alloy C3S7 gives maximum values of 6.5 tons/in.², with 25 per cent. elongation on 2 in. and a Brinell hardness of 34.

The authors have shown that there is an approximate linear relation between tensile strength and Brinell hardness for all heat-treated rolled alloys. A different relation exists for alloys rolled and self-annealed. The difference is probably connected with grain-size, since the self-annealed alloys always have much smaller grains than heat-treated specimens.

Further investigations on these alloys are being carried out by the authors. These include tests at elevated temperatures, the study of the effect of different degrees of cold-work, casting temperature, and grain-size, and the effect of small additions of other metals.

ACKNOWLEDGMENTS.

This research has been carried out for the International Tin Research and Development Council, to whom the authors are indebted for financial assistance and for permission to publish the results. They are particularly grateful to Mr. D. J. Macnaughtan, Director of Research to the Council, for his keen interest in the work.

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ADDITIONAL NOTE.

Some further tests on the permanence of the values obtained after different treatments have been completed since the publication of the paper. The results (Table V) show the effect of allowing the alloys to stand at room temperature (18° C.) for 2½-3 years, after the various treatments.

The results for rolled alloys (columns A) indicate that alloys with less than 5 per cent. of antimony had self-annealed completely after the first 6 weeks at room temperature. Alloys with higher antimony content retain work-hardening for much longer periods, but not permanently.

TABLE V.

Composition.		Brinell Hardness.			Composition.		Brinell Hardness.		
Cadmium, Per Cent.	Antimony, Per Cent.	A.	B.	C.	Cadmium, Per Cent.	Antimony, Per Cent.	A.	B.	C.
3	1	12.1	18.2	20.1	5	4	21.4	27.0	28.5
	2	14.4	21.9	22.0		5	22.4	29.8	30.5
	3	17.4	24.0	24.0		7	23.0	29.3	31.5
	4	21.0	25.3	27.0		9	25.2	27.5	31.5
	5	20.5	25.8	30.0	6	1	12.5	19.0	—
4	7	23.0	27.5	34.0		3	17.5	23.8	—
	9	24.8	29.5	30.5		5	22.6	27.5	30.0
	1	12.2	18.3	21.2		7	25.0	30.5	31.0
	2	14.6	21.9	23.2	7	1	12.5	18.6	—
5	3	17.7	24.0	24.4		3	18.5	24.6	—
	4	21.1	27.0	27.3		5	23.4	30.0	30.0
	5	23.0	28.3	29.5		7	24.2	31.5	30.8
	1	12.4	18.5	20.1	8	5	22.0	27.5	—
5	2	14.8	21.7	23.6		7	25.5	29.8	30.0
	3	18.6	24.8	26.0					

A. Rolled : Self-annealed (18° C.) for 3 years.

B. Rolled : Annealed at 170° C. Tested after 2½ years at 18° C.

C. Rolled : Quenched from 190° C. Tested after 2½ years at 18° C.

The results in columns B show that the annealing treatment at 170° C. succeeded in producing equilibrium (permanently stable) values in all alloys except for a few which lie in or near to the eutectoid valley : these have softened slightly.

Columns C give the results for quenched alloys after 2½ years at 18° C. They are substantially the same as those obtained by tempering the quenched alloys for 24 hrs. at 100° C., and confirm that the hardening produced by supersaturation of the alloys with respect to the α phase, is permanent at ordinary temperature.

The best alloy of the series is that containing 3 per cent. of cadmium, with 7 per cent. antimony. This has a permanently stable hardness of 34, which represents an improvement of 50 per cent. over the fully self-annealed condition.

APPENDIX.

TABLE VI.—MECHANICAL PROPERTIES OF CHILL-CAST ANTIMONY-CADMIUM-TIN ALLOYS (ANNEALED AT 170° C. AND FURNACE-COOLED).

Composition.		Brinell Number.	Results of Tensile Test.		
Cadmium, Per Cent.	Antimony, Per Cent.		Ultimate Tensile Strength, Tons/in. ²	Elongation, Per Cent. on 2 in.	Remarks.
1	1	15.9	3.02	46	"Ductile" fracture.
2		19.0	3.99	44	" "
3		19.5	4.75	28	" "
4		21.4	4.83	10	Ductile fracture; broke at blow-hole.
5		22.5	4.90	16	" "
6		24.2	5.12	33	" "
7		27.5	5.08	25	" "
10		20.7	3.96	12.5	" " broke at blow-hole.
20		25.0	4.83	25	Fibrous ductile fracture.
25		25.0	4.98	53	" " "
28		24.6	5.16	43	" " "
33		25.0	5.00	35	" " "
38		24.0	4.96	52	" " "
43		24.2	4.91	53	" " "
33	0.5	22.2	4.82	33	" " "
5	1.5	24.6	4.32	23	Ductile fracture.
1	2	17.3	2.90	35	" "
2		23.1	4.44	37	" "
3		22.9	5.02	19	" "
4		24.1	5.42	18	" "
5		25.6	5.38	28	" "
6		23.4	4.21	18	" "
12		22.1	4.47	32	" "
20		27.1	5.67	22	" "
1	3	17.9	3.30	44	" "
2		23.7	4.56	42	" "
3		25.0	5.45	16	" "
4		27.0	5.17	27	" "
5		27.6	5.41	10	" "
6		28.2	5.56	34	" "
7		30.0	5.77	34	" "
8		27.1	5.03	23	" "
10		24.3	3.09	10	Fibrous. B.O.P.
14		25.4	4.12	8	" "
16		29.0	5.03	15	Fibrous ductile.
20		28.5	5.89	22	" "
25		28.5	5.65	29	" "
28		28.6	5.72	48	" "
33		27.5	5.69	23	" "
38		27.3	5.52	45	" "
43		26.5	5.57	40	" "
1	4	18.7	3.25	50	" "
2		24.5	4.38	38	" "
3		28.3	5.48	24	" "
4		29.3	6.05	16	" "
5		27.2	5.91	12	" "
16		28.6	6.10	7	" "
1	5	21.0	3.50	58	Fine "brittle" fracture. Fractures of this series change gradually from very ductile fractures, i.e. with great reduction of area to fine-grained brittle fractures, i.e. with little local reduction of area.
2		24.7	4.67	35	
3		30.4	6.15	22	
4		27.3	6.23	22	
5		28.5	6.10	16 *	
6		33.0	6.62	25	
7		32.5	6.55	24	
8		33.5	6.35	10	
10		28.0	4.98	8	* Fractured at blowhole.

TABLE VI (*contd.*).—MECHANICAL PROPERTIES OF CHILL-CAST ANTIMONY-CADMIUM-TIN ALLOYS (ANNEALED AT 170° C. AND FURNACE-COOLED).

Composition.		Brinell Number.	Results of Tensile Test.		
Cadmium. Per Cent.	Antimony. Per Cent.		Ultimate Tensile Strength. Tons/in. ²	Elongation, Per Cent. on 2 in.	Remarks.
12		27.5	5.00	6	Fine fibrous fracture.
14		27.0	4.83	5	" " "
16		29.3	5.46	6	Fine brittle fracture.
20		29.0	5.42	15	" " "
28		29.1	4.78	1	" " " at blow-hole.
33		29.0	4.76	4	Fine brittle fracture.
43		27.1	—	—	
1	7	23.7	4.31	52	Ductile fracture.
3		31.8	6.04	16	Fine fibrous fracture.
5		33.3	7.04	15	" " "
6		36.2	7.13	13	" " "
7		35.5	6.89	11	" " "
8		36.2	6.6	10	" " "
10		31.0	5.82	4	Fine brittle fracture.
12		28.0	5.32	2	Coarsely crystalline brittle fracture.
14		31.0	5.74	3	" " " "
16		29.3	5.49	4	" " " "
20		30.3	3.94	3	" " " "
25		31.3	—	—	
38		29.3	3.48	0	" " " "
1	9	25.0	5.34	36	Ductile fracture.
3		31.0	6.01	18	Fibrous ductile fracture.
5		34.0	7.00	6	Brittle fracture of extremely fine texture.
6		36.5	7.16	8	" " " "
7		38.0	7.32	10	" " " "
8		37.0	6.66	6	Fine brittle fracture.
10		33.5	6.05	3	Fine brittle fracture; blow-hole.
25		31.5	3.48	0	Very coarsely crystalline fracture.
33		34.0	3.30	1	" " " "
38		31.8	3.28	1	" " " "
1	10	29.3	5.95	18	Fibrous ductile fracture.
2		34.5	6.87	13	" " " "
3		33.5	6.49	5	" " " "
5		32.8	6.90	3	Very fine brittle fracture.
7		34.5	6.20	3	" " " "
10		33.3	6.10	2	" " " "
12		32.2	6.20	3	" " " "
14		30.8	6.20	3	" " " "
16		30.8	2.54	1	B.O.P.
20		31.3	1.16	1	Blow-holes.
3	12	33.5	5.90	3	Fine brittle fracture.
5		32.8	6.01	3	" " "
7		30.5	6.95	2	" " "
10		31.5	6.17	2	" " "
12		32.0	6.07	2	" " "
14		34.2	3.00	0	Very coarse fracture; blow-holes.
25		34.5	1.75	1	Very coarse crystalline fracture.
1	14	31.8	5.8	4	Very fine brittle fracture.
2		31.8	6.10	5	" " " "
3		31.5	6.43	4	" " " "
5		33.5	6.25	2	" " " "
7		34.5	4.70	3	Rather coarsely crystalline fracture.
10		35.3	4.80	2	" " " "
12		34.0	4.35	1	Very coarsely crystalline fracture.
20		33.8	1.8	0	Very coarse crystals; blow-holes.
33		36.5	1.73	1	Very coarsely crystalline.

DISCUSSION.

(Condensed.)

DR. R. GENDERS,* M.B.E. (Member of Council): I have no criticisms of detail to offer on this work, but I should be glad to know of any applications of the relatively high-strength heat-treated alloys which are described in the paper; whether, for instance, we have now in the tin-rich alloys a bearing material or a workable alloy for pressing, &c., of higher strength than the tin alloys which we have used up to the present time.

MR. J. CARTLAND,† M.C., M.Sc. (Member): In his Autumn Lecture, Mr. Pye said that, as regards aircraft, all the metals which we produce are "top weight" at the moment; the development of the internal combustion engine is limited by what metallurgists can provide for it. That is particularly true in the case of bearings. Manufacturers have had to resort to alloys of copper and lead, which have certain difficulties in their application; therefore any improvement which can be made in normal bearing metals is of the utmost importance. This paper initiates a systematic study of how that can be done.

Already bearings have been improved by the addition of cadmium to the ternary alloys of tin, antimony, and copper. So far, only approximately 1 per cent. of cadmium has been added to such bearing alloys in practice, because there is another difficulty—that of the bonding to the shell. Have the authors carried out any experiments on the bonding of the alloys containing higher cadmium to steel shells.

DR. PELL-WALPOLE (*in reply*): As regards possible practical applications of these alloys, we scarcely reached that stage, since this was more in the nature of a pioneer investigation to ascertain which compositions might prove most useful. I believe that some further research is being undertaken regarding the possible use of the strongest of these alloys, as such, or with minor modifications, for tin-rich bearing alloys, but we have no results at the moment.

We have not carried out any tests on the effect of cadmium on the bonding properties of these alloys. It is possible that if they were used in a heat-treated state, such as is necessary to obtain their best properties, the cadmium might not be such a disadvantage in that respect as when the alloys are used in the ordinary cast state, since in the latter case it is possible that there are traces of a low melting point eutectic present which might interfere with bonding.

CORRESPONDENCE.

MR. H. H. A. GREER,‡ J.P. (Member): This is an important paper for engineers, because the usual custom at present is for bearings to be of gun-metal lined with white-metal. In Diesel engines we use steel bearings and the white-metal run into it, so it is becoming very important to engineers that something harder and something more durable should be made than the tin-antimony-copper alloy which has been used hitherto. I suggest that the Admiralty, for instance, should confer with the authors as to whether the use of cadmium in these white-metals will or will not be beneficial, so that if it is beneficial, the specification can be changed from its present form to that which the authors suggest.

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

‡ Glasgow.

Dr. HUGH O'NEILL* (Member): The authors will have noticed, in comparing Figs. 1 and 2, that when the alloys were annealed for 1 week at 170° C., the tenacity contours in the alloys of high cadmium content had their crest in a very different position from the crest of the Brinell hardness contours. For example, in alloys containing more than 28 per cent. cadmium, the maximum hardness value of 36 occurred at the 14 per cent. parallel of antimony, whilst the maximum tenacity crest of 5.5 tons/in.² occurred at the 3 per cent. parallel of antimony. This difference may be due to the possibility that relationships between Brinell hardness and ultimate stress do not obtain throughout the whole range of the compositions, or simply to premature fracture of the tensile test-pieces. The last is probable, and compression tests would therefore be interesting.

The conditions which were chosen for making the hardness tests deserve comment. The authors used a Vickers machine and went to the trouble of replacing the diamond pyramid by a 2 mm. ball working under a load of 10 kg. If they felt that there were good reasons for using the Brinell ball test it was to be recorded that they had not chosen standard loading conditions, values of $L/D^2 = 1$ or 5 being usual for alloys of this kind. They employed a loading ratio of $\frac{L}{D^2} = 2.5$, which was not a standard, and consequently the relationships between tenacity and Brinell number which they had elaborated for rolled alloys could not necessarily be applied to Brinell numbers determined according to British Standard loadings. I wonder why the authors departed from using the diamond pyramid test, for it gives truly comparable hardness results on a scale which is likely to become a basis for most hardness testing. Correlations between tensile and pyramid values would, therefore, have been very welcome. That the pyramid test can be employed on white metals is shown by the values obtained on alloys of the compositions given in Table A. For comparative purposes Brinell ball values at the authors' and at a standard loading ratio were also obtained. It will be observed from Table A that

TABLE A.

Specimen.	Composition.					Pyramid Hard- ness. H _D /10/ 15.	Brinell Hardness.			
	Cu.	Sn.	Pb.	Sb.	Cd.		L/D ² = 2.5. 2/10/ 15.	L/D ² = 5.		L/D ² = 1. 10/100/ 15.
								2/20/ 15.	5/125/ 15.	
Diesel bearing after service	—	—	0.13	—	1.08	30.0	28.8	29.5	31.8	30.6
No. A Babbitt	5.4	84.3	0.3	10.0	—	31.4	31.2	30.8	31.8	30.0
No. A + Cd	5.4	83.2	0.3	9.9	1.0	34.5	34.7	36.2	36.2	33.5
No. B	2.6	58.0	29.9	9.5	—	21.3	20.9	19.7	20.4	19.0
No. B + Cd	2.6	57.0	29.8	9.5	1.1	24.0	23.4	22.8	24.8	23.5

the results on the specimens which were available showed considerable variations, due quite possibly to the heterogeneous nature of the alloys. In view of these variations, it is suggested that the loading ratio used by the authors is sufficiently near to a standard value to make their Brinell-tensile relationships of general application.

The AUTHORS (*in reply*): We are glad that Mr. Greer considers that this paper is important from the engineer's point of view, since the object of the

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research was to develop stronger alloys of tin than those available at present, and if possible to produce a stronger substitute for the antimony-copper-tin alloys which are used for lining bearings. There are, however, some practical limitations to the amount of cadmium which can be added to a bearing metal, as was pointed out by Mr. Cartland in the oral discussion on the paper.

We are pleased to have Dr. O'Neill's communication on the hardness-strength relations and the conditions of hardness-testing for these alloys. It is stated in the discussion of results, that the relation between Brinell hardness and tensile strength breaks down completely in the case of brittle alloys which contain primary ϵ phase. It is probable that compression tests would give more interesting results for these brittle alloys, as Dr. O'Neill suggests.

We agree with Dr. O'Neill that generally the pyramid is more suitable than the ball for indentation hardness-testing, but with these tin-rich alloys, very coarse-grained specimens are obtained after certain heat-treatments, and it was found that in such cases the pyramid gave erratic results due to smallness of the indentation relative to the size of the individual grains. The impression obtained with the 2-mm. ball is much larger, and gave more consistent results with these alloys. In the case of the harder alloys of this system which have much finer grain-size the pyramid is quite satisfactory but it was found experimentally that the difference between the results when using the diamond and the ball was no greater than the variations obtained in a number of tests with either indenter on the same specimen. The same conclusion was arrived at with variation of P/D^2 ratio, hence it seemed that the use of the 2-mm. ball with a load of 10 kgm. would be suitable for the whole series of alloys tested. This assumption is confirmed by Dr. O'Neill's own figures for similar alloys given in Table A.

THE METHODS OF TESTING ZINC COATINGS.*

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SYNOPSIS.

The measurement of the protective value of zinc coatings on iron and steel, other than by accelerated corrosion tests, is carried out by examination of certain properties of the coating, namely, average weight, uniformity, structure, and porosity. Under these four headings, the various methods which are in use or which have been proposed for carrying out this type of determination are described, together with their respective advantages, limitations, and in certain cases suggested modifications.

Methods for determining average weight mostly depend on direct weighing of the sample before and after the coating has been removed. Other methods make use of the heat developed or the gas evolved during the dissolution of the coating in acid. In the recently developed electrolytic test (Britton's test) the time taken to remove the coating with a known current density is used. Chemical methods of dissolution, depending on a time factor for the determination of thickness, are not applicable to coatings partially or entirely composed of alloy layer, because of variation in the rate of dissolution with composition. They may be suitable, however, for the measurement of uniformity, as is the case with the copper sulphate (Prece) test. The electrolytic test, on the other hand, removes the same weight of coating per unit time irrespective of composition.

Structure is preferably determined by metallographic examination while the weight of the component layers of the coating may be measured by the electrolytic test using potential measurements. Several proposed tests for porosity are described, although this property does not assume for zinc coatings the same importance as for coatings electropositive to iron.

The requirements of zinc coatings to withstand corrosion vary with the conditions of exposure and while for atmospheric attack the life is almost entirely dependent on the total weight of the coating (including alloy layer), for immersed conditions there is evidence that the composition of the coating plays an important part. The particular advantages of certain methods for evaluating the various requirements for both types of conditions are discussed.

I.—INTRODUCTION.

ONE of the most common methods adopted for protecting iron and steel from corrosion is the application of some form of zinc coating. Since

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such coatings vary considerably in quality and composition, the necessity arises for some test or tests which can be applied to the coating to indicate its protective value under the conditions to which it will be subjected in service. A method which is sometimes employed for this purpose is an accelerated laboratory corrosion test by means of which the coatings are exposed to corrosive conditions designed to simulate, in the space of a few weeks, the attack which would be met with in years of normal service. Although certain tests of this type have been shown to be of value, especially as regards atmospheric corrosion, the results obtained are apt to be very misleading, and in general their interpretation is to be approached with some caution, unless the method employed has previously been subjected to very careful correlation with actual service life.

A much more satisfactory type of measurement is the determination of what are believed to be the most important properties of the coating from a corrosion-resistance point of view, namely, weight, thickness, uniformity, structure, composition, and porosity, and the present paper is concerned with a description and review of the various methods which have been proposed for this purpose. Even this type of measurement, however, suffers from the disadvantage that the relative importance of the properties mentioned above depends on the conditions of exposure. For example, for atmospheric conditions it has now been established that, compared with thickness, the composition * is relatively unimportant, but for other types of exposure the most desirable qualities of a coating are still incapable of clear definition, and until such knowledge is forthcoming, indirect tests, while of considerable value, do not provide an entirely satisfactory means for assessing the protective value of a zinc coating.

II.—DETERMINATION OF AVERAGE WEIGHT OF COATING.

A. Loss in Weight Methods.

This type of test serves as an accurate means of determining the average weight of a zinc coating, but gives no indication of its uniformity or composition. It consists in immersing the weighed sample in a suitable reagent which will strip off the whole of the coating without attacking the underlying base. After stripping, the sample is washed, dried, and reweighed, the loss of weight representing the total weight of the coating. The average weight per unit area is obtained by dividing this loss in weight by the area of the sample. In routine testing of sheet it is often

* Coatings produced by hot-galvanizing have a layer of iron-zinc alloy between the zinc and the steel. Throughout this paper, the coating is regarded as including the alloy layer as well as the outer zinc layer.

found convenient to cut samples exactly $2\frac{1}{4}$ in. square, in which case the loss in weight in grm. is numerically equal to the average weight of the coating in oz./ft.². Should it be desired to know the weight of the coating on each side separately, it is necessary of course to protect one side by wax or some similar substance while the reverse side is being stripped.

Methods which have been proposed for determining the average weight of coating by loss in weight measurement are :

(i) *Sulphuric Acid-Arsenious Oxide*.—This reagent, proposed by Bauer,¹ is prepared by adding 20 grm. of concentrated sulphuric acid (sp. gr. 1.84) and 2 grm. of arsenious oxide to 500 c.c. of distilled water, heating until all the arsenious oxide has dissolved and diluting to 1 litre with distilled water. The addition of arsenious oxide inhibits the attack of the underlying steel by reason of the fact that arsenic, separated by the reducing action of the hydrogen evolved, forms a protective film on the iron.

In practical work, however, the solubilities of zinc and zinc-iron alloys in dilute sulphuric acid are so much greater than that of iron that the addition of arsenious oxide may be omitted without seriously affecting the accuracy of the test. Burgess,² so far back as 1905, proposed the use of dilute (3 per cent.) sulphuric acid without inhibitor for determining the weight of zinc coatings, whilst in the standard specifications of the American Society for Testing Materials³ it is considered that uninhibited acid is of sufficient accuracy for ordinary weight of coating determinations, the concentration specified being 40 c.c. of concentrated acid (sp. gr. 1.84) mixed with 960 c.c. of distilled water.

Moreover, when it is intended to determine the amount of iron in the coatings by chemical analysis of the solution left after stripping (Section IV, C), arsenic, if present, must first be removed, a separation not without difficulties and liable to affect the accuracy when determining very small amounts of iron. On the other hand, when dealing with an uneven coating, even allowing for the fact that the solubility of iron is far less than that of the coating, if areas of iron are bare at the thinnest parts of the coating some considerable time before the thickest parts have been stripped, some iron will necessarily go into solution unless the acid is inhibited. Whilst this amount of iron may have little effect on the figure for the weight of coating, the value obtained for the iron content of the coating will not be accurate.

Geyer and Cohn,⁴ in order to prevent attack of the underlying base in uninhibited sulphuric acid (1 : 10), suggest placing the samples to be tested in contact with a zinc slab, so as to give electrolytic protection. As an alternative, they suggest making the sample cathodic, using a carbon or other inert anode, the potential being adjusted so that

when the coating is removed, the pure iron is polarized by a film of hydrogen. These authors also recommend the use of dilute sulphuric acid with the addition of an organic inhibitor, as used for pickling.

For general purposes, the present author recommends the use of a solution containing 100 c.c. of concentrated sulphuric acid (sp. gr. 1.84) and 5 grm. of arsenious oxide per litre. This solution gives very accurate results and has the advantage of being considerably more rapid in its action than the solution originally proposed by Bauer.

(ii) *Hydrochloric Acid-Antimony Chloride*.—This solution, similar in principle to the sulphuric-arsenious acid described in the preceding section, was proposed by Aupperle ⁵ and has been adopted by the American Society for Testing Materials ⁶ as the standard method for determining the average weight of zinc coatings. The solution consists of concentrated hydrochloric acid (sp. gr. 1.19) to 100 c.c. of which is added 5 c.c. of an antimony chloride solution, prepared by dissolving 20 grm. of antimony trioxide or 32 grm. of antimony chloride in a litre of concentrated hydrochloric acid (sp. gr. 1.19). The end-point is easily determined by the cessation, usually quite sudden, of the violent effervescence. In fact, Cushman ⁷ considers that for ordinary testing the addition of antimony chloride is unnecessary, the end-point being reasonably sharp without the presence of an inhibitor. Witt ⁸ also recommends the use of uninhibited acid of a 1 in 1 concentration at a temperature not exceeding 45° C. For accurate work, however, the present author does not recommend the use of uninhibited hydrochloric acid, particularly for coatings which are not uniform.

(iii) *Basic Lead Acetate*.—The following reagent was suggested by Patrick and Walker,⁹ and has been adopted by the American Society for Testing Materials ¹⁰ as an alternative method for determining the weight of zinc coatings: 400 grm. of crystallized lead acetate are dissolved in 1 litre of water and to the solution 4 grm. of finely powdered litharge are added. After thorough agitation the liquid is allowed to settle and the clear portion decanted for use.

The method depends on the fact that lead is electro-positive to zinc; thus zinc displaces lead from a solution of its salts, the lead being precipitated in metallic form and the zinc going into solution. The same principle governs the Preece test (Section III, A), in this case a copper salt being employed which attacks the coating, while metallic copper is deposited. The Preece test, however, cannot be used for determining the weight of coating, since, when the coating has been removed, the copper deposits on the bared iron in an adherent form and thus upsets the weight determination. In the basic lead acetate method, however, lead does not adhere firmly to the iron, provided that care is taken when

washing the sample that a burnishing action does not occur. Nevertheless, it is often a matter of some difficulty to remove all traces of lead, especially from irregularly shaped articles, and the method suffers some disadvantage for this reason.¹¹

(iv) *Other Methods*.—Several other solutions, described below, have been proposed, but none of them appears to be of great practical utility.

Alkali or alkaline earth bisulphates or bisulphites have been proposed by Broemme and Steinau.¹² Meyer¹³ has used boiling sodium peroxide solution. Heise and Clemente¹⁴ carried out an extensive investigation of a large number of stripping solutions. In addition to the standard methods described in the preceding sections (i) to (iii), they found that acetic acid and 25 per cent. phosphoric acid gave accurate results, as also did certain salts of lead, cadmium, copper, cobalt, chromium, and aluminium. Korpiun¹⁵ proposed anodic dissolution of the coating in 10 per cent. potassium cyanide using a current density of 0.5–1.0 amp./dm.². Walker¹⁶ reports that zinc, exclusive of zinc-iron alloy layer, may be removed quantitatively by the action of hot caustic soda solution.

B. *Electrolytic Tests.*

The weight of coating may be determined electrolytically by Britton's method,¹⁷ in which the sample under test is made the anode of an electrolytic cell. By employing a fixed current density, the weight of coating removed from a given area is directly proportional to the time during which the current has been flowing. Since the electro-chemical equivalents of iron and zinc are approximately equal, the weight of coating removed in a given time is independent of the amount of zinc-iron alloy present. The only drawback to the method is that a uniform current density must be applied to all parts of the coating being tested. This condition is easily satisfied for wire and sheet, but for more complicated shapes it might be a matter of some difficulty and would, in any case, necessitate a specially designed cathode.

In carrying out the test on wire, a cylindrical glass jar is used, the cathode being a roll of perforated zinc gauze sprung tightly against the curved sides of the jar. The wire to be tested is fixed vertically in the centre of the jar, which is then filled with a solution having 20 parts of sodium chloride and 10 parts of zinc sulphate in 100 parts of water, so that the wire is immersed to a depth of 4 in. The cell is then connected to a d.c. supply, the sample being made the anode and the current adjusted to give a current density of 1 amp./in.², i.e. a current (in amps.) of 12.5 multiplied by the diameter of the wire in inches. This current removes 0.104 oz./ft.² of coating per minute.

To determine the weight of coating, the current is run for a short

time, after which the wire is removed, immersed in 10 per cent. copper-sulphate for 5 seconds and, if no bright red deposit of copper is formed, the wire is rinsed, replaced in the cell and subjected to a further period of stripping. This process is repeated until failure occurs, as indicated by the appearance of a red deposit when the wire is dipped in copper sulphate. The total time of stripping in minutes multiplied by 0.104 gives the minimum weight of coating in oz./ft.².

In applying the method to sheet, the sample is held in a frame made on a similar principle to a photographic printing frame. This is fitted at one end of a rectangular cell, the cathode, a piece of sheet zinc, being placed at the opposite end. If the test is being used to determine whether or not the thinnest parts of the coating are of specified weight, the current is maintained for the appropriate time, after which the sample is removed and, if no red deposit is obtained with the copper sulphate dip, the coating may be considered as meeting its specification.

A test for wire similar in principle to Britton's test has been designed by Glazunov,¹⁸ using a platinum cathode and a concentrated solution of zinc sulphate as the electrolyte.

Heise and Clemente¹⁴ state that stripping may be satisfactorily accomplished by making the sample the cathode in sulphuric acid or making it the anode in concentrated caustic alkali solutions, such as sodium hydroxide.

C. Hydrogen Evolution Method.

A drawback to the loss-in-weight method for determining the average weight of coating by means of stripping in acid is the fact that this frequently means the mutilation or destruction of the article in order to remove a sample suitable for testing. A method which overcomes this objection was proposed by Cushman,⁷ and consists in measuring the volume of hydrogen evolved from a known area of the coating when stripped in acid. The method is carried out by clamping an inverted cup to the surface under test, this cup being connected with a gas burette and levelling bottle. Hydrochloric acid containing antimony chloride is introduced into the cup and, when the effervescence has ceased, the gas is collected in the burette and measured at atmospheric pressure by suitable manipulation of the levelling bottle. Since 2.72 mg. of zinc liberate 1 c.c. of hydrogen, measured at 20° C. under atmospheric pressure, it is possible, knowing the area of the spot stripped, to calculate the average weight of the coating per unit area. Although the volume of hydrogen evolved depends on the structure and chemical composition of the coating, it has been calculated that the errors arising on this account are relatively small and the results which are obtained are

stated to check very closely with those obtained by the hydrochloric acid-antimony chloride loss-in-weight method.

The stripped spot, after washing and drying, may be either painted or sprayed so that the article does not suffer permanent damage. A further advantage offered by the method is that it can be applied to articles *in situ*. Moreover, when it is necessary to determine the weight of coating on each side of a sheet, this method obviates the necessity, required by loss-in-weight methods, of waxing one side, a lengthy and tedious process when dealing with a large number of samples.

The method has been developed by Goeke¹⁹ and also by Keller and Bohacek,²⁰ whilst a convenient testing apparatus involving this principle has recently been patented.²¹

D. Thermal Method.

This method, due to Strickland,²² also involves stripping the coating in acid, but makes use of the temperature increase resulting from the chemical reaction that takes place. Each degree increase in temperature is assumed to be directly proportional to the weight of coating dissolved, so that by recording the total increase in temperature the total weight of coating on the sample can be calculated.

To carry out the test a measured volume of concentrated hydrochloric acid (usually 200 c.c.) is poured into the testing jar (preferably about 2½ in. in internal diameter with a capacity of about 400 c.c., flared at the top to prevent overflow of the acid). The acid is stirred and the temperature measured by a thermometer (graduated in 0.1° C. and with a range of about 50° C.), after which the sample is immersed in the acid. The temperature is watched during the process of stripping and the maximum temperature is recorded. From a table of factors prepared for the equipment and the volume of acid used, the weight of coating dissolved can then be calculated. For very light coatings, the volume of the acid used is reduced to 100 c.c., in order to obtain an appreciable increase in temperature, but with coatings of 2½ oz./ft.², or heavier, 300 c.c. is necessary. To standardize the equipment, a weighed sample of known area is immersed in the acid and after the temperature increase has been recorded, the loss in weight of the sample is determined by re-weighing. A number of samples are tested in a similar way, and the mean of the determinations used for calculating a conversion factor (*i.e.* for converting increase in temperature to weight of coating).

Strickland has published apparently convincing figures regarding the accuracy of the method, but it would appear in principle to be liable to several errors. In the first place, the assumption is made that increase in temperature is proportional to the weight of coating dissolved, no

account being taken of the composition of the coating. Since, however, the relative heats of reaction of equal weights of zinc and iron are 56-37, it will be seen that alloy coatings will give erroneously low results compared with pure zinc coatings of the same weight. Secondly, the heat evolved depends on the heat capacity of the system. This is a constant regarding the equipment itself and is allowed for in the conversion factor, but a variable is introduced by the size and consequent heat capacity of the article being tested. For example, in the case of a thin coating on a heavy base, the increase in temperature of the small volume of acid which would necessarily have to be used, would differ considerably from that obtained with a similar coating on a thin base.

These objections, however, can no doubt be overcome to some extent by choosing a conversion factor which has been calculated from samples of a similar type to the one being tested.

The advantages of the method are its simplicity and particularly its rapidity, since a complete determination may be carried out in less than 3 minutes.

E. Magnetic Methods.

Magnetic methods, which naturally can only be applied to coatings on iron and steel, have recently made their appearance. Radchenko and Shestakovskii²³ carry out the test by measuring the current necessary to detach a magnetized needle from the article. The force required decreases less rapidly than a linear inverse function of the coating thickness. The greatest sensitivity is stated to occur with coatings from 0.0005 to 0.02 cm. in thickness. A similar method,* developed and recently exhibited by the Post Office Engineering Research Station, London, consists in comparing, by means of a spring balance, the pull of an electro-magnet when applied to a piece of polished iron and when applied to the article under test. The accuracy is stated to be ± 15 per cent., and increases with the thickness of the coating.

F. Chord Method.

This method, due to Mesle,²⁴ and developed by Blum and Brenner,²⁵ depends on just cutting through the coating, a grinding wheel of known radius being used for a flat surface and a fine file for a curved surface. The thickness of the coating T is given by the expression $\frac{C^2}{8R}$, where C is the width of the cut and R is the radius of the wheel or the curved surface. The results are stated to be accurate within about 10 per cent.

* Catalogue of the Physical Society's 27th Annual Exhibition of Scientific Instruments and Apparatus, 1937, 176-177.

III.—DETERMINATION OF UNIFORMITY.

In assessing the value of a metallic coating it is desirable to know, besides the average weight, something of the way in which it is distributed, since the protection afforded by the coating will depend to a large extent on its minimum thickness. With certain of the methods described above for determining the average weight of the coating, it is possible to obtain a very rough idea of the degree of uniformity by watching carefully the progress of the stripping operation, but it would be quite impossible by this means to form any quantitative estimation of the minimum thickness. For this purpose a method is required which will, first, strip the coating at a uniform rate and, secondly, reveal the base metal directly it is exposed. The methods which have been proposed for carrying out this type of determination are described below.

A. *Copper Sulphate (Preece) Test.*

This test was described by Pettenkofer ²⁶ in 1857, but was brought into general use about 1880 by Sir W. H. Preece, by whose name the test is now commonly known. The reagent used is a neutral solution of copper sulphate, having a sp. gr. of 1.170 at 60° F. and containing approximately 33 gm. of crystalline copper sulphate in 100 c.c. of distilled water. The solution is neutralized by agitation with a small amount of copper hydroxide and is then filtered or allowed to settle before use. In carrying out the test, the article is immersed in the solution, maintained at 60° F. ($\pm 1^\circ$) and is subjected to successive 1-minute dips. After each dip the sample is rinsed immediately in running water, wiped dry, and examined. The test is continued until a bright red adherent deposit of copper is obtained, indicating that iron has been exposed.

The Preece test has been adopted as a specification,²⁷ and coatings to comply with it are required to withstand a stated number of 1-minute dips, often referred to as the Preece Test Number. Although the test affords an excellent indication of uniformity, its adoption as a specification is open to severe criticism, since the assumption is made that all zinc coatings are attacked to the same extent by a 1-minute immersion in the copper sulphate solution. That this is an erroneous assumption has been proved by numerous authors,^{9, 28-31} who have shown that the rate of solution in copper sulphate decreases with increase in the iron content of the coating. Thus, coatings composed mainly of alloy layer (e.g. galvanized and sherardized) withstand more dips than relatively pure coatings (e.g. electrodeposited and sprayed) of the same thickness.

Groesbeck and Walkup ³¹ have suggested that this objection might be overcome by altering the time of the standard dip for each type of

coating, thus making the number of dips comparable. For example, if the period of immersion for electrodeposited coatings were retained at 60 seconds, then, in order that all types of coatings of the same thickness should withstand the same number of dips, the periods of immersion should be, approximately, 55 seconds for sprayed coatings, 80 seconds for hot-dipped coatings, and 120 seconds for galvanized coatings. Even this arrangement is not completely satisfactory, however, since such a rigid classification takes no account of variations in composition which exist between coatings of the same type. This is particularly the case with hot-dipped coatings which show a wide variation in the relative thicknesses of the constituent layers.

Another serious fault of the Preece test is the production of premature end-points, i.e. the appearance of an adherent red copper deposit before the iron is actually bared. This difficulty is lessened, according to Britton,¹⁷ by a preliminary dip of 15 seconds in 2 per cent. sulphuric acid, followed by rinsing in water. Care should also be taken that the article remains stationary during testing, otherwise the rate of stripping will be accelerated and low results obtained.

B. Hydrogen Peroxide-Acetic Acid Test.

Another test on similar lines to the Preece test, but which has only been suggested in connection with electro-deposited coatings, is due to Wernlund.³² The reagent for this test is a solution composed of 140 c.c. of 3 per cent. hydrogen peroxide and 20 gm. (19.1 c.c.) of glacial acetic acid made up to 1 litre with distilled water. In carrying out the test, the sample is immersed in the solution heated to 95° C. and the time taken for the first appearance of iron rust. The actual weight of this minimum thickness is read off from a graph showing the relationship between weight of coating and time of test. The method, like the Preece test, assumes uniform removal of the coating and the results, even with electrodeposited coatings, are affected by the method of application of the coatings. Thus, coatings prepared from cyanide baths dissolve at a slower rate than those deposited from sulphate baths. Consequently, although the test may have some value as a rapid plating shop test, it would not appear to be suitable for general application.

C. Sulphuric Acid Test.

Diakonova³³ has proposed a specification test for zinc coatings on wire in which the sample under test is immersed for a certain time in sulphuric acid containing arsenious oxide. The sample is then removed, washed, and placed in a concentrated solution of ammonium sulphide, the appearance of black spots being taken as evidence of insufficient

coating. Alternatively, after the acid treatment the wire is placed for a short time in concentrated acetic acid and after removal, if no colour is obtained on adding potassium ferricyanide, the wire is considered as having an adequate coating.

D. Dropping Test.

The dropping method for determining the local thickness of electrodeposited coatings, which is due to Clarke,³⁴ consists in allowing a specified solution to drop at a uniform rate on the coating under test, the thickness being obtained from the number of drops required to perforate the coating. Clarke used the method for determining the thickness of cadmium coatings by means of an aqueous iodine solution, whilst Hull and Strausser³⁵ have shown that it may be successfully applied to zinc coatings. The solution, which consists of 100 gm. of iodine and 200 gm. of potassium iodide per litre, is allowed to drop at a uniform rate of 1 drop per second on to the coating under test, held at an angle of 45° ; 22 drops are required to remove 0.0001 in. of zinc. Thus the number of drops required for penetration of the coating, divided by 220, gives the thickness of coating at the spot tested in thousandths of an inch. The end-point is readily determined by the contrast between the stained surface of the zinc and the bright exposed steel. Hull and Strausser³⁵ have developed a similar test, using a solution containing 100 gm. of ammonium nitrate and 55 c.c. of concentrated nitric acid per litre. With 80 to 120 drops per minute at room temperature the rate of stripping is 0.00001 in. per second. Thus the time for penetration of the coating (in seconds) divided by 100 gives the thickness of coating at the spot tested in thousandths of an inch.

Normally the dropping test can only be applied to electrodeposited coatings, since the rate of solution of zinc-iron alloy will differ from that of pure zinc.

E. Jet Test.

A similar type of test to the dropping test, described above, has recently been invented by Clarke³⁶ for testing electrodeposited zinc coatings, but in this case the corroding liquid impinges on the article to be tested in a steady stream instead of a succession of drops. The solution employed consists of 70 gm. ammonium nitrate and 8.1 c.c. concentrated hydrochloric acid (sp. gr. 1.16) per litre. The rate of flow is regulated to about 20 c.c./minute and at room temperature this strips approximately 0.00002 in. per second.

F. Electrolytic Test.

All the methods described above for testing uniformity, suffer from the disadvantage that the rate of chemical dissolution is dependent on

the composition of the coating. While it is possible to standardize these methods for electrodeposited coatings, the same rates of solution would not apply to coatings composed partly or wholly of zinc-iron alloy, such as hot-dipped galvanized and sherardized; nor is it easy to introduce modifications of the tests for these coatings, since the composition of coatings in each class, particularly those produced by the hot-dipping process, often shows a wide variation. The only method which will strip all zinc coatings at a uniform rate irrespective of their composition is the electrolytic test,¹⁷ as described previously (Section II, B). With this method, it is possible to determine not only the uniformity, but the exact value of the maximum and minimum weight of a coating. Unfortunately, it is difficult to apply the method to articles which are not uniform in shape but, where applicable, the author strongly recommends the method.

IV.—DETERMINATION OF STRUCTURE AND COMPOSITION.

A. Electrolytic Test.

Britton's test¹⁷ (Section II, B) is also capable of measuring the actual weight of the alloy and outer zinc layers of coatings on wire and sheet. The test is carried out in the ordinary way, except that a voltmeter is connected between the cathode and the sample (which is the anode), readings of the voltmeter being taken every half-minute during the course of the stripping. Changes in voltage are associated with changes in composition of the coating. Thus, in the case of a hot-dipped coating, the potential difference remains constant so long as the outer zinc layer of the coating remains intact. When, however, sufficient zinc has been removed to expose some of the zinc-iron alloy, the potential begins to increase and continues to do so until all the outer zinc layer has been removed. An arrest then occurs until sufficient alloy layer has been removed for the iron base to be exposed, when the potential begins to increase again, finally reaching a steady value when all the coating has been stripped. By plotting a potential-time curve it is thus possible, knowing the exact weight of coating that is removed per unit time, to determine the weight and, if necessary, the thickness of the component layers of the coating.

B. Metallographic Examination.

The most direct method for investigating the structure of zinc coatings is by means of microexamination. The preparation of specimens for this work, however, needs a considerable amount of care if satisfactory results are to be obtained. One of the greatest difficulties

is due to the difference in hardness between the iron or steel base and the coating, so that there is a tendency during the polishing operation to wear away the softer zinc. To obviate this so far as possible, it is essential to embed the samples in some material before polishing. For this purpose, Finkeldey³⁷ has suggested clamping the specimens between thin sheets of soft zinc or in the case of irregularly shaped specimens he advises placing them in a small mould and pouring in molten zinc at a temperature just above the melting point. Low melting point alloys have also been suggested, but these have the disadvantage of being easily smeared over the sample. Winter³⁸ advises copper plating the specimen in a copper potassium cyanide bath, using a low current density, and then embedding in Rose's metal. Hajda and Popofe³⁹ have suggested fixing the specimens in ebonite, whilst the author has found Bakelite mouldings very satisfactory.

To prepare micro-specimens of sheet samples the author recommends clamping one or more specimens, cut to approximately 2 cm. square, between pieces of steel about 2 mm. thick, by a nut and bolt passing through the centres. One side is then filed flat, taken down on emery paper to "0000" stage, polished with alumina on the wheel, and finally very lightly polished with magnesia on parchment. Too much attention should not be devoted to removing all the scratches or there will be a tendency to wear away the softer portions of the specimens.

Alternative polishing technique has been published by Finkeldey.³⁷

After polishing, the structure is more clearly defined by the application of a suitable etching treatment; several have been suggested for this purpose. Finkeldey³⁷ has recommended an 8 seconds' dip in a solution containing 20 gm. of pure chromic acid and 1.5 gm. sodium sulphate in 100 c.c. of water. Hajda and Popofe³⁹ suggest the prolonged use of Kourbatoff's reagent; this is composed of 1 part of acetic anhydride containing 4 per cent. nitric acid and 10 parts of a mixture of equal volumes of methyl, ethyl, and isoamyl alcohols. Walker⁴⁰ used 0.5 per cent. nitric acid in 95 per cent. alcohol, whilst Rawdon, Grossmann, and Finn⁴¹ used a solution of 1 per cent. iodine in alcohol. Winter³⁸ has proposed a polish etch consisting of treatment for 5 minutes on parchment with jewellers' rouge and a 2 per cent. aqueous solution of ammonium nitrate.

The author has found that a dip for 5 seconds in a solution containing 50 gm. of chromic acid and 4 gm. of sodium sulphate per litre is a very satisfactory etching treatment. The use of 1 per cent. iodine in alcohol is apt to give trouble from staining.

It is possible, by preparing specimens in this way, to measure the total thickness of coatings and, in the case of hot-dipped coatings, the

thickness of the component layers. A magnification of 250 diameters is very suitable for this purpose.

C. Chemical Determination of Iron.

A good indication of the structure of coatings may be obtained by determining the iron content after stripping in acid, sulphuric acid being the most suitable for this purpose (Section II, A (i)).

In the procedure advised by the American Society for Testing Materials⁴² the sample, after stripping, is scrubbed and washed with a jet of water from a wash bottle, the washings being allowed to run into the container. 15 c.c. of 5 per cent. mercuric chloride are then added and the solution titrated with 0.1 *N* standardized potassium permanganate solution. The solution should not be allowed to stand more than 5 minutes before titration, otherwise incorrect results will be obtained from excessive oxidation.

It should be noted, however, that if the determination of iron is contemplated at the time of stripping, it is advisable to avoid the use of arsenious oxide as an inhibitor, but if, for any reason, this has been used, arsenic must be separated before the determination of iron can be proceeded with. This may be effected by diluting the solution and precipitating with hydrogen sulphide. The filtrate, after boiling, can then be examined for iron, as described above. An alternative method, which the author recommends, is to precipitate the iron with ammonium chloride and ammonium hydroxide. The precipitate is then redissolved in hydrochloric acid, reduced with stannous chloride and titrated with potassium dichromate. If the iron precipitate is very small, however, it should be redissolved, the solution made up to a standard volume and aliquot portions tested colorimetrically.*

For accurate work, in order to prevent the dissolution of iron from the base, by other means than arsenious oxide inhibitor, Cohn⁴³ recommends the methods published by Geyer and Cohn,⁴ as described in Section II, A (i). Where an organic inhibitor has been used, this must be removed before the iron determination can be carried out. To do this the solution is oxidized by evaporation to dryness, nitric and perchloric acids then being added. After dilution and reduction, the iron is then titrated with standard potassium permanganate solution.

D. Hydrogen Evolution Method.

Various authors,^{44, 45} have proposed to determine the structure of zinc coatings by measuring the rate of evolution of hydrogen at intervals

* The author is indebted to Mr. B. W. Drinkwater, B.Sc., F.I.C., for details of the chemical analysis described in the foregoing paragraph.

during the course of the stripping process. Vondracek⁴⁶ in particular has determined the structure of coatings on wire by this method, and claims that solution curves can be established that determine the structure of the coating with an accuracy frequently exceeding that of micrographic examination. The rate of evolution depends largely on the iron content of the coating, the higher the iron content the greater being the rate of evolution. Presumably, care should be taken that the heat of reaction does not cause the temperature of the acid to increase, otherwise an increased rate of reaction will occur, having no connection with change in composition.

V.—DETERMINATION OF POROSITY.

A common method for determining the porosity of certain coatings is the ferricyanide test, first introduced by Walker⁴⁷ for testing tin coatings. In its original form it consisted of applying a warm reagent containing potassium ferricyanide (1 part), sulphuric acid (1 part), and water (450 parts), with sufficient gelatin (50 parts) to enable it to set rapidly to a jelly when applied to the coating. Pores in the coating produce blue spots of ferrous ferricyanide by the interaction of the reagent with the bare iron. This type of test is, however, normally only applicable to those coatings which, like tin, are electro-positive to iron. Zinc coatings, being electro-negative to iron, cannot be tested in this way, since any pores or bare spots in the coating are protected by the adjacent zinc and do not react with the reagent to give a blue colour. Various modifications of the test have been proposed, however, to render it applicable to zinc coatings. The chief of these consists in making the whole sample to be tested anodic, by the application of an external e.m.f. Under these conditions, the protection afforded by the zinc is overcome, and ferrous ions are produced at the bare spots.

Koehler and Burford's⁴⁸ method for carrying out the test is to cover the surface with a ferricyanide-gelatin or ferricyanide-agar-agar type of reagent, connecting the positive pole of a battery to the sample under test and the negative pole to a metal plate placed on the surface of the reagent. The reagent may be applied to the sample either direct or in the form of sensitized paper. For direct tests, a solution consisting of 60 gm. sodium chloride, 6 gm. potassium ferricyanide, 30 gm. of agar-agar, and 300 c.c. alcohol made up to 1 litre with water was found most suitable, but for tests with sensitized paper, gelatin-base solutions were found to give the best results.

Garre⁴⁹ uses a liquid cell with a 4-v. accumulator and a platinum cathode. The electrolyte consists of 20 gm. potassium ferrocyanide and 1 gm. magnesium sulphate in 500 c.c. of water. It is claimed that

by this means pores may be detected which would take 5 days to distinguish by a salt-spray test. It is also claimed that no blue colour is produced by iron and iron-zinc inclusions in the coating. Garre⁴⁹ states that the ferricyanide test may be satisfactorily modified purely by chemical means by the addition of oxalic acid and hydrogen peroxide. In this case, iron inclusions as well as pores give rise to a blue coloration, but there is said to be no difficulty in differentiating between them.

Another method for testing porosity, due to Garre,⁴⁹ is to immerse the sample in a dilute ($\frac{1}{250}$ to $\frac{1}{1000}$ *N*) solution of potassium permanganate. The permanganate is reduced where the iron base is bare, giving a black coloration of manganese dioxide.

Walker¹⁶ proposed the use of a boiling solution of sodium hydroxide for revealing pinholes, the location of discontinuities being shown by a stream of tiny bubbles of hydrogen. The results obtained, however, are open to criticism because of the rapid attack of the coating which takes place.

CONCLUSIONS.

In view of the large number of tests which have been described, this concluding section has been written with the object of indicating some of the more practical methods and their particular advantages.

The choice of methods which will most satisfactorily provide the necessary information for assessing the protective value of zinc coatings depends on several factors. In the first place it is important to know the conditions of service under which the coating in question will be exposed. If atmospheric exposure is intended, the decision is considerably simplified, since recent work⁵⁰⁻⁵² has shown that under these conditions the life of a zinc coating is almost entirely dependent on its total weight per unit area (*i.e.* including any alloy layer). The composition of the coating has little significance apart from the fact that for æsthetic reasons, alloy coatings possess a slight disadvantage in showing rust or discoloration before the coating has actually failed. The distribution of the coating is of course of considerable importance, for although discontinuities, either in the original coating or as a result of corrosion at thin parts, are to some extent protected electrochemically by adjacent zinc, this protection only extends for a limited distance. Thus, in most cases of atmospheric exposure, pores in the coating are not so detrimental as relatively large areas of thin deposit. Marine atmospheres appear to be an exception, owing to the formation of a film of basic zinc chloride which reduces the rate of corrosion of zinc but at the same time suppresses its electrochemical protective action over iron. Generally speaking, however, it may be stated that the protective value of a zinc coating as regards atmospheric exposure, other things being equal,

is proportional to the minimum weight of the coating, but approximating to the average weight as areas of thin deposit or uncoated spots decrease in size.

The most satisfactory method yet published for measuring the properties of weight and distribution, provided that the material is in the form of sheet or wire, is Britton's electrolytic test (Section II, B), since this method possesses the particular advantages of providing a quantitative evaluation of the distribution of the coating, as apart from the average weight figures given by chemical stripping methods.

For coatings (other than electrodeposited) on irregularly shaped articles, which cannot be tested by the electrolytic method because of the difficulty of arranging a suitable cathode, no single alternative method is entirely satisfactory. In such cases, determination of the average weight of coating by stripping in acid, as described in Section II, A (i), is to be recommended, and if several determinations are carried out on fairly small samples, some indication of uniformity will also be obtained. In the case of large structural shapes or other materials which cannot be sampled without complete mutilation, the hydrogen evolution method (Section II, C), which can be applied without cutting the material, would appear to be the most satisfactory alternative, and with the recently developed apparatus ²¹ the method seems capable of being employed as a works test. Information regarding distribution of a purely qualitative nature may be obtained by the application of the Preece test (Section II, A) but micro-examination (Section IV, B) should be resorted to if an accurate determination is required.

Owing to their relative uniformity of structure and composition, the measurement of weight and distribution of electrodeposited coatings, even on articles of irregular shape, presents much less difficulty. Clarke's jet test (Section III, E) and Hull and Strausser's dropping test (Section III, D) each give accurate determinations of both these properties.

In specifying the weight of coating necessary to provide adequate protection against atmospheric attack, consideration must be given to the type of atmosphere, since a coating which may be satisfactory under certain conditions may be very short lived in others. Exposure to clean rural and marine atmospheres gives a much longer life than the polluted air of industrial neighbourhoods. Thus, in the field tests being carried out by the American Society for Testing Materials ⁵³ galvanized coatings of 1.25 oz./ft.², which showed rust in 30 months in an industrial atmosphere, lasted 84 months in a marine atmosphere and showed no rust after 96 months in a relatively dry rural atmosphere. Similarly, in tests being carried out by Britton and the present author the average time for the appearance of rust on coatings exposed to an industrial

atmosphere has been 31 months per oz. per ft.² and in a marine atmosphere 84 months per oz. per ft.².

For exposure to immersed conditions, the exact requirements of a coating are not at present completely known, but it is thought⁵⁴ that the outer zinc layer of the coating has a greater protective value than the alloy layers. It is also possible that under these conditions discontinuities in the coating are more serious than in atmospheric exposure. Hence, it would appear that the requirements are a thick coating with as little alloy layer as possible and freedom from pores and discontinuities.

To test for thickness and composition, the electrolytic method, employing the potential measurements as described in Section IV, A, is recommended where possible. In other cases, average weight determinations by chemical stripping is advised, supplemented by microexamination and/or chemical analysis of iron in the stripping solutions (Section IV, C). Discontinuities and general distribution of the coating may be conveniently investigated by means of the Preece Test.

In the matter of routine testing of zinc coatings, the author is fully aware that the claims made for the Preece test regarding simplicity and rapidity are undeniable, but in view of the serious shortcomings of the test it should be subjected to a correction factor for the type of coating being tested and, in addition, checked periodically by some method of actual weight determination. In this capacity, the electrolytic test is already being used in this country.

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DISCUSSION.

(Condensed.)

DR. W. H. J. VERNON,* (Member): The policy of the Institute in sponsoring general surveys of particular subjects receives ample justification in the present paper, which seems to me to constitute a model of what such a paper should be. I shall not attempt to go through the individual methods that the author has mentioned, although personally I should very greatly welcome

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statements of experience from users of these methods, particularly under industrial conditions. After reading the paper I am left with the impression that there is room for still more work in the correlation of the properties studied by these methods with the service behaviour of the materials. Much depends on environment, and the results of tests which indicate satisfactory performance under one set of conditions may be misleading under others. I would endorse the author's statement that, under conditions of open-air exposure, thickness of coating transcends in importance factors such as porosity and composition, but at the same time I would place added emphasis on the importance of ensuring a coating of a certain minimum thickness.* The building-up of basic protective films on zinc surfaces, for which there seems to be evidence under certain conditions of exposure, takes appreciable time. In the early stages soluble corrosion products greatly predominate—insoluble products tend to appear at a later stage. Hence, the coating should be at least sufficiently thick to survive this early period. The importance of this factor is frequently overlooked, and, in my view, too much emphasis is usually placed on "sacrificial protection" afforded by the coating. After all, a coating is of no use when it has been sacrificed, and a longer life of the coating should surely be the objective.

A word of caution may perhaps be added as to the importance, in comparing the behaviour of coatings, of ensuring comparable conditions both in respect to the underlying metal and also the shape of the test-piece or article under test, both of which factors may seriously affect the performance of the coating. Naturally, the author will not claim to have exhausted all possible methods of testing, and here it may be observed that changing conditions may call for other tests. In illustration of this—and it is merely an illustration—an incident came to my knowledge recently which is of interest. A well-known numismatist, Mr. Garside, of Teddington, showed me some sherardized iron coins issued in Austria during the War; this is an instance of the unexpected applications to which these coatings can be put. I mention this merely as indicative of the need for bearing in mind possible changes, and the need for having a variety of methods of testing available for various conditions. For all ordinary practical purposes the methods enumerated in the present paper are amply sufficient.

Mr. T. H. TURNER,† M.Sc. (Member): This paper must be of practical interest to many users. The user of a wire is probably generally satisfied with the Preece test, and I doubt whether Britton's or the other tests help him very much; I think that the Preece test gives the information which he requires. He often also takes the weight of zinc, but I am inclined to think that that is measured rather with the idea of the storekeeper getting what he pays for, than with the idea of the engineer getting what he wants, and I think that the Preece test is better from that point of view.

Recently I obtained samples of each of the wires which we use. I found that I had 41 different kinds of zinc-coated wire to test, and I could not help wondering whether the weight should not be considered in relation to the diameter. When you are confronted with large- and small-diameter wires, and remember that this zinc has come as molten material crystallizing from, and at right angles to, the surface of the steel wire, there is reason to think that merely measuring the weight of zinc will not give the same picture of the

* Note added since Meeting: For the sake of clearness it should be observed that "minimum thickness" is here used in a different sense from "minimum weight of coating" referred to by the author on p. 241.

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corrosion-resistance, or the way in which the metal will react to chemical influences, with the small diameter wire as with the larger one. Many of these tests may fit one given type of article quite well, but not, as a general rule, all kinds of articles. That is brought out very well by the author.

The discussion of the methods at the end of the paper gives a clear picture and is of definite value. I notice one omission from the long list of references. Mr. D. M. Smith carried out some work in 1929 at Birmingham University with the spark spectrograph, and obtained some useful results by sparking zinc-coated wires. I carried out photomicrographic tests on the specimens, which seemed to show that that might be a useful test. I have not tried it in practice, because the B.S.I. carefully-specified Preece test seems to meet our requirements.

The author's remarks, in his conclusion, with regard to the effect of different atmospheres are absolutely true. The extreme case is a very smoky tunnel with a great deal of sulphur dioxide, where zinc coating is of relatively little value. In open country it is of great value, but I believe that it is quite wrong to rely solely on zinc; we know that zinc corrodes, so why should we rely on it? Engineers seem to think that to put a non-ferrous coating on a piece of steel liable to corrosion is to overcome the corrosion problem, but it only takes us a little stage further. We can put on more noble metals, like nickel, or base metals, like aluminium or zinc; the latter give sacrificial protection, but only for a limited period of time. The smooth-coated zinc cannot be painted at the beginning, but it can be painted or doped after it has roughened up in weathering or by deliberate preparation. In the aircraft industry it is common practice to apply dope over a metallic protective coating, but that is not the case in general engineering. I think that it would pay the engineer not to be satisfied without further protecting a galvanized wire or sheet. He must realize that there are two groups of protective metallic coatings: the first, like nickel and chromium plate, giving a good appearance in public places where the articles are regularly cleaned; the other is zinc, cadmium, or aluminium coating, which is used merely to retain the engineering strength of the steel article and to stop corrosion accelerating the mechanical failure of the steel. In the latter case we are not concerned with appearance; let us by all means have the sacrificial value of the aluminium, zinc, or cadmium coating, but let us add on, as soon as that is roughened, a dope—varnish, paint, or whatever it may be—and keep it there as long as possible.

Dr. W. H. HATFIELD,* F.R.S. (Member): If you are dealing with the sacrificial method mentioned by Mr. Turner, you can buy steel sheets with a thicker coating, and that means that the sacrifice takes a longer period. That is a point of some consequence. These discussions turn largely on meeting the situation created by abnormal economies as regards the added layer. Speaking as a member of the Corrosion Committee of the Iron and Steel Institute, as Mr. Turner is also, we know that there are sheets made to-day which will give a life of 20 to 30 years.

The PRESIDENT: This paper well repays study; personally, I am very glad to have such an admirable summary of methods of testing. Many years ago, I was interested in comparing zinc coatings carried out by the ordinary so-called dipping process, misnamed galvanizing, with electrolytic coatings, and at that time we had to use the Preece test, as being almost the only officially recognized test. It is interesting and helpful now to have the results of the trials and errors of the intervening years in the testing of zinc coatings put before us so admirably as is the case in this paper.

* Director, Brown-Firth Research Laboratory, Sheffield.

The AUTHOR (*in reply*): I agree with Dr. Vernon that there is further need for the correlation of these tests with actual service experience and, as a matter of fact, I am now engaged on such experiments, the results of which I hope to publish at a later date.

Mr. Turner referred to the omission of the test devised by Mr. D. M. Smith. I am familiar with this work, since I collaborated with Mr. Smith on that occasion, but, although the spectrographic method proved of value in solving a rather special problem, it is doubtful whether it could be developed into a standard method of testing. For that reason it was not regarded as within the scope of this paper. Mr. Turner tends to give the impression that zinc does not provide a very satisfactory coating. Whilst conditions undoubtedly exist under which zinc suffers rapid attack, the fact remains that zinc coatings have been used successfully for many years. Dr. Hatfield has mentioned that a life of 20 to 30 years is not uncommon.

Dr. Hatfield raised the question of putting on a thicker coating, since this seemed the obvious way of obtaining an increased life. The American Zinc Institute has realized this by its "Seal of Quality" campaign, providing the buyer of galvanized sheet with a guaranteed coating of a minimum thickness of 2 oz./ft.² (total of both sides). The comparatively modern production of thin coatings, with their consequent short life, has been largely responsible for the recent tendency to under-estimate the value of zinc as a coating.

CORRESPONDENCE.

MR. S. C. BRITTON,* M.A. (Member): If, when I described the electrolytic test for zinc coatings,† I had surveyed the methods of tests available, the result would have differed little in its essential contents and conclusions from the survey which Mr. Kenworthy now sets out. I have since seen no reason to change my mind, and the few disconnected points I wish to raise are all supplementary rather than detractive.

In his conclusion, Mr. Kenworthy mentions only the marine type of atmosphere as one in which pores in zinc coatings are objectionable. The action which he describes as occurring in such atmospheres is apt to result in the formation of some rust at pores. The loss is, I believe, largely an aesthetic one, the life of the coating and of the base metal, so far as mechanical strength is concerned, being little reduced. On the other hand, in acid atmospheres, where no protective film of corrosion product forms and the electro-chemical protective action of zinc over iron can operate unhindered, the effect of porosity may be to increase the rate of corrosion of the coating. I have no direct evidence of this effect, but the results of Patterson ‡ on the relative corrosion of electrodeposited and hot-dipped coatings under different conditions, can be explained by such an action if the greater liability of the electro-deposits to contain pores is considered. In other comparisons of the rates of atmospheric corrosion of various zinc coatings, little difference has appeared, no doubt because the coatings used have all been sound; but few examples of the sprayed coatings, which are now finding a more extended use, have been included. Variations in porosity and oxide content may be produced by the different processes of metal spraying, and by individual operators of the same process. It is likely, therefore, that, in resistance to some atmospheric conditions and to immersed conditions, sprayed coatings will differ among themselves as well as from other types of zinc coating. It may be necessary

* London, Midland, and Scottish Railway Research Laboratory, Derby.

† *J. Inst. Metals*, 1936, 58, 211.

‡ *J. Soc. Chem. Ind.*, 1928, 47, 313*π*.

to exclude sprayed coatings from the general rule that, for atmospheric exposure, weight of coating is supremely important, and to use separate tests for them, including one for porosity.

Chemical dissolution methods can be used to obtain satisfactory values for minimum thickness of coating on irregularly shaped articles, if loss of weight, instead of time of solution, be used as the "yardstick." It is essential, of course, that the test-piece should be withdrawn from the stripping solution within a few seconds of the appearance of bare iron, but this can be arranged after a little experience. The test-piece is withdrawn from the solution every 15 seconds or less when the end-point seems to be near. Copper sulphate seems the best solution to use, as it gives the most easily visible end-point, which is even more definite if the solution is slightly acidified. The adherence of copper does not appear to introduce any error, when the method is used to determine only the minimum thickness; in fact, it should help to compensate for the solution of zinc which occurs in any overshooting of the end-point. Some error does no doubt arise, as the rates of solution of the coating from surfaces, having different curvatures, are not likely to be the same.

I have been unable to obtain satisfactory results with Mesle's chord method for zinc coatings, owing to smearing of the coating over the exposed base metal. If, however, conditions can be arranged so that this difficulty is overcome, the method might be extremely useful in the investigation of structure and distribution.

No tests for brittleness or adherence of the coating are mentioned by Mr. Kenworthy. No doubt an adherence test is not so important for zinc coatings as for coatings of cathodic metals, but resistance to cracking may be important for corrosion-resistance at least under some conditions, and, in the case of wire for some forms of service, for fatigue-resistance.

Has Mr. Kenworthy any views on the need for special tests for brittleness, or does he think that investigation of structure alone is sufficient?

MR. H. L. EVANS,* M.Sc. Tech. (Member): This paper has a direct bearing on the practical importance of the use of zinc coatings in protecting iron and steel from corrosion, and this point is fully recognized by the interesting oral discussion which it provoked.

The author mentions that the protection afforded by zinc coatings in service is proportional to the weight of zinc per unit area, assuming reasonable uniformity. Some American work, however, tends to show that the increase in service life is more than proportional to increase in coating weight.† ‡

Most users of galvanized sheet have no conception of the importance of coating weight. To them galvanized iron is an ordinary article of commerce, and the possibility of specifying a definite coating weight, and the advantages to be derived thereby, have probably never been considered. Dr. Hatfield referred to the importance of coating weight in considerations of service life and mentioned that there are sheets made to-day that will give a life of 20 to 30 years. It may be well to stress this aspect, and to indicate that considerable economies may be effected by the use of heavy zinc coatings. By far the greatest amount of galvanized sheet sold has only $1\frac{1}{4}$ oz./1 ft.² of zinc, i.e. including both sides. Two-ounce sheet involves an additional initial cost, including erection, of only about 4 per cent. for the same surface area to be covered. Assuming only a linear relation between coating weight and service life, this additional 4 per cent. will yield 60 per cent. longer life.

Mr. Turner asked why we should rely solely on zinc since we know that

* Chief Alloy Investigator, National Smelting Company, Ltd., Avonmouth.

† *Proc. Amer. Soc. Test. Mat.*, 1935, 35, (1), 89; 1936, 36, (1), 107.

‡ Bartells and Ekblaw, "Production and Use of Roofing Sheets," *Agric. Eng.*, 1932, (Feb.), 47.

it corrodes, and suggested that it might pay the engineer to apply a paint or similar finish on top of the zinc. It seems probable that Mr. Turner has not enquired very closely into the economies at issue. To the user the vital point is the cost of protection per annum, and this resolves itself merely into a consideration of whether it is cheaper to erect good quality galvanized sheet, and to scrap and re-sheet at the end of its normal service life, or else to erect sheet of a lighter coating weight and to maintain a surface paint covering in good condition.

The following figures have been estimated on the use of 24-gauge corrugated galvanized sheet, of 2-oz. coating weight in the one case and of $1\frac{1}{4}$ -oz. in the other. A unit of 10×10 ft. superficial surface area is taken as a convenient basis for comparison. The cost of this area of 2-oz., 24-gauge sheet, erected, is about £2 9s., this being an average for roofing and siding for a fairly large building. Assuming a rural location, a life of 20 years may be expected. Taking into account depreciation and 5 per cent. interest, an annual cost is involved which closely approximates to 4s.

In the case of the sheet to be painted, although Mr. Turner does not give any indication of what he would consider a reasonable period for service life, it must be assumed that, in practice, for various reasons, some limit would have to be set to the expected life, and an obsolescence period of 50 years may, with fairness, be assumed. The initial cost of the same area of $1\frac{1}{4}$ -oz. 24-gauge corrugated sheet is about £2 7s. On the basis of interest at 5 per cent. and depreciation over a 50-year period, an annual cost of 2s. 8d. would be involved for the sheet alone. To this must be added the cost of painting. The variation between different painting contractors' prices, and the possibility that paints differing in quality and price may be used, makes a fair average figure somewhat difficult to determine. The assumption has been made, however, that two coats of good quality lead paint would be used, which would need renewing at intervals of 3 years under the rural conditions postulated. A figure of 10s. 3d. has been taken as a contractor's price for painting a 10×10 ft. superficial area of corrugated sheet with two coats of good quality lead paint. Applied every three years, this would involve an annual cost of 3s. 9d. Added to the annual cost of the sheet alone this makes a total annual cost of 6s. 5d., which compares very unfavourably with the figure of 4s. for 2-oz. unpainted sheet.

Obviously, in practice the matter would not be quite so simple as expressed above. Unpainted buildings would require patching in parts before the building as a whole needed re-sheeting, and similarly, in the other case, some parts would need re-painting at more frequent intervals. Under urban or industrial conditions the 2-oz. sheet would have a life somewhat less than 20 years, but similarly a paint coating would need to be renewed more frequently. Cheaper paints would considerably reduce the cost of any one application, but it is highly probable that they would be dearer than good paints in the long run.

With all these possible variations in mind, an attempt has been made with the figures given above to arrive at a fair estimate of respective costs, and I have no doubt that in actual practice the divergence would be at least as great as these figures indicate.

Quite apart from considerations of protection, appearance is often important and the use of paint on galvanized iron must be separately considered. Mr. Turner referred to the necessity for roughening the surface of galvanized sheet by weathering or deliberate preparation before painting. The lack of adherence of paint to zinc in the normal way is not a question merely of the smoothness of the new surface, but involves the chemical interaction of the zinc with the paint vehicle. There are some phosphate processes available for the immediate pre-treatment of galvanized iron and other zinc surfaces

which give excellent adherence to subsequent paint coatings, but it is not widely known in this country that a priming coat of a metallic zinc dust paint is equally effective. By this means additional zinc protection is afforded, and the necessity for an ordinary priming coat dispensed with.

Dr. U. R. EVANS,* M.A. (Member): This review of methods for estimating the thickness of zinc coats will be universally welcomed. On practical points it may be taken as authoritative, and I have no wish to challenge the conclusions.

I would point out, however, that the use of electro-chemical measurements for determining the end-point is not necessarily confined to cases where the form of the zinc-coated materials is geometrically simple (*e.g.* wire or plate). If, as in Britton's method,† the zinc coat is dissolved away by anodic action, geometric simplicity is essential for obtaining a uniform rate of removal. It is possible, however, to remove the zinc coat in acid, using the measurement of the potential *merely to ascertain the two end-points* at which (*a*) the removal of the pure zinc coat, and (*b*) the removal of the alloy coat, become complete. Some curves which I published 9 years ago‡ showed that this method can be used to ascertain whether an alloy layer is present or absent, and even to measure its thickness and that of the pure zinc layer. Admittedly, in the case of coats bearing an alloy layer, the end-point is not so sharp as one would like, but with a little practice it could probably be used.

It is fully realized that such a method involves weighing the specimens and must therefore be relatively slow, but if, in each experiment, the counter-poise used in weighing the specimen consists of the specimen to be used in the next, the total number of weighings can be roughly halved; moreover, the time of each weighing will thus be greatly reduced, since it is much quicker to determine the difference in weight between two nearly equal specimens than to determine the absolute weight of a single specimen. If it is desired to avoid weighing altogether, I believe that the observation of the amount of heat evolved when the coating is dissolved away in acid (the principle of Strickland's method), could be made fairly accurate for specimens of nearly equal form and weight. Undoubtedly, the heat evolution from a zinc coat will not be the same as that obtained from an alloy coat of equal thickness; but when the two layers are being determined separately, this fact would not necessarily involve any error.

It would doubtless involve considerable work to develop and standardize a test on these lines. I do not intend to do it myself, and I do not know whether it would be worth while for anyone else to do so. In my opinion, the amount of time now devoted to designing new tests is somewhat out of proportion to the value of the tests when they arrive. If some of this time were devoted to more fundamental work on ascertaining the root cause of failures, the benefit to users might be greater, and possibly the urgent need for the tests would cease to exist. This, however, is a matter on which there is room for honest differences of opinion.

Mr. J. W. NORRIS§: I agree with the author's implied conclusion that for a test to be satisfactory it must afford information from which the actual protective value of the zinc coating as a whole can be assessed. Tests can, in general, be classed as (1) academic (research laboratory) tests, or (2) commercial (works) tests, and it is the latter in which I am particularly interested,

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† S. C. Britton, *J. Inst. Metals*, 1936, 58, 211.

‡ U. R. Evans, *J. Inst. Metals*, 1928, 40, 121.

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as a representative of an important body purchasing considerable quantities of engineering stores for export.

It is axiomatic that in specifying that articles shall be galvanized what we expect and pay for is protection from corrosion, and it is the duty of the Inspector to ascertain, as far as is possible before accepting the materials for shipment, that the coating is likely to prove satisfactory. At the present moment, for a large proportion of galvanized work, we have to rely wholly on a determination of the weight of the coating, as ascertained by weighing in the black and then again after galvanizing, making an allowance of 2 per cent. for loss in pickling and the absence of acid spots or other bare places, the presence of which is detected by rusty patches after exposure to the air for a period of 14 days. Other articles are dealt with by the copper sulphate test, which, it is agreed, gives only a limited amount of information regarding the quality of the zinc coating.

I had hoped, therefore, that the paper might have contained information regarding a more satisfactory test from the Inspector's point of view. Unfortunately, the many tests described in the paper fall in the category of research laboratory tests, and there is no test suitable for commercial application, with the possible exception of the magnetic test, which is being developed by the Post Office, and the copper sulphate test, which, for want of a better, is the only test at present specified by the British Standard Institution.

The electrolytic test advocated by Mr. Kenworthy, and on which he places such reliance, is so entirely dependent for its results on the use of accurately-calibrated electrical measuring instruments of an order of accuracy that is not likely to be found in the average works, that it cannot be considered as a commercial test.

With regard to the copper sulphate test, I note with interest the author's reference to the necessity for the adjustment of the time of the standard dips to suit the type of coating under examination. So far as I am aware, no such suggestion was put before the Committee of the British Standard Institution dealing with this test, and I am under the impression that sherardizers have accepted the test as it stands in B.S.S. No. 729, without any amendment.

I hope that the discussion of this paper may eventually lead to the development of a more suitable commercial test which will give an index of the protection afforded, that can be applied to articles for which the copper sulphate test is not suitable.

The AUTHOR (*in reply*): Mr. Britton raises an important point in connection with the variable composition and porosity of sprayed coatings, and it would seem very desirable that a comprehensive study of the protective value of sprayed zinc coatings should be undertaken. I was interested to note that he considers that the copper sulphate dip test might be used as a loss-in-weight test, without appreciable error. His experience with the Mesle chord method is also of interest. Tests for brittleness or adherence were purposely omitted from the present paper, not because of their unimportance, but because they were regarded as preliminaries to the actual testing of the coating. Mechanical tests should be designed to subject the coated material to the degree and type of deformation likely to be met with in service by that particular material. If the coating fails in this process by flaking or cracking, phenomena which may usually be detected visually, the application of the tests described in this paper would, of course, become unnecessary.

Mr. H. L. Evans has interpreted the results of the A.S.T.M. field tests as indicating that increase in the weight of a zinc coating results in a more than proportional increase in service life under atmospheric conditions. This, however, is a matter which depends entirely on the definition of the term "service life." If one regards a coating as having failed at the first appearance

of rusting of the iron base, and this appears to be the reasonable definition, then the relationship between life and average weight is, in fact, linear as shown graphically in the papers quoted by Mr. Evans.* I agree that if the time taken for 50 per cent. rusting to occur is regarded as the point of failure, then the life is more than proportional to the average weight, since, although the *degree* of uniformity may be the same for all thicknesses of coating, the actual excess of average weight over minimum weight will be considerably larger for thick coatings than for thin. Thus, it was observed in the tests of the A.S.T.M., previously mentioned, that iron rust having once appeared, spread rapidly over the surface of the lightly coated specimens, but more slowly over those which had been heavily coated. To avoid ambiguity, therefore, we may say that the useful life of a coating, before the appearance of rusting of the iron base, is proportional to its average weight when exposed to atmospheric conditions.

It is undoubtedly true that most users of galvanized sheet, having no conception of coating weight, never consider the possibility of specifying a definite weight of coating, but this is largely to be attributed to the attitude of the wholesale and retail distributors of galvanized goods, and to some extent to the manufacturers themselves. Even an enlightened member of the public would gain little satisfaction by brandishing specifications before the local ironmonger.

I quite agree with Mr. Evans on the subject of painting, and I am very pleased that he has placed the economics of the problem on record in such a clear manner.

I thank Dr. U. R. Evans for directing attention to the fact that, by combining potential measurements with a chemical dissolution method, it is possible to estimate the structure of zinc coatings even on articles of irregular shape.

Mr. Norris raises the problem of finding a more suitable commercial test than the Preece test, the assertion being made that the more accurate methods which exist suffer from the commercial disadvantages of slowness and complexity. Assuming this to be the case, then clearly the question to decide is to what extent do the inaccuracies of the Preece test warrant the expenditure of time and money on the adoption of a more accurate method. But whatever the decision reached, let it not be said in 1937 that an ammeter was the stumbling-block to progress.

* *Proc. Amer. Soc. Test. Mat.*, 1935, 35, (I), 92; 1936, 36, (I), 110, 112.

A STUDY OF THE DEFORMATION OF THE 779 MACROSTRUCTURE OF SOME TWO-PHASE ALLOYS BY COLD-ROLLING.*

By HERMANN UNCKEL,† Dr.-Ing., MEMBER.

SYNOPSIS.

The deformation, on rolling, of alloys consisting of several phases having different yield-points, differs from that of alloys of homogeneous structure. Harder particles imbedded in a softer matrix deform less, and softer particles somewhat more, than the matrix. A secondary flow is thereby caused round the inclusions. Experiments with some two-phase alloys are described. It is shown that the deformation takes place in such a way that the work of deformation becomes a minimum value.

INTRODUCTION.

THE deformation phenomena occurring during the rolling process have been investigated by a considerable number of authors.^{1, 2, 3, 4} In these investigations the material was assumed to be homogeneous. As however the rolling process is widely employed for alloy systems which are not homogeneous but consist of particles with different hardness, such materials merit consideration.

Apart from a theoretical interest, the problems involved have a distinct practical importance for they concern, for example, the occurrence of stresses and cracks within the structure or the change in shape and arrangement of the second-phase particles brought about by deformation.

Considering first a single-phase alloy, the material mostly consists of a great many crystals with random orientation; we might in this case consider the whole mass of metal as approximately homogeneous with respect to deformation, for, the greater the number of crystal grains per unit volume the less do the vectorial restrictions of the lattice against deformation prevail and the more numerous are the crystallographic possibilities allowing deformation as in a uniform mass. Approximately at least, a one-phase multi-grain metal might therefore be regarded as homogeneous.

The case becomes quite different, however, if we consider an alloy

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with phases of different hardness, and it might be expected that such a composition will not deform in the same way as a homogeneous metal.

LITERATURE.

Siebel ² states that hard constituents frequently remain undeformed or are broken into pieces, whereas softer constituents undergo a correspondingly greater deformation. Benedicks and Löfquist ⁵ give certain data on the plasticity of slag inclusions, and Schnell and Scheil ⁶ have studied more especially the deformation of slag inclusions in steel and noted a different plasticity of the slag inclusions in different parts of the metal. If, for instance, sulphide inclusions lay near the surface of the specimen they proved to be very brittle, but they were plastic if situated more inside the metal mass and therefore exposed to pressure from all sides. Mention might also be made of an interesting paper by Scheil ⁷ on the investigation of structures by statistical methods.

SCOPE OF THE PRESENT PAPER.

The subject apparently opens quite a new and wide field for investigation, but this paper deals only with some of the many aspects of the problem. In addition to certain general considerations, some experiments with a few two-phase alloys are reported as examples, and finally some of the results are treated mathematically in further consideration of the problem.

SOME GENERAL CONSIDERATIONS REGARDING THE DEFORMATION OF INCLUSIONS OR SECOND-PHASE PARTICLES.

Without committing great error, the deformation effected by rolling may be considered essentially as a compression process, as has been shown by the experiments of the authors mentioned above. The deformation is the same and quite evenly distributed through the thickness of the sheet, and is caused substantially by compressive stresses acting perpendicularly to the surface of the sheet. The flow in the direction at right angles to the direction of rolling is negligible, so that the problem is a two-dimensional one.

If the piece of metal consists of crystals belonging to different phases, the part present in the smaller amount may be considered as inclusions in a groundmass. The crystals of one phase, *e.g.* the inclusions, may be softer or harder than the matrix in which they are imbedded. By soft or hard, respectively, is meant lower or higher resistance to plastic deformation or, in other words, the yield-point. The softer or harder particles may either be plastically deformable or brittle. Thus,

the inclusions can be harder than the matrix but plastic, as for example β crystals in α brass; they may be harder than the matrix but brittle, as most of the intermetallic compounds in aluminium alloys; they may be softer than the matrix and plastic, as lead in brass; or, finally, softer but brittle, as graphite in grey iron. In special circumstances, an otherwise brittle substance may show plasticity, for example, where the brittle substance is subjected to sufficient pressure from all sides superposed on the deforming stresses. Th. v. Karman, in his experiments in 1912, succeeded in plastically compressing material as fragile as marble, and Scheil observed that brittle sulphide slag showed plasticity if surrounded by the steel matrix.

As brittleness is often observed, however, even with imbedded inclusions, the all-side pressure is obviously effective only to a certain extent. It can be understood that the flow of a softer matrix mass round the corners of a hard and brittle inclusion exerts a pressure towards its corners and thereby creates a certain normal pressure on the glide planes within the inclusion, which pressure depends on the relative hardness of inclusion and matrix and on the different kind of flow round the inclusion.

Distribution and Size of the Second-Phase Particles.

The second-phase particles in alloy systems may vary greatly in size and distribution according to composition and treatment of the alloy. The particles may thus occur isolated from each other, or they may form a continuous network. In the first case, if the inclusions are relatively small, they will cause only little disturbance in the flow of the matrix; in the second case, however, the skeleton-like net-work must give way if the whole piece of metal is to be deformed.

Considering now inclusions of *equal volume but different shape*, the disturbance is greater if for example an elongated inclusion is arranged with its long side in the direction of compression. Assuming a *hard* particle, the matrix mass above and beneath the inclusion has to undergo greater specific compression than the material ahead of the particle. A compression for example by an amount ΔH of the whole specimen, is shared by a thickness of material H if there is no inclusion, whereas the same compression ΔH above and beneath an inclusion has to be taken up by the thinner layer $H - h$. (Here it is supposed that the inclusion does not participate at all in the deformation.) Conversely, with a particle arranged with its flat side perpendicular to the direction of compression, the disturbance will be less because of the smaller difference of the flow velocities around it, on account of its lesser height. If the atomic connection between inclusion and surrounding mass is loose,

cavities eventually occur at the sides of the inclusion, as illustrated later.

The Flow and Deformation Round an Inclusion.

The flow of the matrix in the neighbourhood of a *hard* inclusion is schematically illustrated in Fig. 1, in which, for simplicity, the particle is assumed to have been square-shaped at the beginning. Supposing a network of vertical and horizontal lines within the test-piece then, after compressing the specimen, the original squares at some distance from the inclusion deform to rectangles. In the vicinity of the particle, however, the flow is disturbed, and the disturbance is levelled out again only at some distance from the particle. It is clear, therefore, that the original horizontal lines are crowded up above and beneath the in-

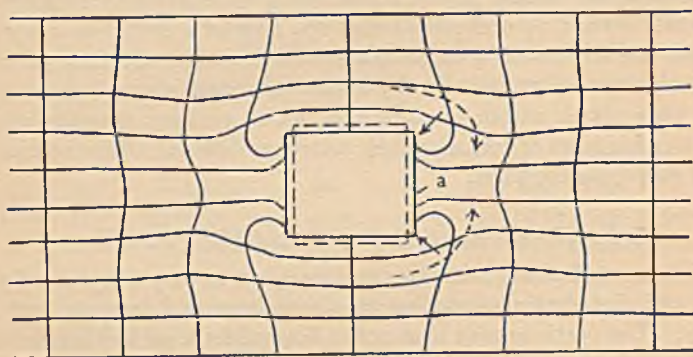


FIG. 1.—The Flow Round a Hard Imbedded Particle.

clusion. Now, since the volume of the particle is constant and supposing the flow to be negligible in the direction perpendicular to the plane of the paper, the area of the original squares is constant during deformation. By drawing the cross-set of lines so that the area of each element is equal, it is found that the horizontals are less distant from each other even at the vertical sides of the inclusion and further, that the deformation is very considerable at the very corners of the particle. As the surrounding material flows with greater velocity at the horizontal than at the vertical faces of the inclusion, a sideward pressure is exerted in the vicinity of the corners which tends to elongate and separate the material at (a) in Fig. 1. Likewise, a pressure is exerted in the direction of the corners of the particle itself. As is shown by means of dotted arrows, a movement takes place in the material from the regions above and beneath the inclusion towards the right and left sides of the particle.

Fig. 2, on the other hand, is intended to give a conception of

the kind of deformation in the neighbourhood of an inclusion which is softer than the matrix. Here again, the disturbance caused by the difference in deformation stress of the two materials diminishes with increasing distance from the particle. As an extreme case, it may be assumed that the inclusion consists of a frictionless liquid. It is clear that the pressure put upon it from above and below is hydrostatically propagated to the sides, as shown by small arrows on one side of the figure. There the elements of the adjoining mass are exposed to a side pressure which leads to an outward bending of the originally vertical lines. By constructing elements again with equal area it is found that the original horizontals drop towards the upper and lower sides of the

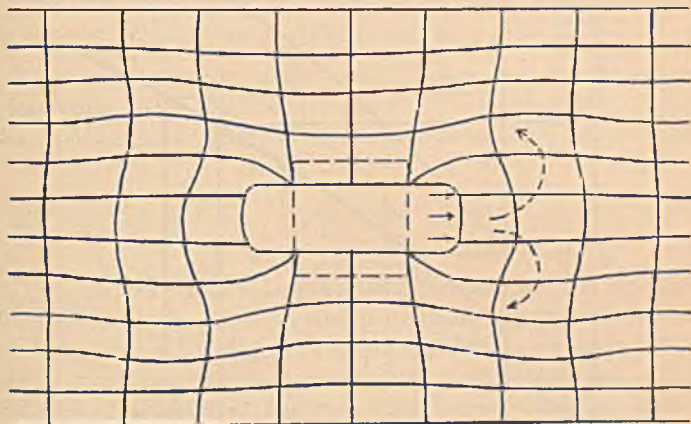


FIG. 2.—The Flow Round a Particle Softer Than the Surrounding Material.

particle and that their distance from each other is greater there. The portions of the surrounding mass adjacent to the vertical sides of the inclusion are stiffened, so to speak, by the horizontal side pressure against the vertical compressive forces, and are consequently compressed to a less degree. As indicated by the curved dotted arrows, flow takes place from the right and left sides to the upper and lower ones.

On the whole it is seen that the total deformation in the matrix is less if the inclusion is softer than the deformation would be if the inclusion had the same hardness. Conversely, the deformation of the matrix is greater if the inclusion is harder. Later in the paper part of the subject is considered mathematically.

Effect of Strain-Hardening.

With most metals and alloys (except those recrystallizing at the rolling temperature), a further complication is involved by the fact that the

yield-point, or the resistance to further deformation, increases with increasing cold-work. This increase of the deformation stress as a function of cold-work varies with different materials and accordingly it is to be expected that the inclusion particles harden differently from the matrix. Assuming for instance an inclusion with an initial yield-point Y_2 , in Fig. 3, which strain-hardens according to the curve *A* and a matrix hardening according to curve *B*. Then, if the imbedded in-

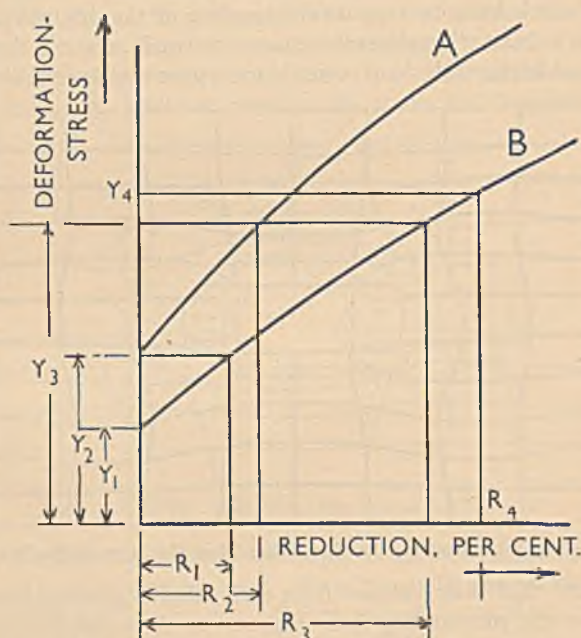


FIG. 3.—Strain-Hardening Curves of Inclusion and Surrounding Material.

clusion behaved as if it were free, it would start to deform after the matrix had already suffered the reduction R_1 corresponding to a stress Y_2 ; depending on the different gradient of curve *B* the deformation of the inclusion thus lags behind that of the matrix.

An imbedded particle, however, is exposed to stresses which differ from the pure compressive stresses as supposed in Fig. 3, because of the special flow around it and, consequently, it behaves otherwise than if not included. Moreover it is uncertain whether the strain-hardening curve of an imbedded particle really is the same as if the same material were free.

EXPERIMENTAL INVESTIGATION.

General Procedure.

Since it is not possible to follow the deformation of definite individual grains, resort must be made to statistical methods of measurement in order to obtain a reliable mean value of the deformation. The actual measurements made were restricted to the plane containing the rolling direction perpendicular to the rolling plane, since the flow of material in the cross-direction is negligible. The measurement itself of the dimensions—height and length of the second-phase particles—was made by means of an eye-piece micrometer consisting of a plane glass, divided into a network of small squares, mounted between the lenses of the ocular. The degree of deformation of a grain is $\frac{h_1 - h_2}{h_1}$, where h_1 designates the height of the particle before, and h_2 its height after, deformation. One might either measure the heights only or the proportion of height to length of the inclusion and therefrom calculate the

height reduction as $1 - \sqrt{\frac{\overline{h_2}}{\overline{h_1}}}$, since the volume is constant, *viz.* $h_1 b_1 =$

$h_2 b_2$ (b_1 = length before, b_2 length after deformation). The latter method yields better results, as it is easier to estimate the proportion of height to length with a fair degree of accuracy, than to estimate the height only in which case the error of observation may be greater. The first method is to be preferred, however, if the length of the individual grain is not clearly determinable, as is sometimes the case with heavier reductions.

Prior to rolling, the distribution and size of the second-phase particles was checked in the cross-plane. It was found with all alloys that the inclusions were approximately equiaxed and evenly distributed in the two perpendicular planes.

In order to obtain reliable results of the average deformation value it is necessary, of course, to measure a very great number of grains in very many different places on the specimen, and thereafter to compute the mean value of all measurements.

In addition to statistical grain measurement, direct microscopical observation of the neighbourhood of the inclusion can often give certain indications of the special flow phenomena which have taken place around it. The deformation of the matrix frequently reveals itself by the special arrangement of the strain marks disclosed by etching or through the displacement of the grain boundaries in the vicinity of the inclusion, as will be illustrated later.

Hardness Measurements.

Two methods were tried to measure the relative hardness of inclusion and matrix, namely scratch hardness tests with a diamond point and indentation tests with a sharp steel needle held in a guide assembly and loaded with definite weights (100 or 150 grm.). The latter method might be considered more adequate, as it measures plastic flow resistance whereas scratching always involves a certain abrasion effect. The needle test, on the other hand, has the disadvantage that the distribution of the second phase particles beneath the surface might be different from that visible in the surface itself.

As these did not prove very satisfactory, measurements were made of the Brinell hardness of all specimens.

Materials Used.

The materials were chosen with one object only in view, namely to represent certain characteristic cases, and not with regard to their technical application. The compositions were selected so that the desired amount of second-phase particles was obtained in the structure.

In order to equalize the structure and eliminate discontinuities, all ingots were rolled or forged and then annealed for homogenizing prior to cold-rolling. The specimens were cold-rolled so far as their capacity for cold-work allowed, *e.g.* until cracking occurred. Samples were taken at different stages of rolling. The etching reagent and treatment were adapted so that both the second-phase particles and the crystal grains of the matrix mass appeared as clearly as possible without giving too much local attack due to electrolytic action at the boundaries of the inclusion and thereby concealing valuable details.

Alloy 1.—Leaded Brass (Copper 63, Zinc 27, Lead 10%).

Lead in brass is a typical example of soft plastic inclusions in a harder matrix. As lead does not form a solid solution with brass, it solidifies last and lies between and partly inside the primary brass crystals.

TABLE I.—*Treatment, Test-Pieces, and Results.*

Dimensions of ingot 120 × 120 × 20 mm.				
Annealed after rolling to 18 mm. thickness, at 750° C. for 2 hrs.				
Average grain-size before rolling		Brass crystals: 0.06 mm.		
		Lead particles: 0.01–0.04 mm.		
Yield-point	"	"	Brass (approx.) 10 kg./mm. ² .	
"	"	"	Lead " 0.3 "	
Specimens taken at	18	16.25	8.30 mm. thickness.	
Brinell hardness	40	84	144.	
	0	9.7	53.3 per cent. reduction in thickness by rolling.	
	0	14.5	54.5	" " " of lead particles.

It appears surprising that the lead particles are compressed only slightly more than the specimen as a whole, in spite of the fact that the yield-point of lead is only 1:30 that of the brass matrix. At the lower reduction the relative deformation of the lead particles was found to be greater than at higher reduction. Typical structures are shown in Figs. 4-7 (Plate IX). The structure prior to cold-rolling is represented by Fig. 4. At 9.7 per cent. reduction the lead particles show a somewhat greater deformation than the α brass crystals. Figs. 6 and 7 show some evidence of the deformation details, and how, for example, twin bands have been bent ahead of lead particles owing to the greater elongation of these in relation to the brass matrix.

Since it is not possible to examine exactly the same place on the specimen before and after deformation, it is easy to commit the error of attributing a certain configuration in the structure, which existed before, to the deformation which would have occurred even if the inclusions had not been present. All conclusions on such observations can therefore only be based on probability.

Besides the displacement of grain boundaries in the matrix material, the strain marks or slip bands developed by etching the polished surface can give some indications of the disturbance caused in the matrix by the second-phase particle, of which Fig. 6 (Plate IX) is an example. In front of a great many lead particles bundles of slip plane traces were observed which can probably be ascribed to a special flow-movement due to the tendency of greater elongation of the lead grains.

It is remarkable that the test-piece broke after 53 per cent. reduction in spite of the fact that both the α brass and the lead are highly plastic if deformed independently of each other and have a much greater capacity for cold-work. The greater brittleness of the alloy may be due partly to special stress accumulations through the discontinuities in the brass structure by the lead particles, which may act like notches. It is highly probable, however, that the side pressure exerted by the soft inclusions on the adjoining matrix material contributes to the cracking.

Alloy 2.— α - β Brass (Copper 63, Zinc 37%).

The β phase in brass is harder at room temperature than the α phase. The latter with its face-centred cubic lattice yields to deformation by gliding on (111) planes (octahedral) in the [011] directions whereas the body-centred β deforms differently, probably gliding on (011) planes in [111] directions.⁸

The alloy was investigated after annealing and quenching from 600° and from 750° C. in order to obtain different β contents. The

composition of the β phase at these temperatures can be read from the phase diagram; at 600° C. the β contains approx. 56 per cent. copper and the α 63 per cent. copper. Consequently the hardness of the two phases can be assumed as being those of an homogeneous alloy with 56 and 63 per cent. copper, respectively.

TABLE II.—*Treatment of the Test-Piece and Results.*

Dimensions of ingot: 150 × 300 × 26 mm.
Homogenized after rolling to 20 mm. thickness at 600° and 750° C., respectively, for 2 hrs.

A. Specimen Annealed at 600° C.

Average grain-size before rolling: Alpha: 0.04 mm.				
Beta: 0.022 × 0.045 mm.				
Yield-point: Alpha (approx.)	12	kg./mm. ² (before rolling)		
" " Beta	23			
Specimens taken at	20.6	17.25	9.15	3.59 mm. thickness.
Brinell hardness	63	107	158	170
	0	16.0	55.7	82.5 per cent. reduction in
				thickness by rolling.
	0	12.5	34.2	55.2 " " " of beta.

B. Specimen Annealed at 750° C.

Average grain-size before rolling: Alpha: 0.062 mm.				
Beta: 0.050 "				
Yield-point: Alpha (approx.)	11	kg./mm. ² (before rolling).		
" " Beta	25			
Specimens taken at	20.33	17.17	9.15	3.55 mm. thickness.
Brinell hardness	68	110	160	182
	0	15.5	55.0	82.5 per cent. reduction in
				thickness by rolling.
	0	10.1	38.4	44.2 " " " of beta.

Because of the irregular shape of the β particles it proved rather difficult to determine their average deformation. This applies especially to the alloy annealed at 750° C. because of its larger β content and the precipitated α needles within the β grains. Since it was not easy to estimate exactly the length of the grains, only the height was measured.

As shown in Fig. 8 (Plate IX) the β grains are elongated before cold-rolling in spite of the homogenizing treatment. The β phase deforms to a less degree than the α . The reduction of β in relation to that of α is, however, nearly the same in both variations of this alloy and therefore might be assumed to be independent of the β content within these limits. At the higher reductions it can be seen (Figs. 9 and 10, Plates IX and X) that β obviously has been deformed less than α , the picture frequently resembling the flow of a liquid round an obstacle, the elongated streaks being gently curved round a region with less plasticity. The β grains, which from the beginning are of more equiaxed shape, seem to withstand deformation better than elongated ones.

Alloy 3.—Complex Brass (Ellis Type) (Copper 55, Aluminium 3, Iron 1.5, Manganese 4, Zinc 36.5%).

Alloys of this type are composed of a hard β solid solution and a hard, round-shaped special constituent. Owing to the complicated atomic lattice and the scarcity or possibly complete lack of definite glide-planes in such intermetallic compounds, their low deformability is easily understood. As with most special brasses, this one is not a cold-working alloy because of the brittleness of the β at room temperature. It is chosen only as representative of this class of alloys.

The test-pieces were annealed before cold-rolling at 600° and 750° C., respectively, and quenched. The amount and size of the special constituent was the same in both cases, only the β grains of the groundmass having grown excessively at 750° C.

TABLE III.—*Treatment of Test-Piece and Results.*

Dimensions of ingot: 150 × 400 × 14.5 mm. as forged.
Annealed after forging at 600° C. and 750° C., respectively, for 2 hrs.

A. Annealed at 600° C.

Average grain-size before rolling: Beta matrix: 0.7 × 1.2 mm.			
Special constituent: 0.005 mm.			
Specimens taken at	" 14.35 "	12.35	10.32 mm. thickness.
Brinell hardness	158	217	245
	0	13.8	27.2 per cent. reduction in thickness by rolling.
	0	2.0	7.1 " " " of special constituent.

B. Annealed at 750° C.

Average grain-size before rolling: Beta matrix: 1 × 2 mm.			
Special constituent: 0.005 mm.			
Specimens taken at	" 14.35 "	12.38	10.38 mm. thickness.
Brinell hardness	139	187	220
	0	13.7	27.7 per cent. reduction in thickness by rolling.
	0	1.0	1.3 " " " of special constituent.

The hard inclusions do not undergo appreciable deformation. It is uncertain, therefore, if the conclusion is permitted that the special constituent deformed less in the specimen annealed at the higher temperature, since the whole deformation is very small.

Figs. 11-12 (Plate X) are given as characteristic. No distinct disturbance in the matrix caused by the hard inclusions could be observed up to the degree of cold-rolling which the alloy allowed before cracking. Fig. 12 shows a typical cold-rolling crack as it occurs in materials which have attained such hardness that the resistance to

further deformation on the glide planes exceeds the resistance to shear on planes inclined at 45° to the direction of compression which planes are exposed to maximum shear stress.

Alloy 4.—Copper with Iron (Copper 94, Iron 6%).

As the solubility of iron in copper is very limited in the solid state, the iron occurs as primary crystals of tree- or star-like form. This alloy is typical of a soft matrix with somewhat harder but plastic inclusions. From the results obtained with this alloy certain conclusions may, however, be reached regarding the behaviour of iron inclusions in, for example, brass.

TABLE IV.—*Treatment of Test-Piece and Results.*

Dimensions of ingot: 110 × 300 × 20 mm.							
Annealed after rolling to 18 mm. thickness at 700° C. for 2 hrs.							
Average grain-size before rolling: Copper matrix: 0.20 mm.							
Iron particles: 0.012 mm.							
Yield-point	"	"	"	Copper (approx.) 5 kg./mm. ² .			
"	"	"	"	Iron 22			
Specimens taken at	18.18	16.79	9.10	6.87	2.32	0.60 mm. thickness.	
Brinell hardness	68	90	112	122	122	139	
	0	7.65	49.6	61.4	87.2	96.5	per cent. reduction in
							thickness by rolling.
	0	3.1	15.4	25.5	41.4	50.0	" " of
							iron particles.

The deformation of the iron particles is less than that of the test-piece as a whole, the difference diminishing, however, with increasing degree of reduction. Consequently, the copper groundmass may either have strain-hardened relatively more than the iron and/or the flattened particles at the higher reductions may have been exposed to greater forces from the surrounding material so that the inclusions kept pace in deformation with the matrix.

Typical structures are shown in Figs. 13–15 (Plate X). The rounded grains composing the iron dendrites are lined up in rows in the course of deformation. Cross-like configurations of the dendritic particles are folded together, the material between the iron grains being squeezed aside. As with the β brass in alloy 2, the deformation of the iron appears to be less with those particles which from the beginning were more rounded than elongated in shape. Particles originally lying extended perpendicular to the rolling direction are, on progressive rolling, pivoted round into the rolling direction. Fig. 14 (Plate X) illustrates disturbance caused by the inclusion in its vicinity. The slip-plane traces clearly show bending and change in direction in the immediate neighbourhood of the iron particle.

Fig. 19 (Plate XI) shows the typical appearance of the structure. As will be seen, the silicon grains frequently break up into small fragments; this was observed especially with particles of elongated shape arranged with the long side in the direction of compression.

It will be noticed also that cavities are formed ahead of the silicon particles, the surrounding aluminium mass separating there from the

TABLE VI.—*Treatment of Test-Piece and Results.*

Dimensions of ingot: $120 \times 120 \times 20.5$ mm.

Annealed after rolling to 19.2 mm. thickness at 500° C. for 12 hrs.

Average grain-size before rolling: Matrix, 0.075 mm.

Silicon particles: 0.024 mm.

Specimens taken at 19.2 " 9.04 6.46 4.20 mm. thickness.

Brinell hardness	30	45	50	53	
	0	52.9	67.0	78.0	per cent. reduction in thickness by rolling.

No plastic deformation of the silicon particles was observed.

inclusion. It should be mentioned, however, that these cavities become enlarged by the action of the etching reagent.

Alloy 7.—Aluminium-Copper Alloy (Aluminium 92, Copper 8%).

In this typical casting alloy the special constituent is the same as in some alloys of the Duralumin type, namely Al_2Cu , but it occurs in greater amount, permitting easier measurement, for which reason this composition was chosen. After annealing at a sufficiently high temperature the β constituent, Al_2Cu , coagulates and accumulates in the grain boundaries and within the grains of the solid solution matrix as rounded globules. In addition needle-shaped dark particles occur, apparently originating from the primary eutectic. According to the rate of cooling, the matrix may hold up to 4 per cent. copper in solid solution and thus varies in hardness.

TABLE VII.—*Treatment of Test-Piece and Results.*

Dimensions of ingot: $120 \times 120 \times 20.5$ mm.

Annealed after rolling to 19.4 mm. thickness at 500° C. for 12 hrs.

Average grain-size before rolling: Matrix: 0.64 mm.

Al_2Cu constituent: 0.013 mm.

Specimens taken at 19.0 " 16.60 12.30 mm. thickness.

Brinell hardness	54	65	70	
	0	12.4	34.5	per cent. reduction in thickness by rolling.

No plastic deformation of the Al_2Cu constituent was observed.

As with the aluminium-silicon alloy, the included particles showed extreme brittleness but no plastic deformability whatsoever. Figs. 20 and 21 (Plate XI) show typical structures. The needle-like inclusions are liable to break into pieces which are then displaced in the direction of the flow, as shown in Fig. 20. The rounded particles, on the contrary, seem to withstand the stresses better and remain unimpaired (Fig. 21).

The round-shaped particles gathered at the corners between several adjacent matrix grains are lined up in rows in the course of the deformation of the latter.*

FURTHER DISCUSSION OF RESULTS.

The results of the grain measurements with the alloys investigated are shown graphically in Fig. 22, with percentage reduction of the test piece as a whole as abscissa and percentage reduction of the second phase

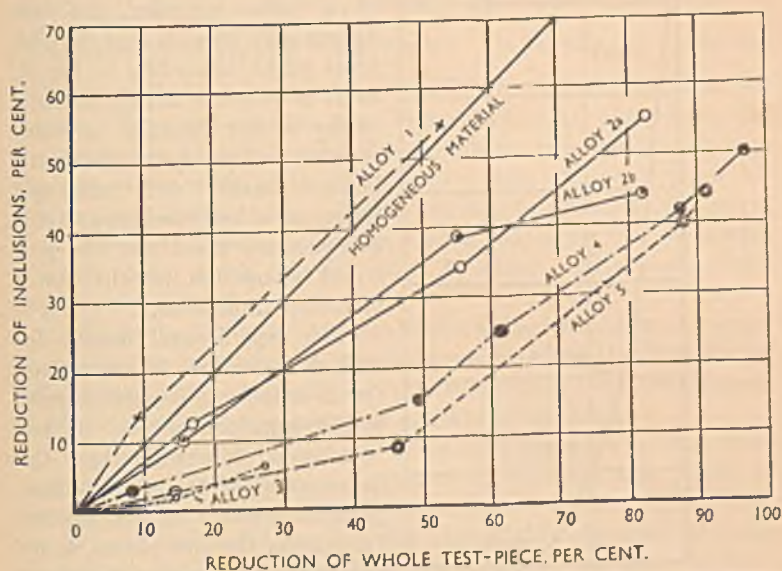


FIG. 22.—Percentage Reduction of Imbedded Particles as Function of Percentage Reduction of Test-Piece.

particles as ordinate. A line, drawn at 45° , divides the diagram in two parts: the deformation of inclusions softer than the matrix lie above that line, the curves for inclusions harder than the matrix material being below it. The 45° line itself represents the deformation curve for a homogeneous material. It is remarkable that all curves show a tendency to approach the 45° line with progressive reduction, indicating that the disturbance caused by the inclusions becomes less pronounced at higher reductions, as already anticipated.

* A paper on faults with pouring and forging aluminium alloys, by W. Schnorrenberg (*Aluminium*, 1936, 18, (9), 422), which appeared after the completion of the present investigation, gives some good examples of fractures of Al_2Cu inclusions.

In the case of inclusions harder than the material in which they are imbedded, it might be that the latter strain-hardens relatively more than the inclusion so that the hardness difference becomes less in the course of the deformation and thereby the deformation more equal; or the inclusion, having gradually been flattened out, then offers a

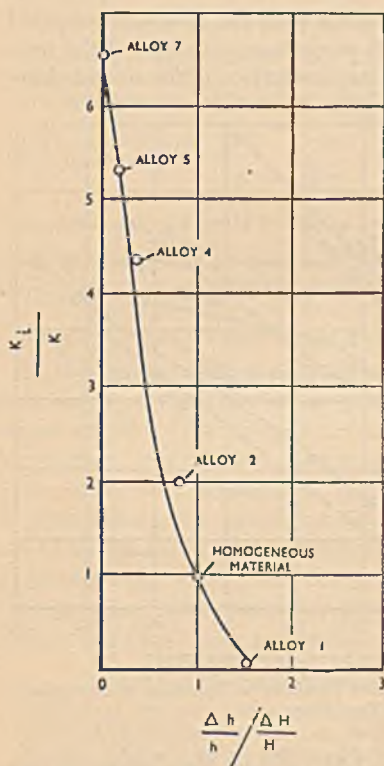
greater surface to the material flowing around it and is more easily stretched out by the action of frictional forces. In the case of a softer inclusion, the conditions may be such that its side-areas which, according to Fig. 2, exert a pressure acting at right angles to the direction of compression on the adjacent material, become smaller with increasing reduction in height wherewith this side-pressure effect and the preferred elongation of the softer inclusions diminishes.

The experimental results described above are, of course, too few in number to permit accurate and definite conclusions. It has been seen, however, that the deformation of the second-phase particles depends on the relative hardness of the two phases, as by the laws of geometric similitude the flow is not influenced by the absolute hardness of the constituents.

FIG. 23.—The Relative Deformation of Inclusions as Function of the Relative Deformation Stresses of Inclusion and Matrix.

of the relative yield-points or deformation-stresses. Plotting the quotient of the deformation-stress of the inclusion and that of the surrounding material, $\frac{K_i}{K}$ as ordinate and the relative compression of

the inclusion to that of the whole specimen $\frac{\Delta h}{h} : \frac{\Delta H}{H}$ as abscissa, where



Δh = the compression of inclusion, ΔH = the compression of whole specimen, h = the height of inclusion before deformation, and H = the height of specimen before deformation, a curve is obtained as shown in Fig. 23. The values for some of the alloys investigated are marked in the figure. It must, however, again be emphasized that the exact establishment of that curve requires much more experimental foundation and further the relative change in yield-point produced by cold-work of the two constituents must be known.

If the hardness of the inclusion is assumed to be equal to that of the matrix, *e.g.* $K_i = K$, the compression of the inclusion Δh is equal to $\frac{\Delta H}{H}h$ and the value $\frac{\Delta h \cdot H}{\Delta H \cdot h}$ is equal to unity. On the other hand, a harder inclusion tends to deform less, and a softer to deform more, than the matrix. For a deformation, given by a reduction ΔH of the test-piece, the plastic flow of matrix and inclusion adjusts itself in such a way that the sum of the work necessary to achieve that total compression ΔH assumes a minimum value. For, according to a general principle in the mechanics of plastic materials, matter adapts itself to the change of outer shape which is forced on it by inner displacements which require least energy.⁹

If the work of deformation were known in analytical terms, it would be possible to calculate the true compression Δh of the inclusion by differentiating the expression for the deformation work with respect to Δh , putting the equation equal to zero and solving for Δh .

Now, suppose the relationship graphically expressed by Fig. 23 to represent the real relative deformation of inclusion and matrix as experimentally established, then, obviously, the work of deformation can be calculated if the graphical function of that experimental curve can be expressed in analytical terms. We shall now calculate the work of deformation which will serve to elucidate further the problem.

Accepting, for simplicity, an exponential form, the graph of which closely resembles the said curve, we might put:

$$\frac{\Delta h \cdot H}{\Delta H \cdot h} = e^{1 - \frac{K_i}{K}} \quad \dots \quad (i)$$

or logarithmically

$$\log \frac{\Delta h \cdot H}{\Delta H \cdot h} - 1 + \frac{K_i}{K} = 0$$

which equation might be multiplied further by an arbitrary factor C . The work of deformation is then, by integrating this equation with respect to Δh as variable,

$$C \cdot \Delta h \cdot \log \frac{\Delta h \cdot H}{\Delta H \cdot h} - 2 \cdot \Delta h \cdot C + \frac{K_i}{K} \Delta h \cdot C + C_0 = W \quad \dots \quad (ii)$$

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The integration constant C_0 follows from the condition that for $K_i = K$. . . $W' = K \cdot l \cdot \log \frac{\Delta H}{H}$ which is the work of deformation for a homogeneous mass (l denoting the length of particle). Considering only small compressions ΔH this becomes

$$W' = K \cdot l \cdot \Delta H.$$

On further making the arbitrary constant $C = K \cdot l$ thus satisfying the dimensions, we finally obtain

$$W = K \cdot l \cdot (\Delta H - \Delta h) + K_i \cdot l \cdot \Delta h + K \cdot l \cdot \Delta h \cdot \log \frac{\Delta h \cdot H}{\Delta H \cdot h} + K \cdot l \frac{\Delta H \cdot h}{H} - K \cdot l \cdot \Delta h \quad . \quad . \quad . \quad (iii)$$

In this equation the first term signifies the work necessary to compress the matrix with the yield-point K by the amount $\Delta H - \Delta h$, the second term accounts for the compression of the inclusion with the yield-point K_i by the amount Δh , and the last three terms denote the additional work which is added by the extra flow round the inclusion which Figs. 3 and 4 illustrate.

The flow always taking place so that $W = \min.$, we find that for $K_i = K$, Δh becomes $= \frac{\Delta H \cdot h}{H}$, the whole work being $K \cdot l \cdot \Delta h$. If $K_i < K$ or $K_i > K$ the sum of the three last expressions in equation (iii) for minimum work will be positive, *e.g.* extra flow takes place in both cases.

On the one hand, it is easier to compress a softer particle. A softer inclusion should consequently be compressed as much as possible, but on the other hand additional flow is then upset in the surrounding material whereby work is absorbed.

This means, in other words, that a soft inclusion undergoes greater deformation than the matrix, but only to a certain limited extent above which the additional flow in the latter would absorb more work than would be gained by a greater deformation of the softer inclusion. Even if the inclusion is infinitely soft, consisting of a frictionless liquid, such a particle is only deformed somewhat more than the groundmass, namely, with the above simplifying assumptions

$$K_i = 0 \quad W_{\min.} \text{ for } \Delta h = e \frac{h \cdot \Delta H}{H}$$

or e times as much as if the particle were of the same hardness as the matrix.

In the case of a hard inclusion, the deformation is less than that of a corresponding mass particle of the matrix, the deformation tending

to be as small as possible. The less, however, is the compression of the hard inclusion, the more considerable is the additional flow around it which also involves work. The harder particle will therefore deform somewhat, its deformation becoming less the harder it is in relation to the matrix.

If the exact curve of Fig. 23 were known, it would be possible to calculate directly the mean pressure values from equation (iii), the pressure being equal to $\frac{W}{\Delta H}$, since the inner work of deformation is equal to the outer work performed by the compressive forces. As is easily seen from equation (iii), and in analogy to the previous considerations, the mean pressure to be exerted on the test-piece diminishes with decreasing K_i and reaches a limiting amount for $K_i = 0$. For if K_i is greater than K and increasing, the pressure increases and reaches an upper limiting value. Since for simplicity an exponential curve has been chosen, this limiting value is approached asymptotically whereas in reality it is a certain definite number.

From the work of deformation it would even be possible to construct the plastic flow round an imbedded particle by graphical methods.

The exponential curve adopted only representing approximately the experimental data, the exact form of the terms in equation (iii) might differ somewhat if we had started from another, and it may be a more accurate, analytical expression for the curve in Fig. 23. The principal features shown by equation (iii), however, remain the same.

CONCLUSIONS.

Embedded particles may be harder or softer than the groundmass and may be plastic or brittle. Through the different relative flow of inclusion and matrix, additional plastic flow must take place in the vicinity of inclusions or second-phase particles.

Thus extra stresses are set up in the material leading to an increase in brittleness, as for example with aluminium, silicon, and brass containing lead.

The deformation of the different-phase particles can be followed by microscopically measuring the mean compression of a very great number of grains by statistical methods.

In alloys consisting of a groundmass with inclusions of a harder phase, the deformation of the embedded particles is less than that of the test-piece as a whole or of the matrix, and becomes nil if the stress necessary for deformation of the inclusion exceeds a certain value.

In alloys consisting of a matrix with inclusions of a softer phase, the deformation of the latter is somewhat greater than that of the matrix.

In all cases the deformation within the material is governed by the principle of minimum work of deformation. The gain in work by a greater compression of a softer particle or less compression of a harder particle being at a certain stage of equilibrium counterbalanced by more additional flow in the matrix.

If the fundamental relationship between the relative deformations of inclusion and matrix and the relative deformation stresses were known exactly by experiment, the work of deformation and the prevailing mean stress could be calculated and the flow round the inclusion found by graphical methods.

ACKNOWLEDGMENT.

The author desires to express his thanks to Mr. Ivar Olsson, Director of the Finspongs Metallverk A.B., for permission to carry out the experiments described, and for works facilities.

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DISCUSSION.

(Condensed.)

THE PRESIDENT: Dr. Unckel was trained at the Darmstadt Technische Hochschule as an engineer, and some time after graduation took a position at the Finspongs brass and copper works in Sweden, at which he has been responsible for a good deal of recent works' practice and works reorganization. He has, therefore, the advantage of an academic training with an appreciable industrial experience. Dr. Unckel's paper deals with a subject which is of very considerable importance to works' metallurgists and engineers.

Professor F. C. THOMPSON,* M.Sc., D.Met. (Member) said: Though I intend to make one or two criticisms of this paper, I should like to say how useful is this contribution to a subject which is of fundamental industrial and academic interest, but which has, up to the present, received very little attention.

* Professor of Metallurgy, Manchester University.

Rolling ← ————— → Direction.

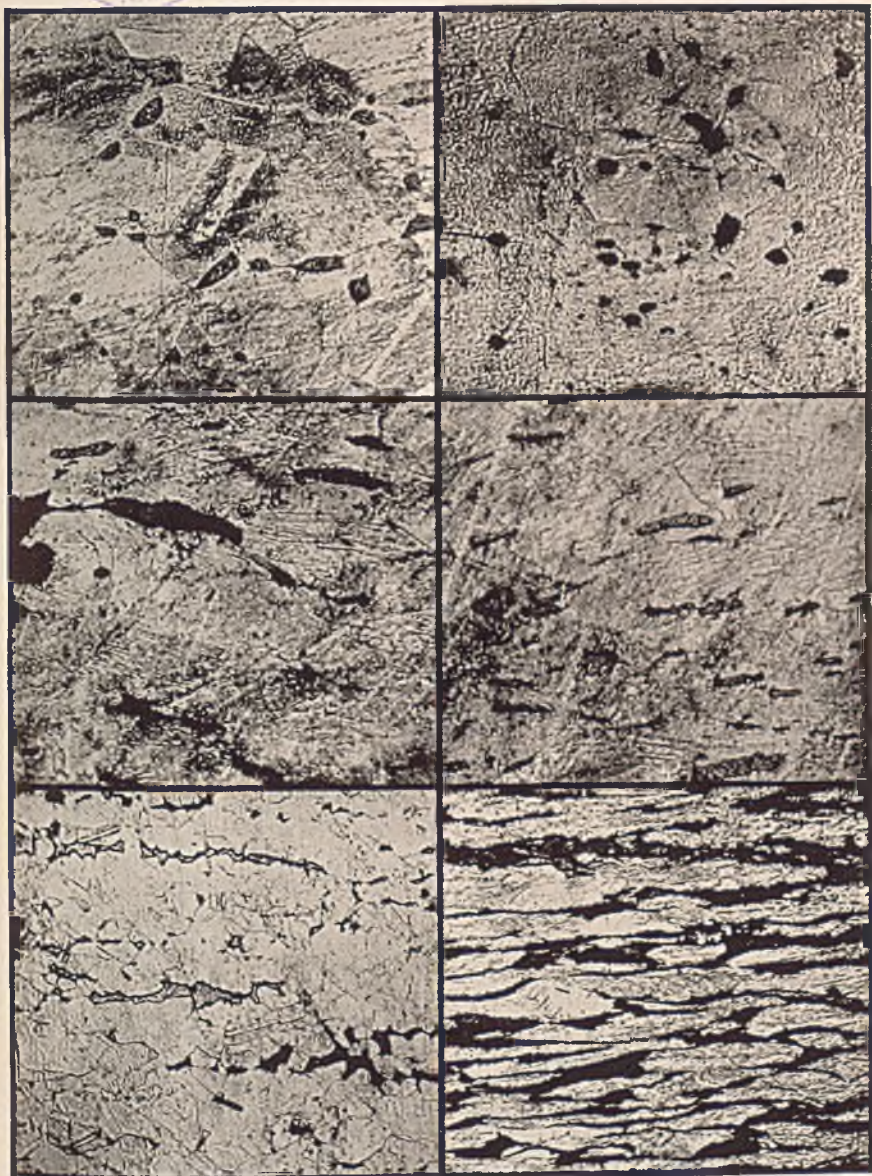


FIG. 4.—Alloy 1. Lead-brass. No Reduction. $\times 350$. FIG. 5.—Same as Fig. 4. 9.7% Reduction. $\times 350$. FIG. 6.—Same as Fig. 5. 53.3% Reduction. $\times 450$. FIG. 7.—Same as Fig. 6. FIG. 8.—Alloy 2. α - β Brass. Annealed at 600°C . No Reduction. $\times 150$. FIG. 9.—Same as Fig. 8. Annealed at 750°C . 55% Reduction. $\times 150$.

Etching Reagents: Figs. 4, 5, 6, and 7, $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$. Figs. 8 and 9, $\text{CrO}_3 + \text{HCl}$.

[To face p. 190.]

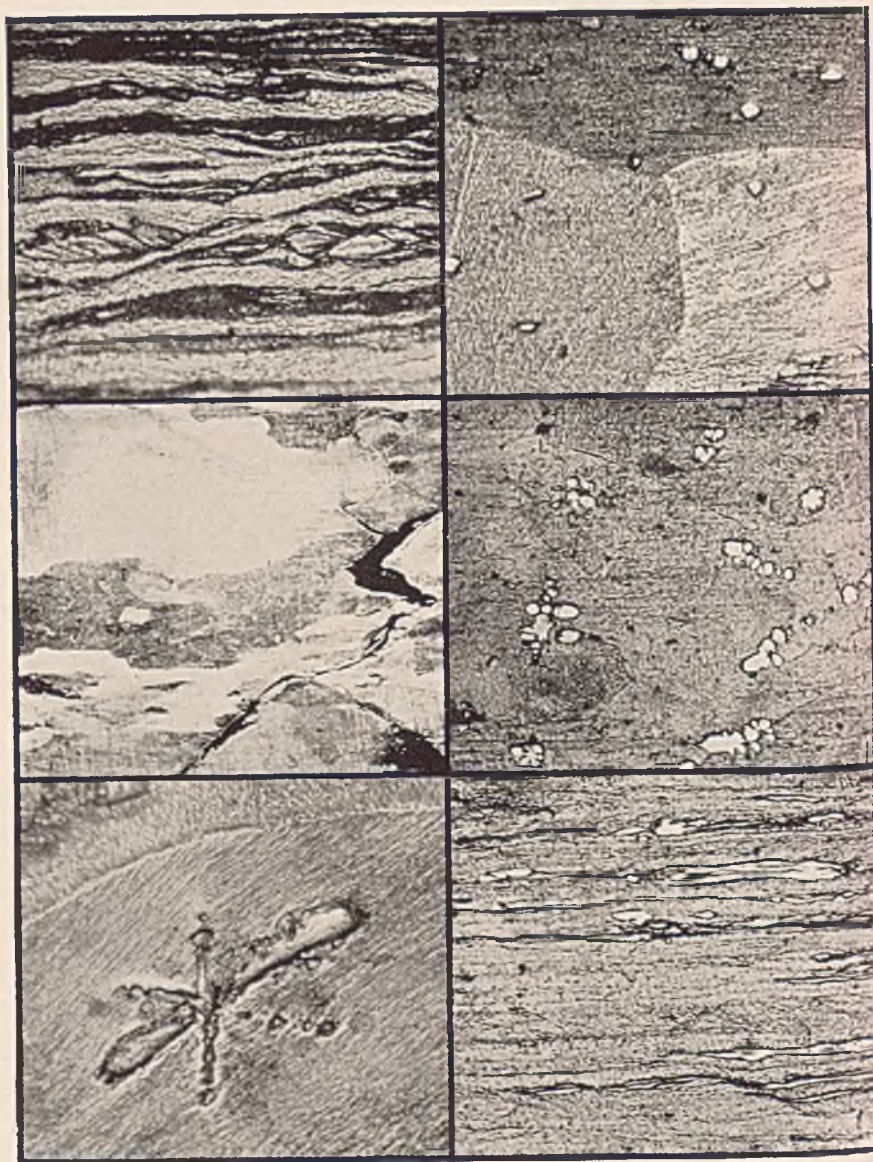
Rolling \longleftrightarrow Direction.


FIG. 10.—Alloy 2. α - β Brass. Annealed at 750° C. 82.5% Reduction. $\times 450$. FIG. 11.—Alloy
 Special Brass. Annealed at 750° C. 13.7% Reduction. $\times 350$. FIG. 12.—Same as Fig. 11.
 $\times 6$. FIG. 13.—Alloy 4. Copper-Iron. No Reduction. $\times 160$. FIG. 14.—Same as Fig. 13.
 7.65% Reduction. $\times 350$. FIG. 15.—Same as Fig. 14. 96.5% Reduction. $\times 150$.

Etching Reagents: Figs. 10, 11, and 12, $\text{CrO}_3 + \text{HCl}$. Figs. 13 and 15, $\text{NH}_3 + \text{H}_2\text{O}_2$. Fig. 14, HNO_3 .

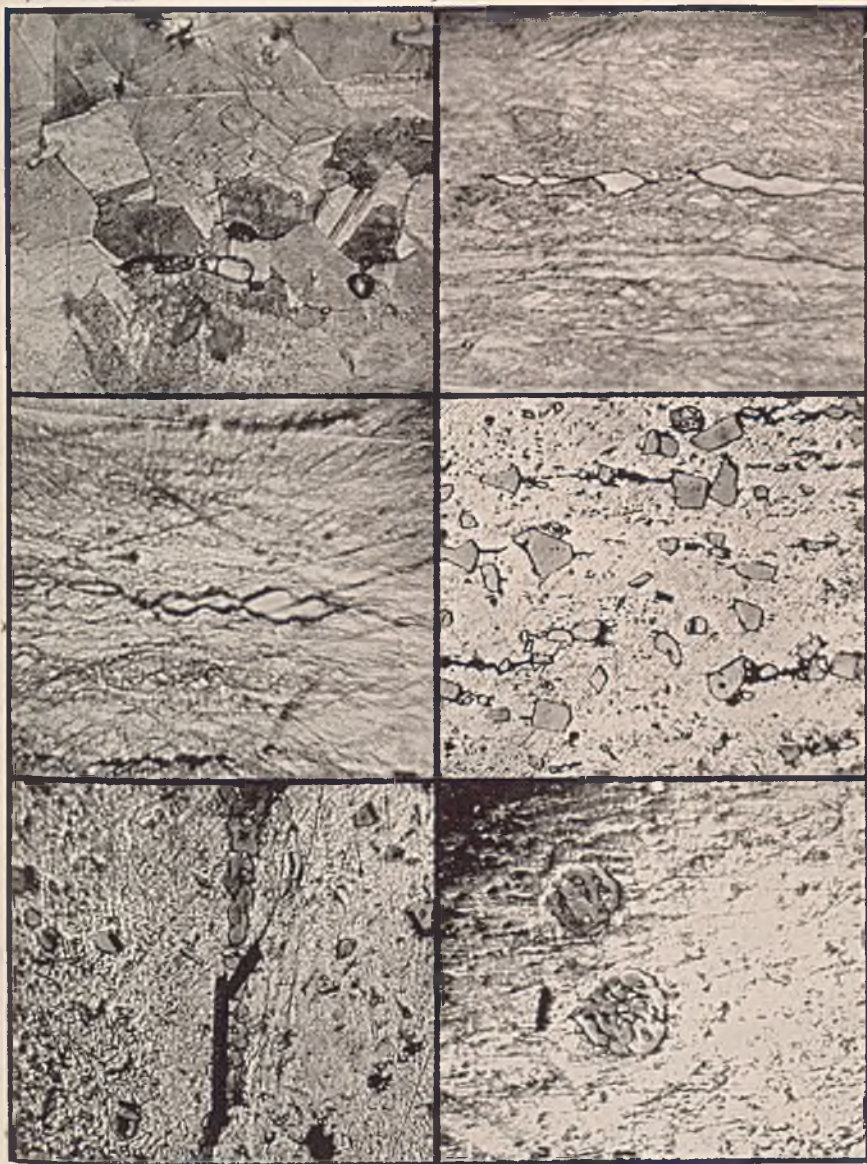
Rolling \longleftrightarrow Direction.

Fig. 16.—Alloy 5. Tin-Bronze. No Reduction. $\times 450$. FIG. 17.—Same as Fig. 16. 87.7% Reduction. $\times 1000$. FIG. 18.—Same as Fig. 17. 90.5% Reduction. $\times 1000$. FIG. 19.—Alloy 6. Aluminium-Silicon. 34.5% Reduction. $\times 350$. FIG. 20.—Alloy 7. Aluminium-Copper. 12.4% Reduction. $\times 350$. FIG. 21.—Same as Fig. 20. 34.5% Reduction. $\times 350$.

Etching Reagents : Figs. 16, 17, and 18, $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$. Figs. 19, 20, and 21, $\text{HF} + \text{HCl} + \text{HNO}_3$.

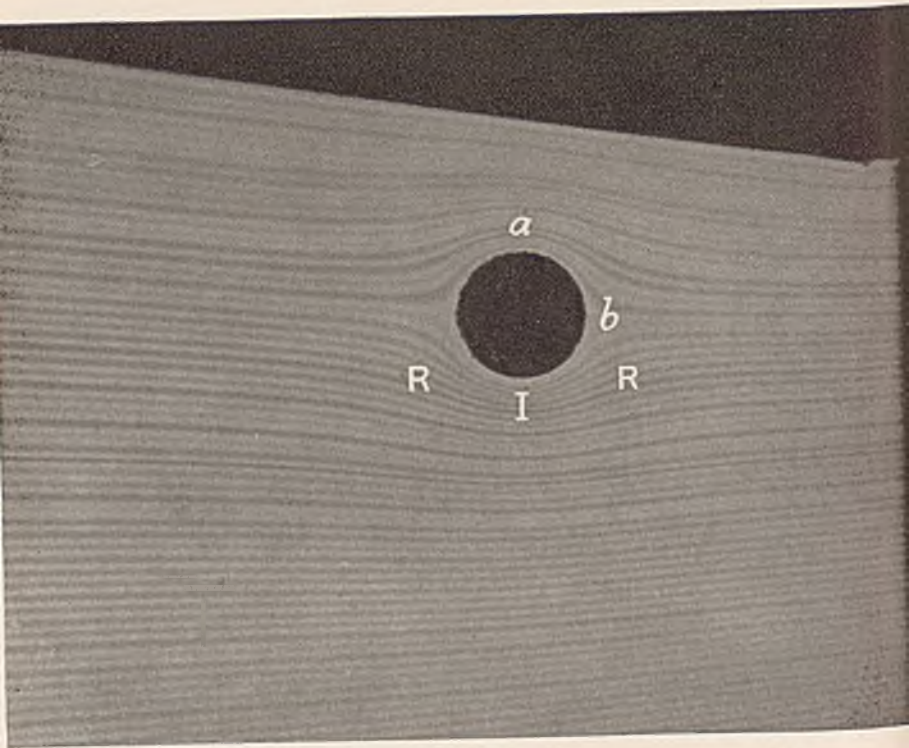


FIG. A. (Illustrating Professor Thompson's discussion.)

I know more about the effect of deformation in cold-drawing than in cold-rolling, but some work was carried out in my laboratories by Mr. Cartwright, which has a bearing on the first part of this paper. The author has assumed, I think without justification, that, in the case of a material consisting of a single phase, the deformation is uniform; in fact, in one part of the paper, he expressly states that that is the case. It is generally recognized that the effect of a stress exceeding the yield-point is to produce a pair of deformation wedges. When those wedges have ultimately met, it may be that, at any rate in many cases, the deformation is more or less uniform, but even then I am uncertain whether that is invariably the case. It is perfectly clear, however, that for reductions which are relatively small, and in which these wedges do not meet, there can be quite considerable variations both of structure and of mechanical properties in a single-phase alloy as one passes from one surface to the other.

Until comparatively recently, it has been generally accepted that segregation in an alloy is to be ascribed to variations of composition caused during the solidification process. Benedicks and Lofquist made quite a novel suggestion when they put forward the hypothesis that, when acting on material consisting of phases of different hardness, the very act of deformation could produce a segregation of those phases. I should hesitate to deny the truth of that hypothesis, but I carried out some experiments some years ago in connection with a rather different problem, regarding the manner in which plasticine would deform when inclusions of harder "play-wax" were inserted, and was unable to find any indication of this type of segregation.

I am not in a position to say what is the nature of the deformation round a square inclusion, but with the Hele-Shaw apparatus I have carried out some qualitative experiments with regard to circular inclusions, which for this purpose must be regarded as being infinitely hard. Such flow-lines are of the character shown in Fig. A (Plate XII). From those it is possible to deduce two facts: (1) that the compression is very much greater at a than at b , and (2) that the velocity of flow of the material round the inclusion varies considerably, being reduced before and after reaching the inclusion, *i.e.* at R, R , but much increased at I . I found no indication, however, of the effects shown in Figs. 1 and 2, where the author suggests that at R, R the flow lines tend to approach each other. I am not exactly sure how the author obtained these figures, and it would be of interest if he would elucidate this point.

Dr. Unckel's method seems to be capable of yielding information regarding the mean effect of these harder or softer inclusions. When all is said and done, however, the mechanical properties of a two-phase or more complex structure are due to the effect of the mean deformation of the material as a whole, together with the effects of the local irregular deformations which occur around the phase interfaces. At the present time, it is very difficult, if not impossible, to say what proportion of the total influence of the deformation is due to the latter factor, but, so far as the ill effects of mechanical deformation are concerned in producing cracks, for example, I am inclined to think that, in some cases at any rate, those local irregularities may have very considerable importance.

Although I have made certain criticisms of this work, I want to repeat that in my view this paper represents a valuable contribution to knowledge.

Dr. C. H. DESCH,* F.R.S. (Vice-President): I agree with Professor Thompson that the great interest of this paper lies in the fact that it opens up a new subject, and I also agree with the criticisms which he has made. I do

* Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

not think that Figs. 1 and 2 represent what will happen in such a case, and information on that point might be gained from experiments, of the kind referred to by Professor Thompson, with the Hele-Shaw apparatus, such as have already been made by engineers in studies of the design of engineering structures. Obstacles of various forms have been examined in that connection, and I believe that the flow lines do not go in the directions shown.

I would mention, however, the possibility of further experimental work. We often refer to the close connection between the ferrous and non-ferrous branches of metallurgy, and I would direct attention to Hanemann's "*Atlas Metallographicus*," in which the actual flow of steel around slag particles and hard masses of cementite is shown in very beautiful photomicrographs. One effect which takes place, and is not mentioned in the paper, is that when the inclusion is of a brittle character it may fracture, and a long inclusion may break up into a chain of small particles, the plastic material then flowing so as to fill the space between. That happens in steels and has been confirmed at Teddington. Then, of course, the deformation described here is very considerably changed.

Dr. Unckel rightly refers to the amount of deformation of hard substances which can be brought about if they are supported all round, and he mentions the work of von Karman on marble. Before that Hall carried out remarkable experiments in which a cylinder of marble was deformed nearly to a sphere merely by supporting it all round. Some years ago I published the photograph of a very hard material, a piece of white iron, which had been caught in the gearing of a very heavy rolling mill. It had been sufficiently supported not to break up into fragments, and it deformed into a wavy material recalling Damascene steel. The deformation of an entirely supported inclusion, therefore, cannot be inferred from the behaviour of such a material when studied in the free state.

If the study of this subject is to be continued, as it certainly deserves to be, the technique of preparation of non-ferrous specimens, in order to show the inclusions, will have to be improved. Steel metallurgists have been very successful in that way; Hanemann's photographs are particularly beautiful, and Portevin has developed the technique of polishing steels to show the inclusions without any accidental concealing of the structure by flow over them. It will be necessary to do that for the non-ferrous metals also, because, although these photographs are very interesting, I am sure that they miss many features which would be developed if the polishing could be improved.

These are minor criticisms. The author deserves great credit for having opened up such an interesting subject, and, though I think that he has carried the mathematical treatment further than the experiments justify at present, Fig. 23 is sufficiently interesting in itself to make it worth while to accumulate more data and to ascertain whether such a general tendency can be confirmed.

DR. R. GENDERS,* M.B.E. (Member of Council): This is a subject which concerns the steel metallurgist equally with the non-ferrous metallurgist. The localized effects of the mode of distribution of the hard carbide in steel on the behaviour of the surrounding soft matrix is a matter of considerable interest. The general subject is one which has not so far been studied fundamentally, and this paper is a welcome beginning. In work on brass carried out some years ago at Woolwich, we examined the effect of rolling a brass ingot on the shape and behaviour of the inclusions of zinc oxide, which are extremely hard particles and very brittle. We found that in the cast ingot the oxide particles were of various shapes, more or less rounded; there were also crystallite shapes which were not common unless the inclusions were

* Research Department, Woolwich.

synthetically produced in large quantities by addition of copper oxide. When the ingot was rolled, the zinc oxide inclusions tended to split without deformation, and to part readily into small separate pieces, enclosed by metal which flowed into the gaps. Eventually, each original ingot inclusion formed a long line of very small separate particles, and it was possible in some cases to see a connecting line of separation through the brass between the particles. The point of importance which seemed to arise was that possibly in this and in other cases of cold-rolled metal, no welding of the material which flowed in between the broken-off fragments occurred, so that to all intents and purposes a string of inclusions might form a continuous line of separation, and not a line of solidly enclosed particles as it appears in an ordinary microsection. In cross-rolled sheet a small plane area of partial discontinuity might be formed in this way.

Dr. W. J. P. ROHN* (Member): As I have previously pointed out, these studies are of great interest from the point of view of the technique of rolling. There has been some question about the shape of the flow lines in the vicinity of the harder (or softer) particles. I think that this shape is influenced not only by the fact that there are two materials in contact with each other which are of different hardness, but also that the adhesion of one material to the other must have some influence. I believe that the shape of those lines at those parts would differ according to whether a harder particle was inserted simply into a hole drilled into the larger piece or whether this insertion was soft soldered or hard soldered into the hole. The forces at the boundary between the two materials may influence to some extent, and perhaps a great deal, the shape of the lines at those places. In any attempt to obtain a clear understanding of what happens in the deformation of such a compound material, those forces between the material and the inclusion should not be overlooked.

CORRESPONDENCE.

DR. FREDERICK N. RHINES† (Member) and Mr. R. WARD,‡ B.S.: The subject of the plastic flow of alloys in the neighbourhood of dispersed second phases seems due to be one of particular importance at the present stage of the development of the metallurgical science.

Although Dr. Unckel's statistical method of investigation appears quite adequate for the present research, we feel that in some instances, at least, a direct observation of the movements occurring about an individual particle might be more revealing. Indeed, the statement appearing in the paper to the effect that ". . . it is not possible to follow the deformation of definite individual grains . . ." seemed to us to be in the nature of a challenge and moved us to devote a few days to work in this direction. As a consequence, we are able to suggest a procedure by which it will be possible to observe the details of plastic movement in a more or less limited number of cases.

The method consists in ruling a grating upon the polished surface of a specimen and observing with a microscope the distortions appearing after successive steps in working. Ruling is accomplished by the aid of a Micro-character hardness tester, the only necessary accessory being a long lever arm on the translation gear of the mechanical stage, to assist in locating the lines compactly. A very light or no load on the cutter was found most satisfactory,

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and straighter lines were obtained by sweeping the cutter rapidly across the sample than by a slow movement.

Examples of the type of grating obtained by this means are given in Fig. B and E (Plate XIII). The photomicrographs following, Figs. C, D, F, and G, show the same areas after cold-rolling to reductions in thickness of 5 and 15 per cent. In both these instances, the alloy is one of approximately 12 per cent. antimony and 88 per cent. tin, in the cast state, and exhibits a matrix of tin-rich solid solution with hard particles of SbSn (β') embedded in it. The sample has been etched, prior to ruling, with 4 per cent. nital. All photographs are at a magnification of $\times 85$, oriented with the direction of rolling horizontal with respect to the page. The surface pictured was, of course, kept perpendicular to the surface of the rolls in order to avoid the erasure of the grating, and to conform to the conditions set up in Dr. Unckel's experiments.

It will be evident that this method is limited by the fineness and closeness of the lines which can be drawn with the equipment at hand, and by the necessity for ruling the grating upon an external surface of the sample. The latter objection might perhaps be avoided by embedding the ruled sample in a plastic matrix, or by some equivalent scheme.

Surface rumpling caused by working interferes, of course, with the photographic recording of the patterns, but visual observation is practicable even with relatively high reductions.

By an inspection of Figs. C and D, one may see quite clearly the distortion about the hard white particle of antimony-tin constituent, and that it conforms closely to that given by Dr. Unckel in Fig. 1 (p. 174). In addition, it will be seen that the rotation of the individual grains of the matrix is quite marked, and readily discernible. Finally, it is noteworthy that some of the most pronounced movements have occurred at the grain boundaries. This latter effect is shown more clearly perhaps by the second series of pictures, (E), (F), and (G).

The AUTHOR (*in reply*): Professor Thompson does not agree that deformation by rolling is uniform, and refers to the formation of deformation-wedges.

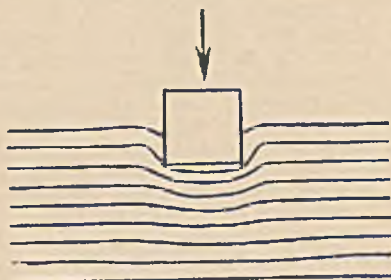
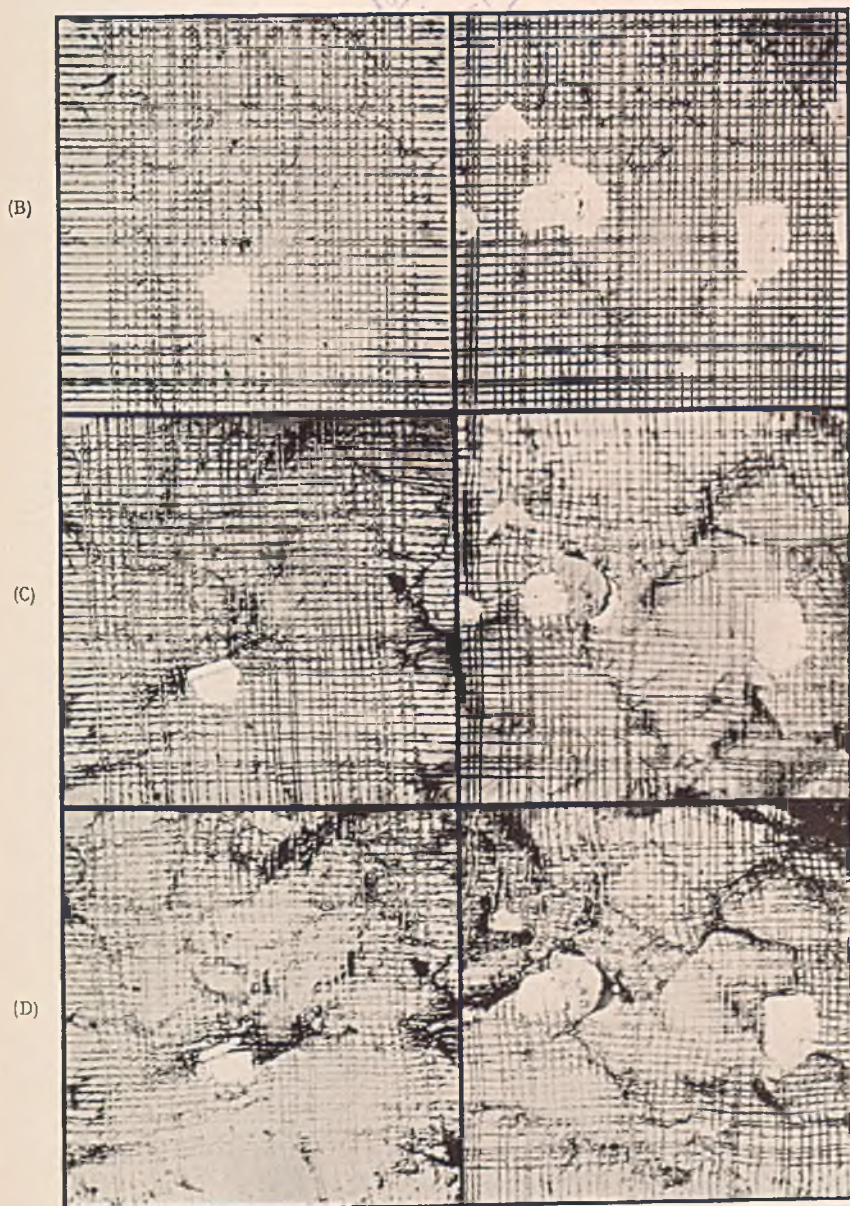


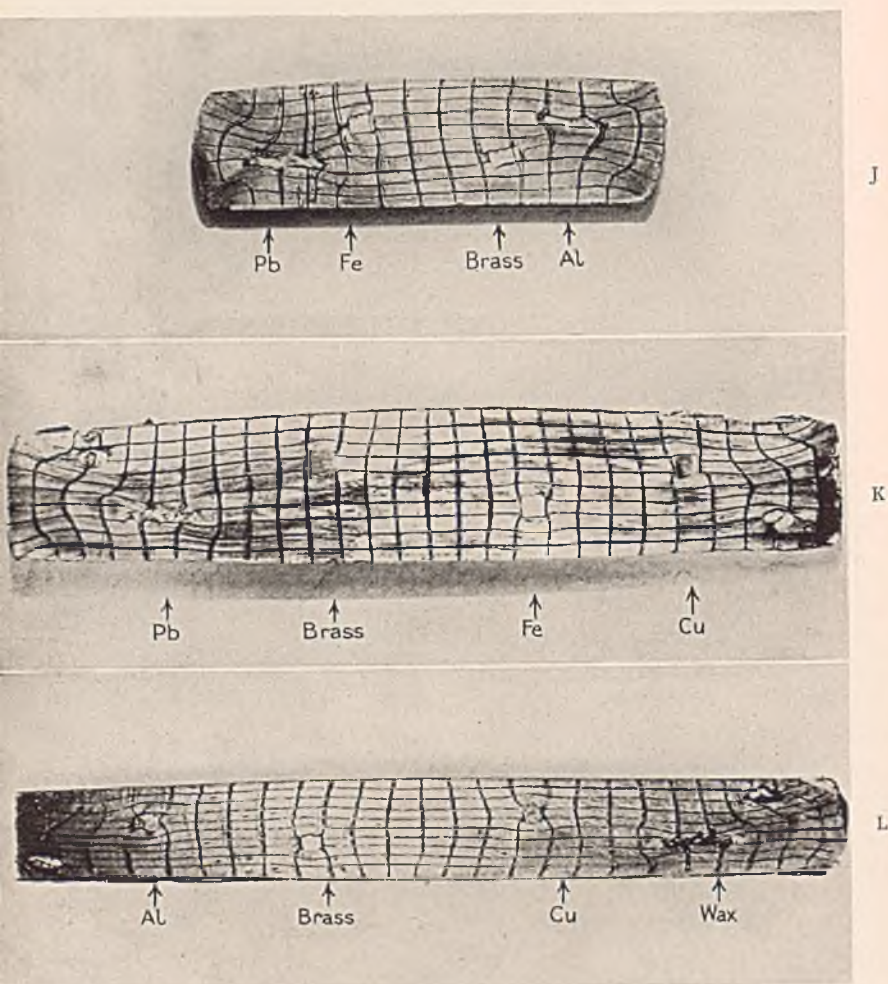
FIG. II.

Experiments by Siebel, Ekelund, Unckel, and others (quoted in the paper) on the rolling process have shown, however, that the deformation may, at least approximately, be regarded as uniform. In a paper * on rolling mechanics I dealt specially with a comparison of the rolling and compression processes. The Hele-Shaw picture given by Professor Thompson is of great interest. I would emphasize, however, that Figs. 1 and 2 of the paper do not represent

* "Flow of Material in the Rolling Process, and Analogies between Rolling and Compressing" (in Swedish), *Teknisk Tidskrift, Ård. Bergsvetenskap.*, 1937, 67, 17-21.



FIGS. B-G.—Alloy of 12% Sb and 88% Sn. Figs. B and E as cast; C and F cold-rolled 5%; D and G cold-rolled 15%. Etched in 4% nital. $\times 85$; reduced in reproduction. (Illustrating Dr. Rhines' and Mr. Ward's communication.)



FIGS. J-L.—Compression Tests with Specimens Divided Along Symmetry-Plane and Provided with Insertions and Cross-Net.

FIG. J.—Copper Specimen with Insertions of Lead, Iron, Brass, and Aluminium; Compressed. Reduction in Height 40%.

FIG. K.—Aluminium Specimen, with Insertions of Lead, Brass, Iron, and Copper; Compressed. Reduction in Height 32%.

(To Extreme Right and Left Aluminium Guide-Pins for Assembling.)

FIG. L.—Lead Specimen with Insertions of Aluminium, Brass, Copper, and Wax; Compressed. Reduction in Height 47%.

(To Extreme Right and Left Lead Guide-Pins for Assembling.)

stream-lines but the *displacements or deformations* of the original horizontals and verticals. The heading on p. 174 might have been better if it had read "Deformation Round an Inclusion."

Regarding the closing up of the horizontals above and beneath a hard inclusion, the following consideration may be helpful. By virtue of the principle of reversibility one can imagine the matrix as being at rest and the inclusion moving towards it. It will be seen from Fig. H that the horizontals close up beneath the inclusion, their distance being smallest in its immediate neighbourhood. Fig. I may show, in exaggerated form, the arrangement of the *stream-lines* on rolling a material with a very hard inclusion. The position of the stream-lines without the presence of an inclusion is indicated by dotted lines. Before entering the rolls (inclusion at position A) all stream-lines are parallel, the velocity being the same throughout the thickness. The same applies to position C after leaving the rolls, the velocity being correspondingly greater. Between the rolls, considerable displacements of material, and thus

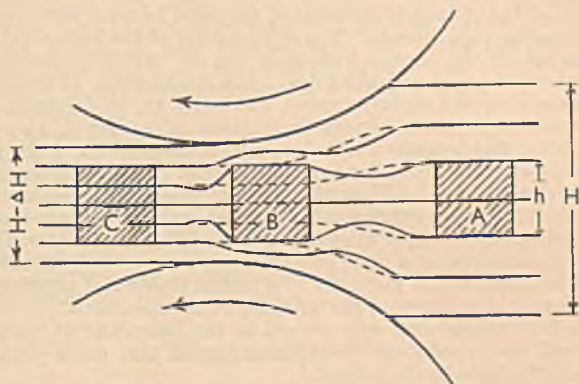


FIG. I.

high velocities, occur above and beneath the inclusion. This diagram resembles Professor Thompson's Fig. A (Plate XII) in some respects. The inclusion being assumed to be very hard, all points within it have the same velocity, which in position B has a value between that in positions A and C. The velocity above and beneath the inclusion is increased, since in the case of a hard inclusion less material (height $H - h$) has to take up the total reduction ΔH , whereas at a distance from the inclusion the compression ΔH is shared by the total thickness H . The distance from each other of the original horizontals (not stream-lines) in Fig. 1 must, therefore, be less above and beneath the inclusion than at its sides. In drawing the diagrams Figs. 1 and 2 it was thus accepted that, in case of a hard inclusion, the original horizontals close up above and beneath it, and conversely open out in the case of an inclusion softer than the matrix. On the other hand, the disturbance caused by the inclusion is certainly levelled out at some distance from it, the original horizontals becoming equidistant. The horizontals were drawn first, closing up in case of a harder inclusion and *vice-versa* with a softer one. (The degree of this closing up was chosen after some arbitrary law in the schematical figure). The verticals were then drawn so that the area of each element (originally quadratic) is the same everywhere (thus satisfying the law of incompressibility). In this way Figs. 1 and 2 were obtained.

To verify experimentally the assumptions made, the following experiments have been carried out since the completion of the paper. Test-pieces of copper, aluminium, and lead consisting of two longitudinal halves were provided with insertions of materials harder and softer than the material of the test-pieces, namely, iron, brass, copper, aluminium, lead, and bees-wax. These inclusions were inserted in square holes through the test-piece halves, and matched each other when the two halves were laid together. Moreover, the dividing planes were provided with a square net of scratch marks filled with lamp-black. These test-pieces as made up were compressed in a special die which allowed two-dimensional flow only, the thickness of the test-pieces remaining the same. Figs. J, K, and L (Plate XIV) show one half of each test-piece after compression. The deformation of the matrix is shown by the distortion of the original squares. It will be seen that the details anticipated in Figs. 1 and 2 are confirmed by this experiment, and especially that the original horizontals are closed up above and below harder inclusions, and conversely with softer ones. The original verticals also show the shape of Figs. 1 and 2. Regarding the deformation of the inclusions themselves, the same features were observed as in the cold-rolling experiments. The deformation of the test-pieces is somewhat disturbed by the surface friction in the die, which appears especially at the front edges (right and left sides of the specimens). (The upper sides of the specimens appear slightly curved, this being due to deformation of the movable press steel-plate.) Apart from these experiments, those of Dr. Rhines and Mr. Ward, referred to below, also confirm Fig. 1 of the paper.

Part of the above refers to Dr. Desch's remarks. Regarding the fracturing of brittle inclusions, I would say that, contrary to Dr. Desch's statement, this fracturing is expressly referred to in the paper in the cases of the aluminium-silicon and aluminium-copper alloys (p. 184, and Figs. 19 and 20, Plate XI). The plastic deformation of a piece of white iron, referred to by Dr. Desch, is a remarkable example of the plasticity of a brittle material if supported on all sides. I accept the criticism of the polishing of the specimens.

Dr. Genders' suggestions with regard to the behaviour of hard carbide particles, and his remarks on the deformation of zinc oxide particles, are valuable contributions to the subject.

Dr. Rohn is correct in stating that the forces at the boundary between the inclusion and the surrounding material must be taken into account. With the test-pieces Figs. J, K, and L (Plate XIV) (shown at the meeting by lantern slides) it is, however, experimentally difficult to obtain intimate contact between the insertions and the matrix. With insertions of iron and brass in the copper test-piece an attempt was made to obtain the contact by soft-soldering. Apparently, the contact is of minor importance in the case of inclusions softer than the matrix, since they tend to elongate more than the surrounding material, and therefore exert a pressure on the latter.

Dr. Rhines' and Mr. Ward's experiments are extremely interesting. Their method is very ingenious and will in my opinion be most valuable in further investigations. The effect of the free surfaces of the specimens could be avoided if the grating were applied at the dividing-plane of a test-piece consisting of two halves, as with my rolling experiments, quoted above, and the compression experiments illustrated in Plate XIV. The two halves might be clamped together, or rolled between guides. In addition, the friction on the rolls would help to hold the halves together. Dr. Rhines' and Mr. Ward's proposal to apply a fine grating to two-phase alloys avoids the difficulties of obtaining good contact between the inclusion and the surrounding material, to which I have alluded in my reply to Dr. Rohn. Naturally, the results will be the more clear and reliable the coarser the grain-size for a given line-distance of the grating.

A NEW INTERMEDIATE PHASE IN THE ALUMINIUM-COPPER SYSTEM.* 776

By A. G. DOWSON.†

SYNOPSIS.

This work was originally undertaken to fix more accurately the position of the boundaries between the β and γ phases in the aluminium-copper system at high temperatures. The copper-rich end of the aluminium-copper equilibrium diagram as at present accepted is shown in Fig. 1. The present investigation is confined to the area enclosed in the rectangle *a b c d*.

A series of alloys containing between 12.5 and 18 per cent. aluminium by weight were examined above 900° C. by thermal, micrographic, and dilatometric methods. A new stable phase between 14 and 17 per cent. aluminium has been shown to exist above 963° C., at which temperature it decomposes into a eutectoid mixture of β and γ . The eutectoid composition is 15.4 per cent. aluminium by weight. The new phase, like β of high aluminium content, cannot be retained by quenching, and it is impossible, therefore, to distinguish the two under the microscope. Both appear half tone with the γ white.

MATERIALS AND MELTING.

THE materials used were the purest obtainable, being not less than 99.99 per cent. pure. The alloys were made under hydrogen by melting most of the copper, adding the aluminium, and then the rest of the copper. Stockdale¹ found that a more homogeneous melt is obtained in this way. The melting was done in Salamander crucibles lined with Alundum. The specimens for microscopic examination were cast in a 1 cm. circular steel mould; those intended for thermal investigation were allowed to cool slowly in the crucible. The specimens examined microscopically were analyzed (see Table I) and in most cases the composition was within 0.05 per cent. of that intended. Iron was just detected in some cases, but the amount of impurities was so small in all cases that the specimens used in the other experiments were not analyzed.

EXPERIMENTAL METHODS.

The liquidus curve and the peritectic line *HD* were determined by cooling curves taken directly on the screen of a water dropper.¹

* Manuscript received January 16, 1937.

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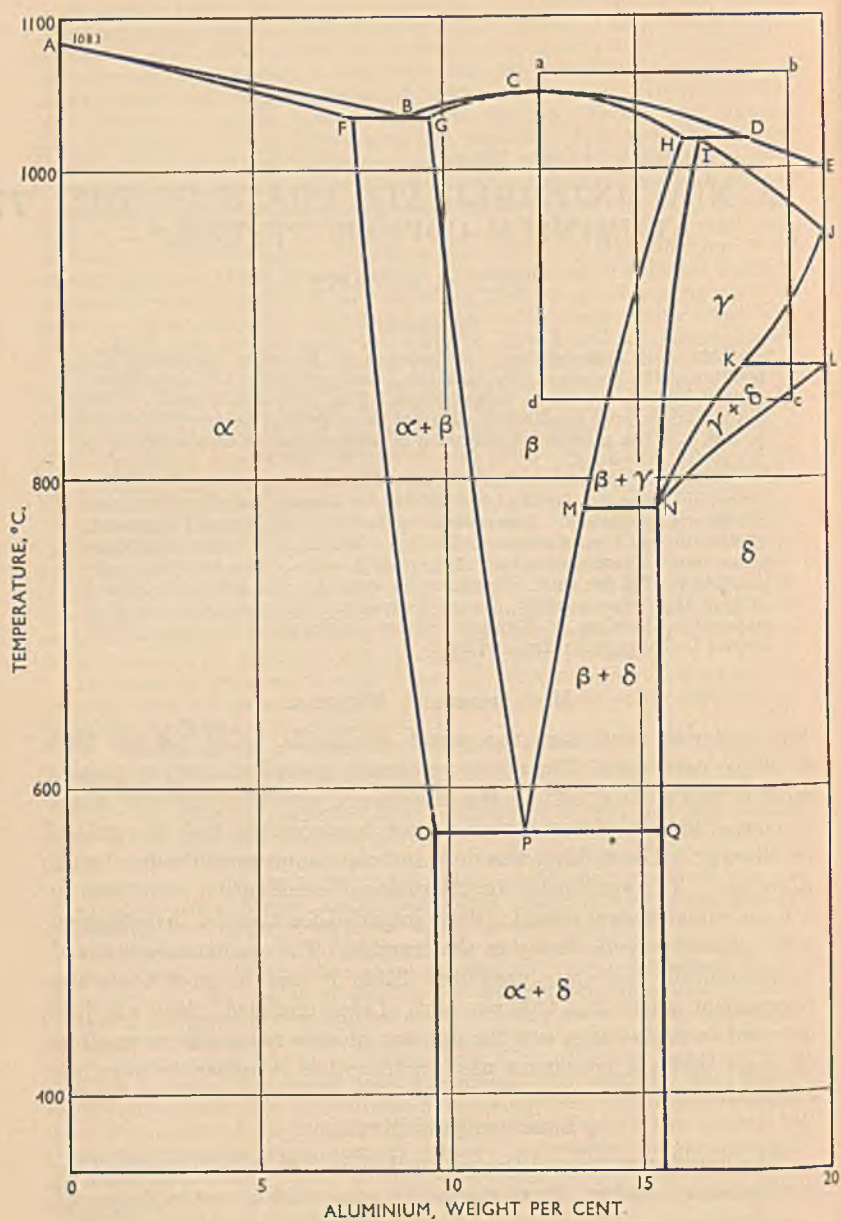


FIG. 1.

Differential heating and cooling curves on solid specimens and more particularly the micrographic examination of quenched specimens were used to determine the other phase boundaries. A dilatometer was used to investigate the positions of certain boundaries which could not readily be detected by other methods.

Temperatures were measured by means of a platinum/platinum-10 per cent. rhodium couple enclosed in a thin-walled silica tube, in conjunction with a potentiometer. This apparatus could detect a potential difference equivalent to 0.2°C . The absolute values given are not claimed to be accurate to this figure, but the temperature

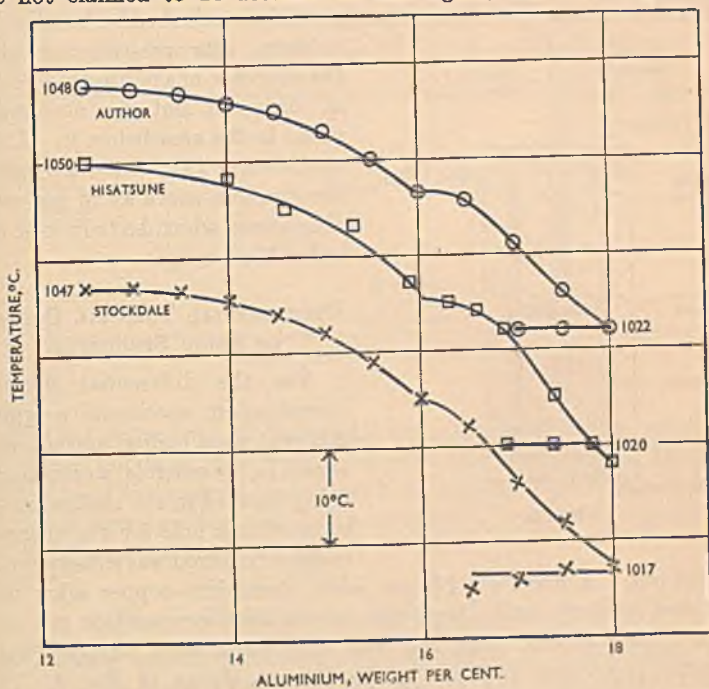


FIG. 2.

differences between points on the liquidus curve are correct at least to the nearest 0.5°C . The agreement, mentioned later, between temperatures found on heating curves with those on cooling curves indicates that the absolute values are probably accurate to this figure, since the thermocouple was checked frequently on the melting point of pure copper, without any variation being observed.

DIRECT COOLING CURVES OF MOLTEN ALLOYS.

Specimens weighing 200 grm. were used, but fresh materials were not employed for each composition, one alloy being "diluted" with copper

to make the next specimen. By this method it was hoped to get the difference between the freezing points more accurately. Three separate melts were made, one for the range 12.5–14 per cent. aluminium, one for 14–15 per cent. aluminium, and the third for the range 15–18 per cent. aluminium.

When the alloy was thoroughly molten the hydrogen was turned off and the current in the furnace reduced so that the alloy cooled at a rate of 1° – 2° C. per minute. The results obtained are plotted on Fig. 2 with the results given by Stockdale¹ and Hisatsune² on the same scale.

It will be seen that all three curves show a break at about 16 per cent. aluminium. This break was apparently overlooked by both earlier workers. Its presence indicates the existence of a peritectic reaction at this point and of a new stable phase in the area below it. J. H. Andrew³ in 1915 found a break in the liquidus curve at 16 per cent. aluminium, which he took to be the end of the β range.

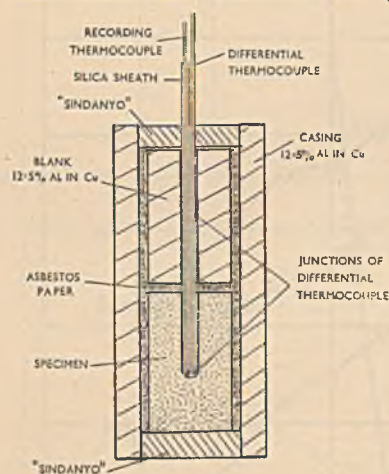


FIG. 3.

DIFFERENTIAL THERMAL CURVES OF SOLID SPECIMENS.

For the differential thermal investigation, specimens weighing 200 grm. were melted and allowed to cool in the crucible, a carbon rod being inserted in the molten metal to provide a hole for the thermocouples. This rod was subsequently

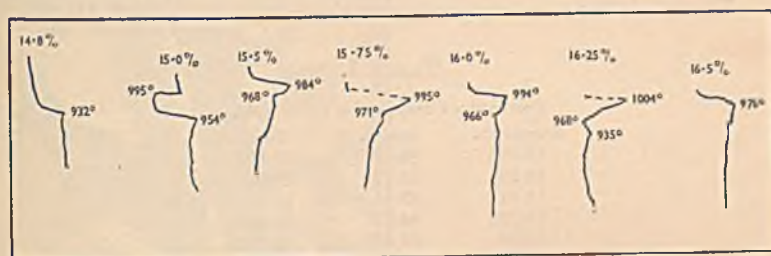
drilled out. A blank of 12.5 per cent. aluminium-copper alloy was prepared similarly, and a large tube of the same composition was cast in a special mould. The specimen and blank were wrapped with asbestos paper and inserted in the tube as shown in Fig. 3. The differential couple was of Chromel-Alumel.

The whole was placed inside a vertical electric tube furnace and annealed for some hours at about 980° C. The current was reduced so that the specimen cooled to about 800° C., where it was maintained for $\frac{1}{2}$ hr., before beginning a heating curve. The heating circuit contained a device for progressively increasing or decreasing the current flowing through the furnace, and by suitable adjustment a fairly constant rate of heating or cooling could be obtained. Most of the curves were taken at a rate of 2° – 3° per minute on a double-thread recorder, one galvano-

meter of which recorded the e.m.f. developed by the differential couple, while the platinum couple was attached to the other. To increase the sensitivity of the latter circuit, a "back e.m.f." was used in conjunction with the platinum couple, so that 8 cm. on the scale represented just over $200^{\circ}\text{C}.$; but even so, the accuracy was not more than $\pm 2^{\circ}\text{C}.$ The heating curves for some of the alloys are shown in Fig. 4.

It was inadvisable to heat the alloys above $1020^{\circ}\text{C}.$ for fear of melting, and therefore, cooling curves did not, as a rule, "settle down" before reaching the temperatures of the arrests on the heating curves. They were, therefore, neglected.

The heating curves show an arrest between 965° and $970^{\circ}\text{C}.$ in four different alloys in the range 15.5-16.25 per cent. aluminium. This



DIFFERENTIAL HEATING CURVES

FIG. 4.

suggests the presence of a eutectoid transformation in this range, and the other points fit in with this. More accurate methods of fixing the positions of the various boundaries were employed later, and, in order to avoid overcrowding, the points obtained by the above method are omitted from the final diagram.

MICROGRAPHIC INVESTIGATION.

A tilting quenching furnace was constructed for this work, a silica tube slightly larger than 1 cm. internal diameter being used inside a refractory tube wound with Nichrome wire. The furnace was constructed so that it rotated about an axis at right angles to the tube which was held horizontal during the heating. To quench the specimen the operator unscrewed the clamp, removed the thermocouple, and rotated the furnace through a right angle. The specimen dropped vertically into a cold aqueous solution of calcium chloride. The 1-cm. diameter cast bars were annealed in the furnace for 5 hrs. at $950^{\circ}\text{C}.$ to ensure homogeneity, and then slowly cooled. Small pieces from the bars were heated at suitable temperature intervals for 1 hr. and quenched. When

so treated, alloys containing 15 per cent. aluminium or more invariably split up into small pieces and, therefore, only one specimen could be handled at a time.

The specimens were etched in a 10 per cent. solution of ammonium persulphate in water. The γ -phase, when present, appears pale blue by comparison with the β , and it is easy, therefore, to detect the presence or otherwise of primary γ in the etched specimen. In alloys containing more than 14.5 per cent. aluminium, the β -phase decomposes on quenching giving an intimate mixture of β of lower aluminium content and γ . These γ crystals, by their small size, cannot be confused with the "primary γ " originally present at the temperature from which the specimen was quenched.

The specimens were analyzed, with the results shown in Table I.

TABLE I.

<i>Percentage Composition by Weight.</i>		
Aluminium.	Copper.	Total.
14.085	85.85	99.935
14.20	85.79	99.99
14.81	85.14	99.95
15.225	84.72	99.945
15.54	84.425	99.965
15.77	84.225	99.995
16.11	83.885	99.995
16.44	83.56	100.02

When the results of this investigation are plotted, they show a break between 960° and 965° C. in the boundary, *MH*, shown continuous in Fig. 1. Fig. 11 shows it stepped, *MR, RS, SH*; *RS* being horizontal.

The existence of this break is further confirmed by the photomicrographs (Figs. 5-10, Plate XIVa). Primary γ appears white and the decomposed β half tone. There is a very small amount of primary γ in the alloy quenched from 965° C., *i.e.* just above the break (Fig. 5), while the same alloy quenched from 960° C., Fig. 7, shows nearly half the field to consist of γ . The alloy quenched from 955° C. (Fig. 9) is practically identical with that quenched from 960° C. (Fig. 7). Comparison of the three photomicrographs at a magnification of 350 shows that the decomposed phase in Fig. 6 is coarser than that in Figs. 8 and 10 and also contains more γ (white).

The experiments described above leave no doubt of the existence of a new phase, as shown on Fig. 11; and, therefore, above the break referred to, the phase which decomposes will not be β , but the new phase. However, since both decompose into an intimate mixture of β of lower aluminium content and γ , it is impossible to distinguish the two under the microscope. Therefore, the expression "break in the β

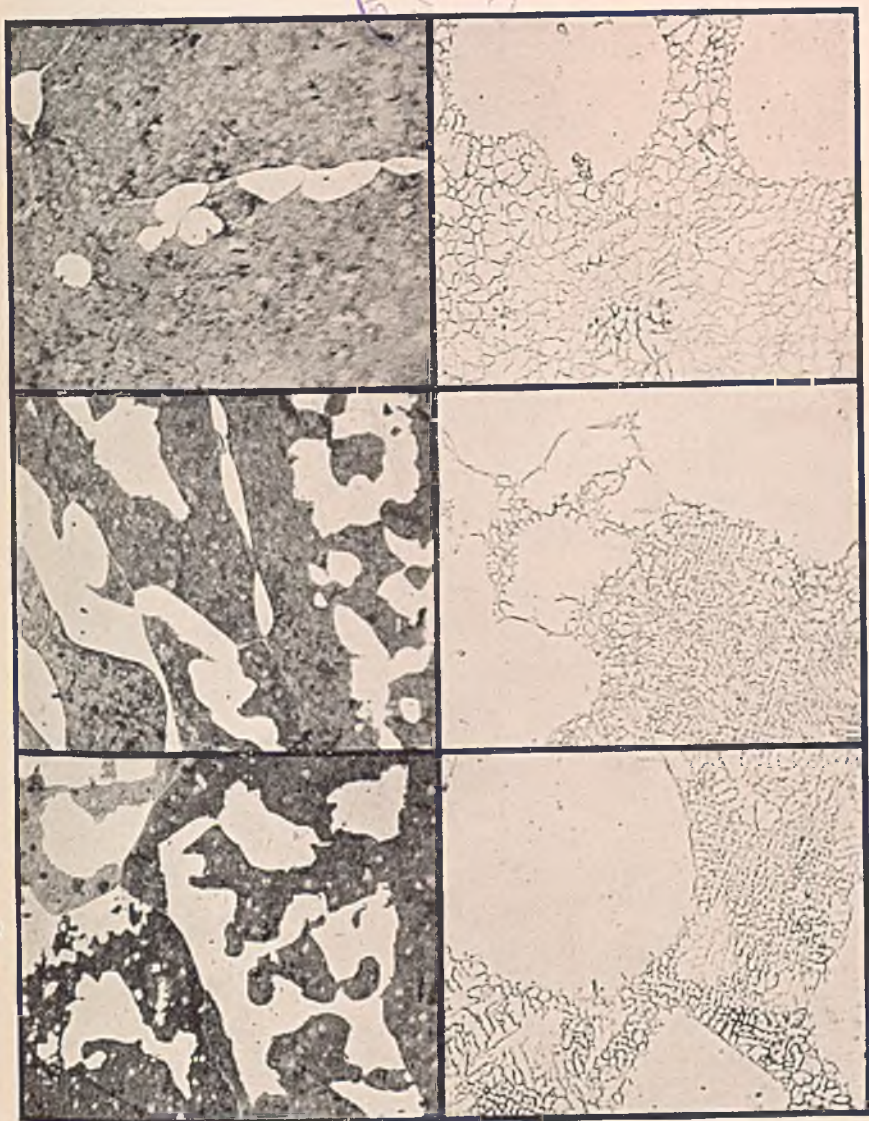


FIG. 5.—15.54% Aluminium. Quenched from 965° C. $\times 30$.
 FIG. 6.—Same as Fig. 5. $\times 350$.
 FIG. 7.—15.54% Aluminium. Quenched from 960° C. $\times 30$.
 FIG. 8.—Same as Fig. 7. $\times 350$.
 FIG. 9.—15.54% Aluminium. Quenched from 955° C. $\times 30$.
 FIG. 10.—Same as Fig. 9. $\times 350$.

All Etched in 10% Solution of Ammonium Persulphate.

[To face p. 202.

boundary," though not a strictly accurate statement, is an adequate representation of the facts as revealed by the microscope.

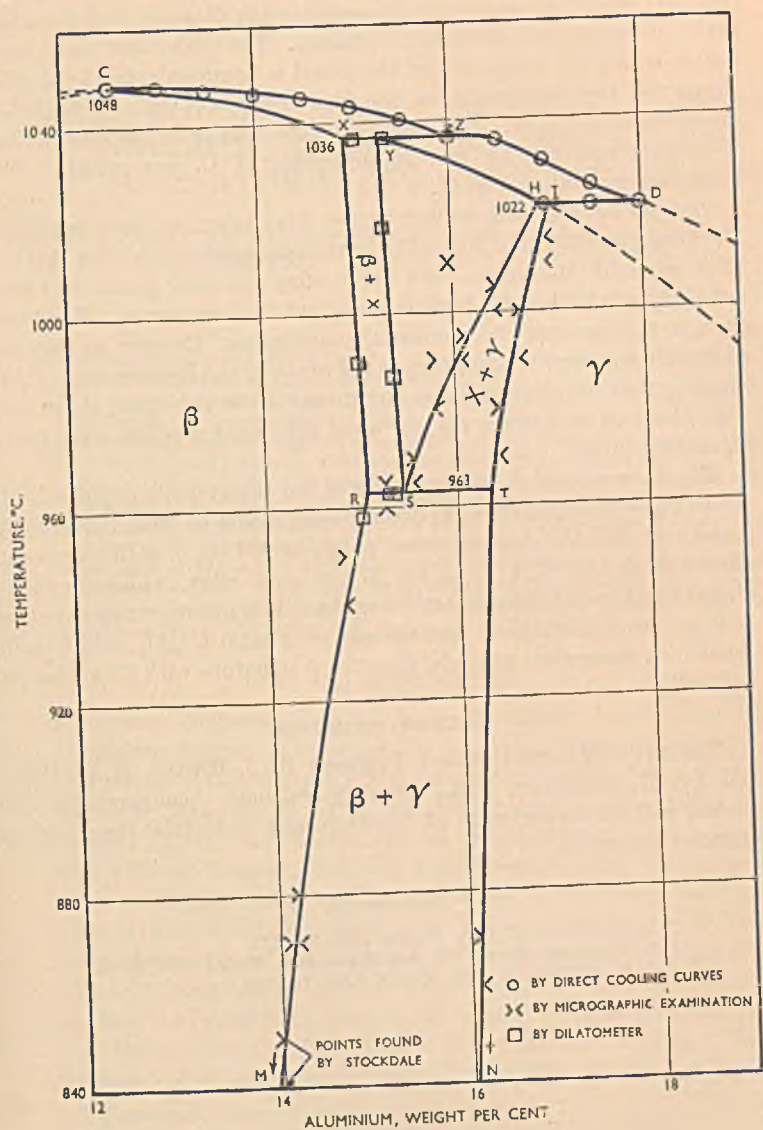


FIG. 11.

EXPERIMENTS WITH THE DILATOMETER.

A dilatometer was used in order to detect the lines *RX* and *SY* (Fig. 11), which are necessary to complete the diagram, but for which little concrete evidence had been obtained. The model used was a small one in which the expansion of the metal is communicated by a silica thrust rod to a tensometer on the dial of which $\frac{1}{16}$ in. represented an expansion of $\frac{1}{10,000}$ in. The specimens were 5 cm. in length, and the rate of heating and cooling was approximately $\frac{1}{2}^{\circ}$ C. per minute. The results are plotted on Fig. 11.

Several heating and cooling curves were taken on each specimen. The points at 1036° and 1035.5° C. in the specimens containing 15.0 and 15.30 per cent. aluminium were found after the other points had been definitely established by both heating and cooling curves. To obtain them it was necessary to sacrifice the specimens. Coming, as they do, at exactly the same temperature as the break in the liquidus curve, they indicate that the temperatures shown can be relied upon, since they were obtained on heating curves, while the liquidus points were found on cooling curves.

Fig. 11 is plotted from the results of the experiments described. It shows a new phase (marked *x*) decomposing into a eutectoid mixture of β and γ at 963° C. Andrew found points at 964° C. in a 15.5 per cent. alloy and at 990° – 981° C. in his 16 per cent. alloy, which points fit almost exactly on to the author's diagram. It is of interest to note that 15.9 per cent. aluminium corresponds to a ratio Cu_9Al_4 , which ratio should, on theoretical grounds, give the γ structure with 52 atoms per unit cell.

ACKNOWLEDGMENTS.

The author desires to thank Professor R. S. Hutton, M.A., D.Sc., and Dr. D. Stockdale, M.A., for very welcome encouragement and advice, and the Department of Scientific and Industrial Research for financial assistance.

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THE CONSTITUTION OF THE COPPER-782 GALLIUM ALLOYS IN THE REGION 18 TO 32 ATOMIC PER CENT. OF GALLIUM.*

By WILLIAM HUME-ROTHERY,† M.A., D.Sc., F.R.S., MEMBER,
and GEOFFREY VINCENT RAYNOR,‡ B.A., B.Sc.

SYNOPSIS.

The equilibrium diagram of the system copper-gallium has been investigated above 420° C. in the region 18-32 atomic per cent. gallium. Three distinct modifications of the β phase, denoted β , β' , and β'' , are shown to exist above 420° C., and there is evidence that a further modification exists at low temperatures. The β phase, stable at high temperatures, has a considerable range of composition which diminishes rapidly with decreasing temperature until a eutectoid point is reached at 618° C. The phase boundaries for this modification of the β phase agree well with the diagram of Weibke, but, in contrast to the results of this investigator, the eutectoid transformation is not a reaction of the type $\beta \rightleftharpoons \alpha + \gamma$, but $\beta \rightleftharpoons \beta' + \gamma$ where the β' phase exists over a narrow range of composition in the region 22.3 atomic per cent. gallium. The β'' phase is stable above 475° C., at which temperature another transformation takes place with the formation of the β'' phase existing over a narrow range of composition in the region 21.5 atomic per cent. gallium.

(1) INTRODUCTION.

THE system copper-gallium has been investigated by Weibke,¹ whose equilibrium diagram is shown in Fig. 1. This diagram was constructed from results obtained mainly from heating and cooling curves taken at the rather high rate of 10° C. per minute, and was supported by incomplete X-ray and micrographical investigations. In a previous paper,§ Hume-Rothery, Mabbott, and Channel-Evans² determined the α -solid solubility limits, and in the course of this work results were obtained with which the diagram of Weibke could not be reconciled. The β -phase area of this diagram was therefore reinvestigated, and extremely complicated results were obtained. The present paper describes the equilibrium diagram above 420° C., and shows that in this range three distinct modifications of the β phase are formed. There is evidence that a fourth modification of the β phase exists at low tem-

* Manuscript received February 23, 1937.

† Royal Society Warren Research Fellow, Oxford.

‡ Kable College, Oxford.

§ For brevity the authors of this paper will be referred to as H.-R., M., and C.-E.

peratures, and it is hoped to present later a detailed study of this region together with the results of X-ray crystal analyses of the different

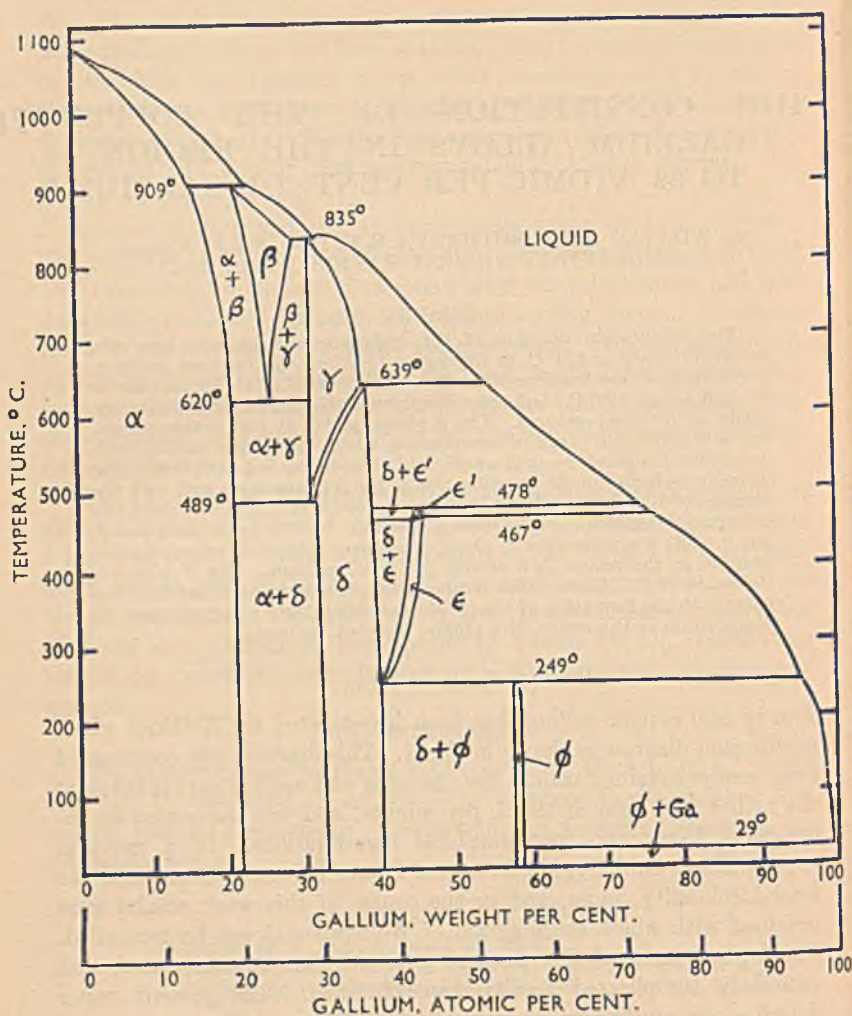


FIG. 1.

modifications. The whole system is so complicated, however, that it was thought advisable to publish the results which definitely establish the high-temperature portion of the diagram.

(2) EXPERIMENTAL DETAILS.

(a) *Materials Used.*

The gallium used for the present work was supplied by the Kaliwerke, Aschersleben, Germany, and was of 99.875 per cent. purity, the chief impurities being zinc 0.07, copper 0.04, and lead 0.01 per cent., with traces of iron and nickel. The copper used for the first four alloys prepared was electrolytically refined metal with a guaranteed purity of 99.95 per cent.; these alloys are referred to in the Tables as the "A" series. For the preparation of the remaining alloys, special copper of 99.99 per cent. purity was kindly presented by the British Non-Ferrous Metals Research Association.

(b) *Cooling Curve Technique.*

The liquidus curve for the β phase was determined by means of cooling curves, using from 50 to 30 gm. of alloy melted in graphite crucibles provided with graphite lids. The experimental methods were those already described³ for the accurate determination of freezing points. The composition of the melt was determined by the analysis of a sample removed shortly before reaching the expected arrest point by suction into a preheated silica tube. The alloy was thoroughly stirred until the arrest point was established, and the rates of cooling used varied from 0.6° to 1.2° C. per minute. The authors must thank Mr. P. W. Reynolds for helping to take these cooling curves.

(c) *Preparation of Specimens for Annealing and Quenching Experiments.*

For the preparation of cast alloys, the copper and gallium were melted together under powdered charcoal in a small Salamander crucible, and were cast into a $\frac{1}{4}$ in. diameter cylindrical mould bored in a heavy copper block. The resulting specimens had fine microstructures, and were free from segregation effects.

(d) *Solidus Determinations.*

Part of the solidus curve for the β phase was determined by the usual quenching methods. For this purpose the specimen, after a preliminary heat-treatment, was annealed in a sealed, evacuated, hard glass tube heated in a well-lagged tubular resistance furnace. The temperature was controlled by hand adjustment of resistances, and was measured by means of a thermocouple, the tip of which touched the tube containing the alloy. By this means the temperature could be kept constant to within $\pm 0.2^{\circ}$ C. for 30 minutes. For some alloys the solidus and liquidus curves were so close together that etching methods failed to reveal the presence of chilled liquid, even though it was clear from

the shape of the specimen that considerable melting had occurred. Two points were obtained, therefore, by means of heating curves using cylindrical specimens approximately $\frac{3}{4}$ in. long by $\frac{3}{8}$ in. diameter. After preliminary heat-treatment, one of these was embedded in a large crucible of charcoal contained in the crucible furnace, and annealed for 4 hrs. at a temperature within the homogeneous range, after which

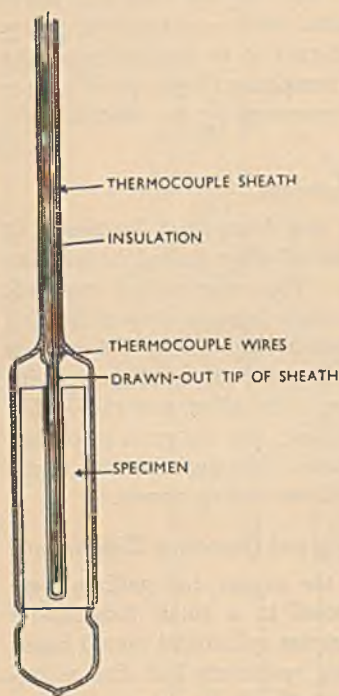


FIG. 2.

the temperature was increased at a rate of about 0.8° per minute. In order to minimize loss of gallium during the experiment the second specimen was enclosed in a partially evacuated quartz tube, into which the thermocouple sheath was sealed as shown in Fig. 2. This was embedded in charcoal as in the previous case. The thermocouple was inserted into a hole drilled along the axis of the specimen, and the composition was obtained by the analysis of sections taken from both ends of the specimen after the experiments.

(e) *Annealing Experiments.*

For the annealing experiments, the alloys, contained in sealed evacuated tubes, were heated in electric resistance furnaces controlled by Foster temperature regulators, and were quenched in a freezing mixture of ice and salt. It was found that in the case of the alloys referred to below, which decomposed on quenching, the

less drastic cooling obtained by the use of cold water resulted in the production of a very coarse decomposition structure, in which it was difficult to detect the presence of small amounts of a second constituent present at the quenching temperature. The general arrangements have already been described,⁴ and the constancy of the temperature control varied from $\pm 1^\circ \text{C.}$ for short periods to $\pm 2.5^\circ \text{C.}$ for periods extending over several weeks.

(f) *Etching Technique.*

As the work proceeded it became clear that it was only within certain ranges of temperature and composition that the high-temperature

modification of the β phase could be retained apparently undecomposed on quenching. In other cases decomposition occurred, resulting in the precipitation of particles of the α or γ phases according to the composition. The structures were always sufficiently coarse for the individual constituents to be identified under a $\frac{1}{8}$ in. or $\frac{1}{16}$ in. objective.

The transformations from one modification to another at the lower temperatures were accompanied by slight changes in composition. Under certain conditions it was very easy to obtain alloys which were not in true equilibrium, but which consisted chiefly of one of the low-temperature modifications of the β phase, with small particles of both the α and γ phases. It was essential, therefore, to be able to distinguish clearly between the α and γ phases, and this was done by means of the reagents shown in Table I. No reagent was discovered which distinguished between the different modifications of the β phase, although the high-temperature modification tarnished most readily with alcoholic ferric chloride.

TABLE I.

Reagent.	Use.	Colour Contrast.
Alcoholic ferric chloride	$\alpha + \beta$ alloys	α light yellow
Aqueous solution (19 per cent. FeCl_3 , 6 per cent. HCl) diluted with twice its volume of absolute alcohol		β dark brown
Ammoniacal hydrogen peroxide	$\alpha + \beta$ alloys	γ white
(2 c.c. 20 vol. hydrogen peroxide in 10 c.c. 0.880 ammonia).		α dark
10 per cent. Aqueous ammonium per-sulphate	$\alpha + \beta$ alloys	β light
		γ white
Chromic acid-nitric acid mixture	$\beta + \gamma$ alloys	α light
(40 per cent. nitric acid, 25 per cent. chromic acid, 35 per cent. distilled water.)		β dark
		γ white
		α and β light yellow
		γ shining blue

(g) Analysis.

A very slight loss of gallium occurred during the melting process, and all alloys were therefore analyzed, both copper and gallium being determined. The alloy was dissolved in nitric acid, and the copper then separated as sulphide, redissolved, and determined electrolytically. The filtrate from the sulphide precipitation was boiled free from hydrogen sulphide, and the gallium precipitated by ammonia. The mixture was then boiled until Sofnol No. 2 indicator showed that it was only feebly alkaline. Under these conditions the gelatinous precipitate became powdery, and could readily be filtered, but the last traces

showed a tendency to stick to the walls of the flask, and were therefore dissolved off and reprecipitated. After ignition to the sesquioxide the precipitate was allowed to cool in a vacuum desiccator, and weighed as quickly as possible, since it tended to gain in weight owing to absorption of vapour or gases. In the determination of phase boundaries above 620° C., the analysis was carried out with the actual specimens annealed at the upper and lower limits of the temperature bracket giving the phase boundary for the alloy concerned. These determinations showed that no loss of gallium occurred on annealing, and for the alloys used in the determination of phase boundaries at low temperatures, the alloys were analyzed after the high-temperature anneal. A slight loss of gallium occurred when alloys were heated above the solidus temperatures, and for the alloys used in the determination of the solidus curve by the quenching method, the compositions were determined by the analysis of the quenched specimens. For the alloys used in the heating curve experiments the composition was obtained by the analysis of the specimen after the heating curve had been taken. Thirty alloys were analyzed, and the totals of the percentages of copper and gallium were between the limits 99.88 and 100.05, with two exceptions where the totals were 99.83 and 100.10, respectively.

(h) *Temperature Measurements.*

As in the previous work,³ temperatures were measured with a platinum/platinum 13 per cent. rhodium thermocouple calibrated against the freezing points of silver (960.5° C.), silver-copper eutectic (778.8° C.), aluminium (659° C.), zinc (419° C.), and lead (327° C.). Intermediate temperatures were obtained by means of a deviation graph used in conjunction with the standard tables of Roeser and Wensel⁵ as recommended by these authors.

(3) EXPERIMENTAL RESULTS.

(a) *The Liquidus Curve.*

The results of the cooling curve experiments are shown in Table II, and are plotted in Fig. 3. The upper peritectic temperature corresponding with the reaction $\alpha + \text{liquid} \rightleftharpoons \beta$ was determined as 915.1° C. by cooling curves, whilst quenching experiments with two-phase alloys in the $\alpha + \beta$ area placed the peritectic horizontal between the limits 914.0° and 915.3° C. These temperatures are considerably higher than the value of 909° C. given by Weibke, who used melts of 25 gm., but are in good agreement with the value of 914° C. obtained by H.-R., M., and C.-E. from a cooling curve using 7 gm. of alloy. The composition of the liquid phase at the peritectic horizontal is 21.5 atomic per cent.

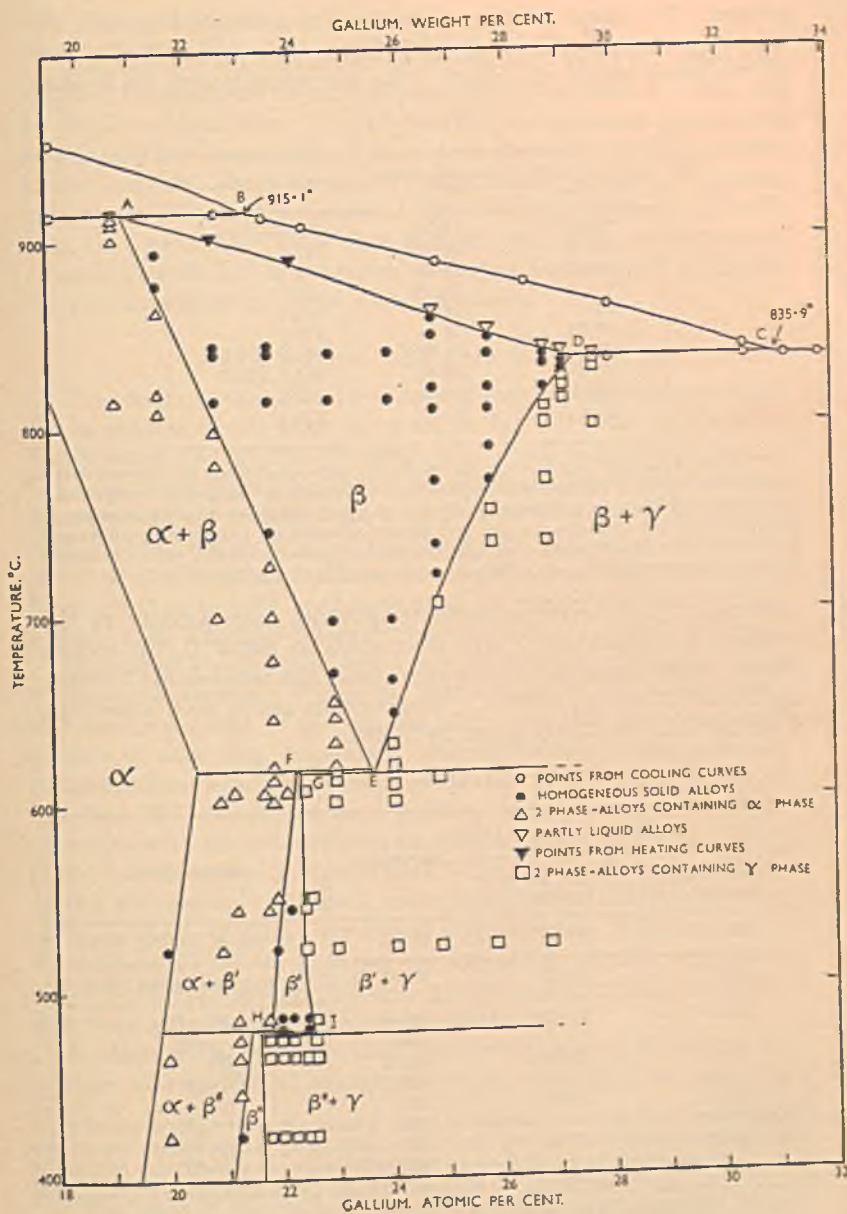


FIG. 3.

gallium. The upper portion of the liquidus corresponding with the deposition of the β phase is about 5° higher than that of Weibke, but for the lower portion the results of the two investigations are in close

TABLE II.

Gallium, Weight Per Cent.	Gallium, Atomic Per Cent.	Arrest Points.
19.48	18.07	953.7, 914.1 †
22.58	21.01	915.1
23.46	21.84	912.1
24.24	22.58	906.7
26.75	24.98	888.1
28.38	26.54	876.7
29.96	28.06	864.0 834.7 †
32.45	30.46	841.0, 835.9
33.215	31.20	835.2
33.816	31.78	835.8

† Since these two alloys were almost completely solid when the second arrest points were reached, stirring was impossible; the crucible was therefore vigorously tapped in order to minimize supercooling. It is very probable that the absence of adequate stirring accounts for the fact that the peritectic temperatures obtained from these two experiments were slightly low compared with the values obtained from experiments during which stirring was possible throughout.

agreement. The lower peritectic temperature corresponding to the reaction $\beta + \text{liquid} \rightleftharpoons \gamma$ was determined as 835.9°C. by cooling curves, whilst quenching experiments placed the temperature between the limits 833.8° and 836.8°C. ; these results are in good agreement with the value of 835°C. given by Weibke.

TABLE III.

Composition.		Temperature, $^\circ \text{C.}$	Microstructure.
Gallium, Weight Per Cent.	Gallium, Atomic Per Cent.		
22.496	20.92	903.1	Arrest on heating curve
23.97	22.32	890.7	Arrest on heating curve
26.64	24.875	861.5	[β] + liq.
		858	
27.69	25.88	851.5	[β] + liq.
		848	
28.71	26.86	841	[β] + liq.
		838	
29.08	27.21	840	[β] + liq.
		837	

Note.—In this table the symbol [β] is used to denote the decomposed β structure typical of alloys quenched from temperatures within the homogeneous β area of the equilibrium diagram.

(b) *The Solidus Curve.*

The results of the heating curves are shown in Table III, which also includes the results of the critical quenching experiments on either side of the phase boundaries. The full details of the additional experiments which confirm these results* have been deposited in the archives of the Institute. In the region 19.5–24 atomic per cent. of gallium the present solidus curve is higher by amounts of the order 5°–8° C. than the figures given by Weibke from the end points of the arrests on cooling curves, but in the region 25–27.4 atomic per cent. of gallium the two investigations are in close agreement.

(c) *The β Phase Stable Above 618° C.*

The results of the critical † annealing experiments which establish the boundaries of this phase are given in Table IV, and are shown in Fig. 3, which also includes the results of the confirmatory experiments. The composition of the β phase at the upper and lower peritectic temperatures and the eutectoid point are 19.3, 27.45, and 23.7 atomic per cent. gallium, respectively, as compared with the values 19.3, 27.32, and 23.98 atomic per cent. gallium given by Weibke. The two investigations are thus in very good agreement as regards the limits of the β -phase area, although the exact temperatures are slightly different.

Interesting observations were made regarding the stability of the β phase on quenching. Within the narrow range of composition 22.5–23.8 atomic per cent. of gallium, the alloys quenched from the homogeneous β area were apparently retained undecomposed, and the microstructures were typical of a single phase. If the β phase contained less than 22.5 atomic per cent. gallium, decomposition occurred on quenching with the production of an acicular type of structure. Fig. 4 (Plate XV) shows the structure of alloy 19.19 after quenching from 914° C. At this temperature the alloy is in the ($\alpha + \beta$) area, and the quenched alloy shows the original α crystals in a ground-mass of decomposed β . Fig. 5 (Plate XV) shows the rather confused acicular structure typical of alloys containing less than 22.5 atomic per cent. gallium when quenched from temperatures within the homogeneous β area.

In alloys containing more than 23.8 atomic per cent. of gallium, the β phase also underwent decomposition on quenching, but with the

* In the later sections the same policy has been adopted, and only the critical results are submitted for publication, whilst the complete tables containing the additional experiments have been deposited in the Library of the Institute; they may be inspected in the Library on application to the Librarian.

† The results of the additional experiments have also been deposited in the Library of the Institute, where they may be inspected, on application being made to the Librarian.

production of a fine rosette type of structure. Fig. 6 (Plate XV) shows the structure typical of alloys in this range quenched from temperatures

TABLE IV.—*The $\alpha + \beta/\beta$ and $\beta/\beta + \gamma$ Boundaries.*

Composition.		Preliminary Heat-Treatment.	Final Annealing Treatment.	Microstructure.
Gallium, Weight Per Cent.	Gallium, Atomic Per Cent.			
20.66	19.19	A	30 minutes 915.3° C.	α + chilled liquid.
	"	A	1 hr. 914° C.	α + $[\beta]$.
21.46	19.94	C	6 hrs. 877° C.	$[\beta]$.
	"	C	6 hrs. 862.5° C.	α + $[\beta]$.
22.51 A	20.94 A	40 hrs. at 600° C.	10 hrs. 815° C.	$[\beta]$.
	"	F	12 hrs. 798.5° C.	$[\beta]$ + a little α .
23.52 A	21.90 A	F	12 hrs. 745° C.	$[\beta]$.
	"	F	12 hrs. 727° C.	$[\beta]$ + α .
24.67 A	22.99 A	F + 30 minutes at 876° C.	48 hrs. 669.5° C.	β .
	"	F	48 hrs. 654° C.	β + α .
25.73 A	24.07 A	E	48 hrs. 647.5° C.	β .
	"	E	48 hrs. 631.5° C.	β + γ .
26.67	24.88	D	10 hrs. 721.5° C.	$[\beta]$.
	"	D	48 hrs. 706° C.	$[\beta]$ + γ .
27.69	25.88	C	10 hrs. 770.5° C.	$[\beta]$.
	"	D	10 hrs. 755° C.	$[\beta]$ + γ .
28.71	26.86	15 hrs. at 600° C.	12 hrs. 820.5° C.	$[\beta]$.
	"	D	10 hrs. 800.5° C.	$[\beta]$ + γ .
29.06	27.21	B	1 hr. 831.5° C.	$[\beta]$.
	"	G	3 hrs. 826°	$[\beta]$ + γ .
29.60	27.73	24 hrs. at 680° + 5 hrs. at 800°	1 hr. 836.8° C.	$[\beta]$ + chilled liquid.
			1½ hr. 833.8° C.	$[\beta]$ + γ .
			1½ hr. 831.3° C.	$[\beta]$ + γ .

The preliminary heat-treatments referred to are as follows: A. 15 hrs. 600° C. + 9 hrs. 901° C.; B. 35 hrs. 610° C. + 12 hrs. 814.5° C.; C. 15 hrs. 600° C. + 12 hrs. 809° C.; D. 15 hrs. 600° C. + 12 hrs. 819.5° C.; E. 40 hrs. 600° C. + 10 hrs. 840° C.; F. 40 hrs. 600° C. + 10 hrs. 815° C.; G. 15 hrs. 660° C. + 10 hrs. 814.5° C.

within the homogeneous β area. Fig. 8 (Plate XVI) shows the structure of an alloy quenched from the $(\beta + \gamma)$ area, and this structure is of interest on account of its very close resemblance to the structures of copper-zinc

alloys when quenched from the corresponding ($\beta + \gamma$) area; an example of this type is shown in Fig. E, Plate LVIII, of the discussion on the paper by Jenkins,⁶ which is reproduced as Fig. 9 (Plate XVI).

Careful etching with the reagents described in Table I showed that in quenched alloys the decomposition of the β phase took place by the precipitation of the constituent which would have separated if the alloy had cooled slowly through the phase boundary. In the structures of Fig. 6 (Plate XV) and Fig. 8 (Plate XVI) the small precipitated particles had the etching characteristics of the γ phase, whilst in the structures of Figs. 4 and 5, the light etching constituent was identified as the α phase.

(d) *The β Eutectoid Transformation and the $\alpha + \beta \rightleftharpoons \beta'$ Reaction.*

The annealing experiments confirmed that the β phase underwent a eutectoid transformation, the composition of the eutectoid point being 23.7 atomic per cent. gallium. Fig. 7 (Plate XV) shows the structure of alloy 24.07 after cooling at a rate of $\frac{1}{2}^{\circ}$ C. per minute from 800° to 530° C., at which temperature the alloy was quenched. Since this alloy contained slightly more gallium than corresponds with the eutectoid point, the structure consists mainly of the finely divided eutectoid with a few crystals of the γ phase deposited in the grain boundaries. Careful etching showed that, in contradiction to the diagram of Weibke, the constituents of the eutectoid were not the α and γ phases, but were the γ phase, and a new phase, the etching characteristics of which closely resembled those of the high temperature β phase. The results of section (e) showed that below the eutectoid temperature of the β phase, alloys containing approximately 22.25 atomic per cent. gallium were homogeneous, and the new phase may be denoted β' . The most probable form of the equilibrium diagram in this region is shown in Fig. 3. The true eutectoid point corresponds with the reaction $\beta \rightleftharpoons \beta' + \gamma$, and quenching experiments gave its temperature as lying between the limits 616° and 619° C., as compared with the value 620° C. given by Weibke.

According to the Phase Rule only three phases can exist in equilibrium at any one temperature, and hence the α phase cannot theoretically be in equilibrium with β' and β phases at the temperature at which these two phases are in equilibrium with the γ phase. The theory therefore demands the presence of a second horizontal line corresponding with the reaction $\alpha + \beta \rightleftharpoons \beta'$, and this is included in Fig. 3. Quenching experiments showed that alloy 22.99 was in the ($\alpha + \beta$) area at 619.5° C., and since the ($\beta \rightleftharpoons \beta' + \gamma$) eutectoid temperature lies between 616° and 619° C., the temperatures of the two horizontal lines cannot differ by more than 3.5° C. The β' phase appears to exist over a small

range of composition which is of the order 0.1 atomic per cent. at 616° C., and increases at lower temperatures. The narrowness of this range prevents the use of heating or cooling curves to obtain the temperatures within more precise limits, since equilibrium in the β' area is attained very slowly.

(e) *The β' Phase.*

The critical experiments establishing the composition and solid solubility limits of this phase are summarized in Table V. The composition of the point *G* in Fig. 3 is 22.4 atomic per cent. gallium, and is thus on the copper-rich side of the β eutectoid point; consequently misleading results were easily obtained unless the annealing treatments were carefully adjusted. Suppose, for example, that an alloy containing 23 atomic per cent. of gallium is quenched from the ($\alpha + \beta$) area, and is then re-annealed below the temperature of the β eutectoid point. The quenched alloy consists chiefly of the β phase with isolated particles of the α phase. On re-annealing, the β phase decomposes to form both β' and γ phases, so that the alloy contains α , β' , and γ phases, and true equilibrium is obtained only by the complete absorption of the α -phase, a process which takes place very slowly. If the preliminary annealing treatment is at a temperature within the homogeneous β area, the same difficulty may be encountered if the quenching is insufficiently drastic to prevent decomposition. At 616° C. the β' phase has a range of composition which does not exceed 0.3 atomic per cent. and which, from examination of the relative amounts of the constituents in two phase alloys, is estimated as approximately 0.1 atomic per cent. At lower temperatures the extent of the β' solid solution increases to about 0.75 atomic per cent. at 480° C.

The β' phase has a yellowish-brown colour, and is soft, and difficult to etch without producing staining or relief effects. It is stable between 616°–619° C. and approximately 475° C. and is retained by quenching alloys within this range of temperature. When, however, a homogeneous β' alloy is re-annealed at temperatures below 480° C. small particles of the γ phase are precipitated, and the composition of the homogeneous alloys changes slightly but abruptly in the copper-rich direction, indicating that a third modification which may be denoted β'' exists below this temperature. The structure of alloy 22.15 when quenched from 486° C. is shown in Fig. 10 (Plate XVI) and shows homogeneous crystals of the β' phase, whilst Fig. 11 (Plate XVI) shows the same alloy after quenching from 465° C. when the structure consists of small particles of γ embedded in a ground-mass of β'' .

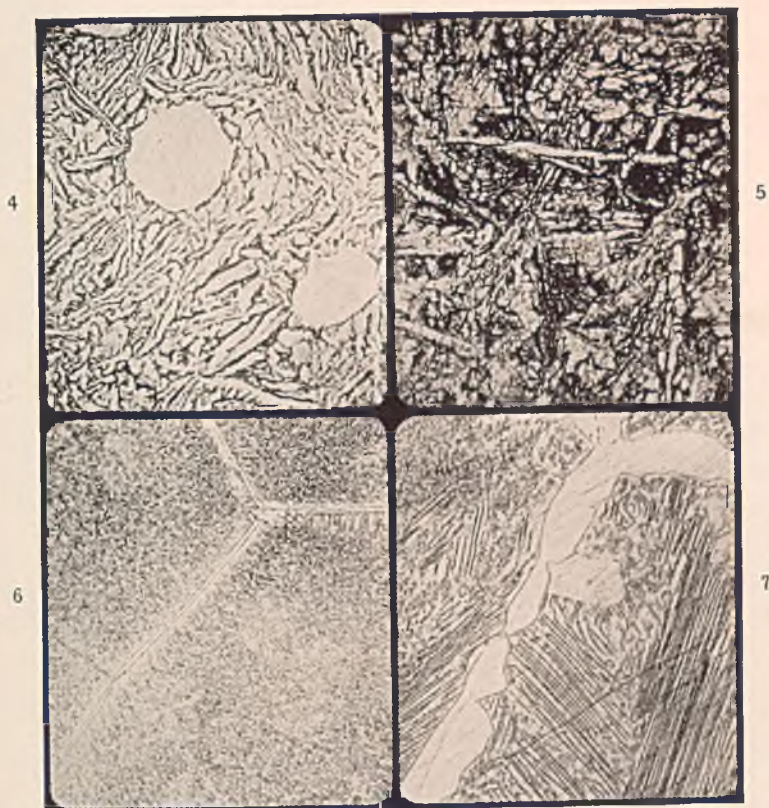


FIG. 4.—Alloy 19.19 Atomic-% Ga Annealed at 914° C. α Crystals in Decomposed β of Acicular Type. $\times 175$.

FIG. 5.—Alloy 20.94 Atomic-% Ga Annealed at 844° C. Decomposed β of Acicular Type. $\times 175$.

FIG. 6.—Alloy 25.88 Atomic-% Ga Annealed at 820.5° C. Decomposed β of Rosette Type. $\times 175$.

FIG. 7.—Alloy 24.07 Atomic-% Ga Slowly Cooled from 800° to 530° C. and Quenched; Primary γ + Eutectoid. $\times 175$.



(To face p. 216.)



FIG. 8.—Alloy 26.86 Atomic-% Ga Annealed at 737.5° C. γ + Decomposed β of Rosette Type. $\times 175$.

FIG. 9.—Cu-Zn Alloy: 46.9 Atomic-% Cu Annealed 2 Days at 734° C. $\times 150$. (Jenkins.)

FIG. 10.—Alloy 22.15 Atomic-% Ga Annealed at 486° C. Homogeneous β' Phase. $\times 80$.

FIG. 11.—Alloy 22.15 Atomic-% Ga Annealed at 465° C. γ Particles in β'' Phase. $\times 175$.

TABLE V.—The β Eutectoid Transformation and the β' Phases.

Composition.		Preliminary Heat-Treatment.	Final Annealing Temperature.	Microstructure.
Gallium, Weight Per Cent.	Gallium, Atomic Per Cent.			
24.67 A	22.90 A	F + 30 minutes at 876° C.	5 hrs. 619.5° C.	$\alpha + \beta$.
24.67 A	22.99 A	E + 48 hrs. at 697° C.	1 hr. 800° C.: then cooled at $\frac{1}{2}$ °/minute to 619° C. and quenched.	Large precipitated α crystals in β phase. No eutectoid.
25.73 A	24.07 A	E + 24 hrs. at 697° C.	1 hr. 800° C.: then cooled at $\frac{1}{2}$ °/minute to 619° C. and quenched.	Precipitated γ crystals in β phase. No eutectoid.
24.67	22.99 A	17 hrs. at 670° C. + 15 hrs. at 840° C.	5 hrs. 616° C.	$\beta' + \gamma$.
26.64	24.88	C	5 hrs. 613° C.	$\beta' + \gamma$.
25.73 A	24.07 A	E + 24 hrs. at 697° C.	1 hr. 800° C.: cooled at $\frac{1}{2}$ °/minute to 609° C. and quenched.	Primary γ + eutectoid.
24.20	22.55	J	2 weeks 486° C.	$\beta' + \gamma$.
24.08	22.43	C C C D	10 days 606.2° C. 10 days 544° C. 10 days 523° C. 2 weeks 486° C.	$\beta' + \text{little } \gamma$. $\beta' + \text{little } \gamma$. $\beta' + \text{little } \gamma$. β' .
23.79	22.15	H H	10 days 606.2° C. 10 days 544° C.	$\beta' + \alpha$. β' .
23.55	21.93	J J	10 days 550° C. 2 weeks 486° C.	$\beta' + \text{a little } \alpha$. β' .
23.52 A	21.90 A	E	10 days 521° C.	β' .
23.35	21.73	H	2 weeks 486° C.	$\beta' + \text{a little } \alpha$.

The preliminary heat-treatments A-G are described in Table IV, and the remainder are as follows: H. 35 hrs. 610 + 12 hrs. 814.5° C.; I. 40 hrs. 625° + 12 hrs. 814.5° C.; J. 40 hrs. 620° + 12 hrs. 814° C.

(f) The $\beta' \rightleftharpoons \beta''$ Transformation and the Existence of the β'' Phase.

The results described above suggest clearly that the β' phase is stable only above about 480° C., and that a further modification exists below this temperature. The critical experiments which establish this part of the diagram are given in Table VI, and are plotted on a large

scale in Fig. 12. These alloys required from 2 to 4 weeks of annealing in order to reach true equilibrium, and no useful information could be obtained by means of cooling curves, since it was shown conclusively

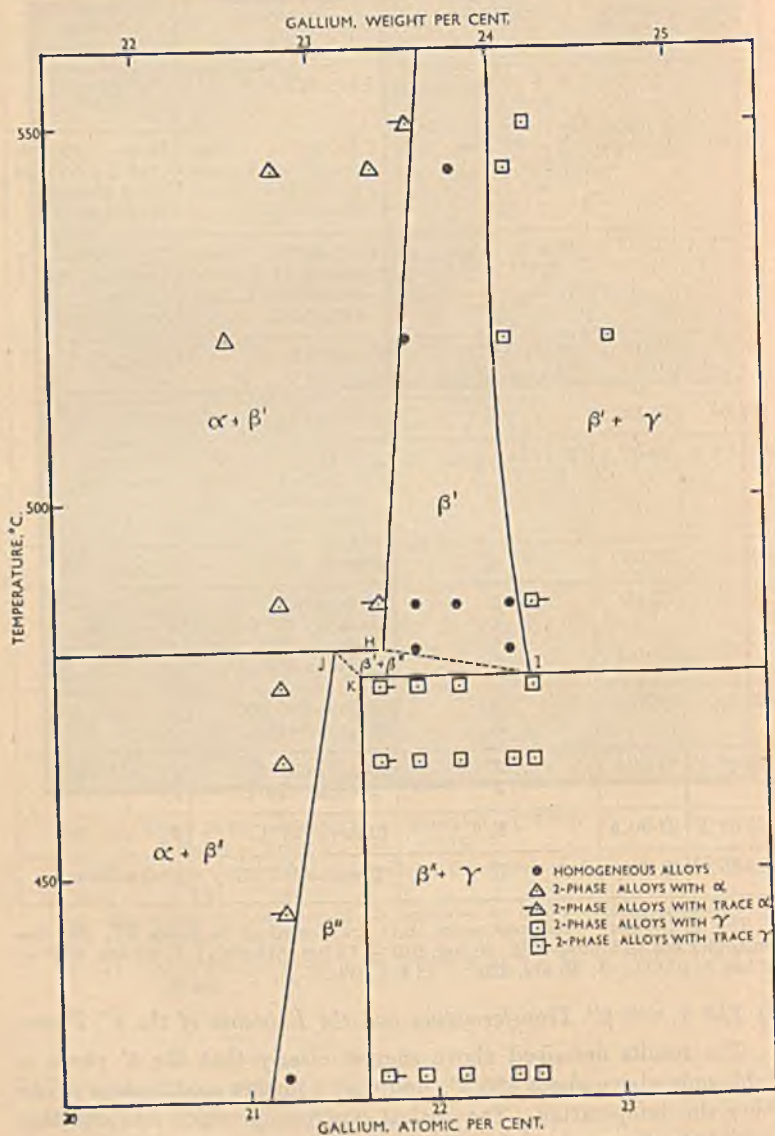


FIG. 12.

by microscopic examination that when cooled at the rate of $\frac{1}{2}^{\circ}\text{C.}$ per minute alloys did not undergo the changes which took place on prolonged annealing. The most critical evidence is given by alloy 21.73. On quenching from 486°C. this consisted of the β' phase together with traces of the α phase, but on quenching from 475°C. the structure was almost homogeneous with traces of the γ phase. Alloys 21.93 and 22.43 consisted of homogeneous β' when quenched from 480°C. but all contained particles of the γ phase when quenched from 475°C. so that the evidence for a discontinuity in the phase boundary is very considerable. It is perhaps significant that the cooling curves of Weibke for all alloys in the range 19.7–29.3 atomic per cent. gallium showed arrests at about 490°C. , which were ascribed to a transformation of the γ phase, but as these experiments began with the liquid alloy cooled at a rate of $9^{\circ}\text{--}10^{\circ}\text{C.}$ per minute, it is not possible to correlate them with the β' and β'' phases which require long annealing to reach equilibrium. A transformation of the γ phase would be expected to lead to a change in direction of the solubility limit of the β' phase on the gallium-rich side. Reference to Fig. 12 shows how improbable any continuous curve appears, and as the $\alpha + \beta'/\beta'$ boundary is also displaced in the copper-rich direction, the conclusion appears inevitable that a third modification of the β phase exists which may be denoted β'' . Since the composition is displaced in the copper-rich direction, the theory again requires two horizontal lines in the diagram, one corresponding with the reaction $\alpha + \beta' \rightleftharpoons \beta''$, and the other with the reaction $\beta' \rightleftharpoons \beta'' + \gamma$.

The annealing experiments show conclusively that the temperatures of the two horizontal lines cannot differ by more than 11°C. Alloy 21.93 when quenched from 480°C. had a large-grained microstructure, and was indistinguishable from alloys quenched from the homogeneous β' area. No etching reagent was discovered which distinguished between the β' and β'' phases, so that it is possible that this alloy was in the $(\beta' + \beta'')$ area at 480°C. The coarse grain structure, however, makes this improbable, since if the transformation had begun, we should expect a diminution of the grain-size, an effect which was observed from alloy 21.20 when this was obtained in the pure β'' form at 423°C.^* The structure of alloy 21.93 at 480°C. suggests, therefore, that the temperatures of the two horizontal lines do not differ by more than 5°C. , and in the absence of apparatus for the measurement of electrical resistance at high temperatures, it does not seem possible to place the limits more precisely.

The β'' phase is soft, and yellowish brown in colour, and closely

* A similar grain refinement was found in the $(\alpha + \beta')$ alloys below the transformation temperature at 616°C.

resembles the β' phase in properties. From the relative amounts of the constituents in two-phase alloys, the range of composition of the β'' phase is estimated as about 0.5 atomic per cent. at 420° C. (21.05–21.55 atomic per cent. gallium), and diminishes to less than 0.2 atomic per cent. at 475° C.

The microstructures of the alloys containing 21.73, 21.93, and 22.15 per cent. gallium after quenching from 423° C. were almost

TABLE VI.—*The β' - β'' Transformation and the Limits of the β'' Phase.*

Composition.		Preliminary Heat-Treatment.	Final Annealing Treatment and Quenching Temperature.	Microstructure.
Gallium, Weight Per Cent.	Gallium, Atomic Per Cent.			
22.79	21.20	H + 3 weeks 423° C.	8 days at 445° C.	β'' + a little α .
	21.20	H	3 weeks at 423° C.	β'' . See Foot-note on p. 219.
23.35	21.73	H	2 weeks at 486° C.	β' + a little α .
	21.73	I	4 weeks at 475° C.	β'' + a trace of γ .
	21.73	I	2 weeks at 465° C.	β'' + a trace of γ .
	21.73	I	3 weeks at 423° C.	β'' + a trace of γ .
23.55	21.93	J + 2 weeks 486° C.	10 days at 480° C.	β' .
	21.93	J	4 weeks at 475° C.	β'' + γ .
23.79	22.15	H	2 weeks at 486° C.	β' .
	22.15	I	4 weeks at 475° C.	β'' + γ .
24.08	22.43	D + 2 weeks 486° C.	10 days at 480° C.	β' .
	22.43	D	2 weeks at 465° C.	β'' + γ .
24.20	22.55	J	2 weeks at 486° C.	β' + a little γ .
	22.55	J	4 weeks at 475° C.	β'' + γ .

identical with those of the corresponding specimens quenched from 465° C. After annealing for 6 weeks at 401° C. and also at 382° C., a further sudden precipitation of the γ phase occurred, suggesting that a fourth modification of the β phase exists at lower temperatures. It is hoped to present a study of this effect at a later date.

(4) DISCUSSION.

In the course of the work described above, alloy 19.94, after annealing at 524° C., was found to consist of the homogeneous α -phase. This agrees with the α solid-solubility curve of H.-R., M., and C.-E., but not with that of Weibke whose results would require this alloy to be within the two-phase area at 524° C.

The present results show clearly that the system copper-gallium is one in which several modifications of the β phase exist, and since the solid solubility limits have been determined in detail, it is of interest to examine the compositions of the critical points in order to see whether these correspond with integral atomic ratios as might be expected from the general viewpoint adopted by Stockdale.⁷

The authors have previously discussed these in terms of the ratio of the number of one kind of atom to the total number of atoms, but in view of Stockdale's request,⁸ we use here the ratio of the number of atoms of the one kind to that of the other. An alloy containing 30 atomic per cent. of gallium contains 30 atoms of gallium to 70 of copper, and the ratio in this notation is therefore $\frac{3}{7}$. The point *B* representing the composition of the liquid at the upper peritectic temperature lies between 21.3 and 21.65 atomic per cent. gallium, and is indistinguishable from the ratio $3/11 = 21.43$. The point *C* representing the composition of the liquid phase at the lower peritectic temperature lies between 30.9 and 31.2 atomic per cent. of gallium, and is thus barely distinguishable from the ratio $5/11 = 31.25$. The eutectoid point *E* at approximately 23.7 atomic per cent. gallium cannot be distinguished from $5/16 = 23.81$. In the β' area the critical point *F* at the higher temperature limit lies between 22.2 and 22.45 atomic per cent. gallium, and cannot be distinguished from the ratio $2/7 = 22.22$. The points *J* and *K* at the head of the β'' area lie between the limits 21.3 and 21.65 atomic per cent. of gallium, and this range includes the ratio $3/11 = 21.43$. The remaining critical points appear definitely distinguished from any fraction involving numbers up to 16, but if numbers up to 24 are permitted as in parts of Stockdale's paper, all but one of the remaining points can be reconciled with some fraction, but in our opinion the possible number of fractions is so great that little weight can be attached to this result. It is, however, interesting to note that if the value (16.5 atomic per cent. of gallium) of H.-R., M., and C.-E. for the α -solid solubility limit at the upper peritectic temperature is correct, the point *A* in Fig. 3 divides the peritectic horizontal in the ratio 4 : 3 so that a simple phase ratio is possible.

ACKNOWLEDGMENTS.

The authors must express their thanks to Professor F. Soddy, F.R.S., for providing laboratory accommodation, and many other facilities which have greatly helped the present work. One of the authors (W. H.-R.) must thank the Council of the Royal Society for election to a Warren Research Fellowship, and for generous financial assistance. Thanks are also due to the Department of Scientific and Industrial Research, the British Non-Ferrous Metals Research Association, and the Fellows of Keble College, Oxford, for grants

made to the authors individually, and to the Aeronautical Research Committee for defraying the cost of some of the apparatus used in this and other research work.

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THE OLD CHEMISTRY DEPARTMENT,
THE UNIVERSITY MUSEUM, OXFORD.

CORRESPONDENCE.

DR.-ING. FR. WEIBKE * (Member): The work of the authors has furnished us with important new knowledge on the decomposition of the β -phase at low temperatures, which subject I was the first to investigate. In this connection I would like to refer them to the work of Zintl and Treusch (*Z. physikal. Chem.*, 1936, [B], **34**, 225), which describes the results obtained in an X-ray investigation of the structure of gallium bronzes and appears to have been in progress simultaneously with the work of the authors. My results indicated that, on cooling, β decomposed into the $\alpha + \gamma$ eutectoid and that the decomposition was probably a complex process passing through intermediate stages such as occur in the decomposition of Cu_3Al . Zintl has shown, by X-ray analysis, that alloys with 20-24 atomic-% gallium, contain an hexagonal phase, $a = 2.594$, $c = 4.229$ A., as well as α and δ , and I considered that this hexagonal phase might be one of the unstable intermediate phases of the decomposition of β . The fact that Zintl and Treusch always found lines due to α and δ , as well as those of the new phase, in the same alloy is probably due to the low reaction velocity of the peritectoid decomposition $\alpha + \beta \longrightarrow \beta'$ or $\alpha + \beta' \longrightarrow \beta''$ and to the displacement of the homogeneity range of the β' and β'' phases further towards the copper side as compared with the β -phase. Zintl and Treusch have also shown that the quantity of new phase present may be increased by heat-treatment.

As regards the position of the solubility line of gallium in copper [the present authors (H.-R. and R.) find a lower solubility at room temperature than at higher temperatures, whereas I found the converse], the differences may be due to faulty establishment of equilibrium conditions, although the sharpness of the lines on my X-ray photograms gave no indication of this. Apart from small differences in the temperatures of the horizontals, there seems to be very good agreement between Hume-Rothery and Raynor's results and my own.

The AUTHORS (in reply): We thank Dr. Weibke for his interesting communication, and agree that the results of Zintl and Treusch can be reconciled with our diagram.

* Dozent, Institut für anorganische Chemie der Technischen Hochschule, Hannover, Germany.

THE TRANSFORMATION IN THE β BRASSES.* 781

By C. SYKES†, D.Sc., Ph.D., MEMBER, and H. WILKINSON,‡ M.Sc.Tech.

SYNOPSIS.

The energy released during the β - β' transformation in brass has been determined as a function of both temperature and composition. The results are compared with those predicted by the theoretical work of Bragg and Williams and of Bethe.

I. INTRODUCTION.

THIS transformation is typical of a large number of transformations which differ in certain essential features from those associated with a change in phase. Tammann and Heusler,¹ in a review of the experimental data available in 1926, emphasized that the transformation occurred without change in phase over a range of temperature of the order of 250° C. and that no recrystallization took place. They remarked on the fact that the magnetic transformation in ferro-magnetic materials produced similar changes in heat content, thermal expansion, and electrical resistance, and concluded that a new type of phenomenon had been discovered in the β - β' transformation in brass. Since that time there has been a considerable amount of speculation as to the mechanism of the transformation, but it is now generally accepted that in the β or high-temperature modification the zinc and copper atoms are distributed at random amongst the atomic sites of the body-centred lattice, whereas in the β' or low-temperature modification a more or less perfect ordered arrangement of the atoms exists with say copper atoms at the cube corners and zinc atoms at the cube centres. Owing to the similarity in scattering power of the zinc and copper atoms, it has not been found possible to verify this view by means of the X-ray diffraction method, but similar transformations in other alloys such as Cu_3Au , FeAl , &c., do produce such ordered structures.

Bragg and Williams,² on the basis of certain assumptions regarding the mechanism of the ordering process, have calculated the amount of energy which should be released and its effect on the specific heat-temperature curve for binary alloys containing equiatomic proportions

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of the two constituents. They have shown that at the temperature at which atomic rearrangement sets in on cooling (the critical temperature) the specific heat should increase to an abnormally high value and then gradually diminish as the temperature decreases and the degree of order increases. Standard cooling curve methods are not particularly suitable for the investigation of transformations following such a course, and in order to make a quantitative determination of the energy involved one of the present authors devised an apparatus for the measurement of instantaneous specific heat.³ The preliminary experiments were carried out on a sample of β brass and the results were compared by Bragg and Williams⁴ with those expected from their own theoretical work and also that of Bethe.⁵

The agreement was satisfactory in that the transformation occurred in a similar manner to that predicted by both theories, but the energy was released too rapidly just below the critical temperature, giving rise to a much higher maximum specific heat than was expected. The total energy involved in the transformation was about 85 per cent. of that predicted by theory. In order to make a more thorough comparison possible, the experiments described in the present paper have been carried out with an improved apparatus which was recently described in this *Journal*.⁶ The specific heat-temperature curves of representative α , $\alpha + \beta$, and β brasses have been measured. These, together with energy content measurements, enable a reliable estimate to be made of the behaviour of a β brass of the composition CuZn (50.7 per cent. by weight zinc). This estimate is then compared with the theoretical work which is primarily concerned with this hypothetical * alloy. The effect of concentration on the energy content is also compared with that predicted by theory. The experimental results are of interest in connection with the fixing of the phase boundaries of the CuZn system.

II. EXPERIMENTAL DETAILS.

(a) *Preparation of Specimens.*

The alloys were prepared from electrolytic copper and distilled zinc, the latter metal having as impurities : iron 0.003, lead 0.002, and cadmium 0.001 per cent. The melting was carried out in a hydrogen atmosphere in crucibles lined with alumina. The ingots were cast in graphite moulds.

The following heat-treatment was given to the ingots : they were rapidly heated to 820° C., soaked for 10 minutes, and quenched in cold

* The β phase ends at about 50 per cent. zinc by weight, i.e. 49.3 per cent. zinc by atoms.



FIG. 2.—Specimen 5. β Brass Showing Traces of α Due to Loss of Zinc. $\times 200$.



[To face p. 224.]

water. A final treatment of 100 hrs. at 450°C . in evacuated glass tubes was then carried out. According to the results of the annealing experiments of Genders and Bailey,⁷ this heat-treatment should be quite adequate to ensure equilibrium at 450°C .

The specific heat specimens (see Fig. 1) were machined from the ingots. Finally, for reasons which will be given later, the specimens were nickel-plated to a depth of about 0.001 in.

(b) Experimental Method.

The methods used for the determination of the specific heat-temperature curve and the measurement of total energy content have been fully described recently in this *Journal*⁶ in a paper on the transformation in the alloy Cu_3Au . For the β brass transformation one

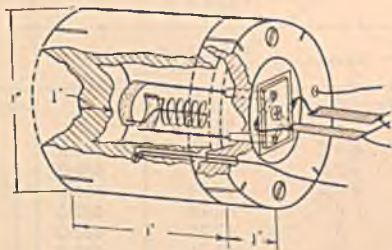


FIG. 1.—Specific Heat Specimen.

minor modification was made to the method: the heating rate used was increased to $2^{\circ}\text{C./minute}$ in order to reduce the duration of the experiments and so minimize loss of zinc. In the initial stages of the investigation trouble was experienced owing to evaporation of zinc from the specimen into the evacuated furnace enclosure. The specimens are heated to a maximum temperature of 500°C . and remain for a period of 3–4 hrs. above 500°C .; consequently the effect of evaporation on the composition of the alloy becomes important. Apart from this, however, the evaporation affects the measurements in two ways. The surface of the specimen changes continuously and its emissivity gradually increases: this leads to a large and somewhat uncertain radiation correction at the critical temperature. The evaporated zinc condenses in cooler parts of the apparatus and gives rise to leakage currents between circuits which are required to be thoroughly well insulated from one another.

These difficulties were considerably reduced by nickel plating the specimens. The polished plated surface has a substantially constant

emissivity which is much smaller than that of a brass surface. Further, the rate of evaporation is considerably diminished. In the case of the specimens containing traces of the γ constituent, however, the apparatus had to be cleaned thoroughly after each run in order to avoid trouble due to leakage effects.

(c) *Homogeneity and Chemical Composition of the Specimens.*

There are many discrepancies in the results of the various investigations which have been carried out to determine the position of the phase boundaries of the copper-zinc system.⁸ Loss of zinc by evaporation and oxidation during the necessary thermal treatment of a specimen leads to uncertainty as to its homogeneity and precise chemical composition. Errors introduced in this way may well account

TABLE I.

Specimen.	Phase.	Weight Per Cent. of Zinc.	T_c .	Cal./gram. 210°-500° C.
0	Pure Copper	0	...	26.2
1	α	36.10	...	27.6
2	$\alpha + \beta$	40.39	455.5	29.7
3	$\alpha + \beta$	42.74	456.0	32.0 ₅
4	$\alpha + \beta$	44.94	454.5	34.0 ₅
5	β	45.76	457.5	34.6 ₅
6	β	47.38	467.0	35.5 ₅
7	β	47.71	467.5	35.7 ₅
8	$\beta + \gamma$ (trace)	49.70	469.0	36.6 ₅
9	$\beta + \gamma$	50.06	469.0	36.1

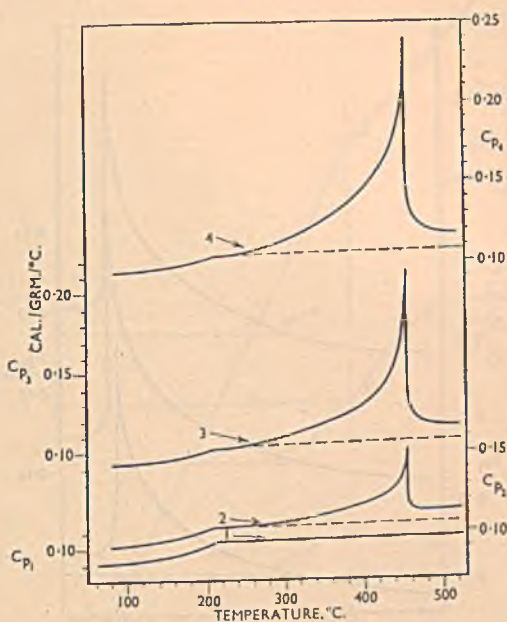
for the lack of agreement in some of the experimental work on this system. Plating the specimens did not entirely prevent evaporation of zinc and it was considered desirable to section the specimens on completion of the experiments and to examine them for homogeneity. The zinc content as indicated visually on an etched section was lower at the surface than in the main body of the specimen. The magnitude of the effect is quite small and may be estimated from Fig. 2 (Plate XVII), which shows the structure of specimen 5 (see Table I) from the edge inwards. This alloy is just inside the β phase and therefore very sensitive to a small diminution in zinc content. The α phase is present in relatively small quantities in a band about 0.010 in. deep parallel to the surface of the specimen. All specimens containing more zinc than No. 5 showed no trace of α constituent.

In order to obtain a thoroughly representative analysis the lids of the specimens were dissolved for analysis at the ends of the tests. The results are recorded in Table I.

III. EXPERIMENTAL RESULTS.

(a) *Specific Heat-Temperature (S.T.) Curves.*

These are given in Figs. 3 and 4 (the number on the curve is also the number of specimen in Table I). Curve 1, Fig. 3, refers to the α brass. Above 200°C. the curve is linear and forms a convenient reference line for the other curves; it is shown dotted in curves 2, 3, and 4 so that the specific heat as modified by the β constituent is more

FIG. 3.—Specific Heat of $\alpha + \beta$ Brasses.

easily recognized. The presence of this constituent alters the shape of the *S.T.* curve, introducing a maximum at about 456°C. The height of the maximum increases as the amount of β constituent in the specimen increases. The temperature at which the maximum occurs is practically constant in the two-phase alloys.

There is an unexplained anomaly in the *S.T.* curve of the α brass starting at 200°C. and proceeding to lower temperatures. This anomaly gradually disappears as the β phase is approached.

In Fig. 4, curves 5 and 6 refer to single-phase β alloys, curve 8 to a specimen which contains a slight trace of γ . The maxima in these curves are higher than those for the two-phase region, and the critical

temperature increases slightly as the zinc content is increased. Curve 8 for the alloy containing 49.73 per cent. zinc is probably very close to the *S.T.* curve for the ideal alloy CuZn (50.7 per cent. zinc), and is the best approximation which can be realized experimentally.

(b) *S.T. Curve of the Quenched Alloys.*

Various investigators have concluded that the β - β' transformation in brass is not appreciably retarded by quenching. The authors have

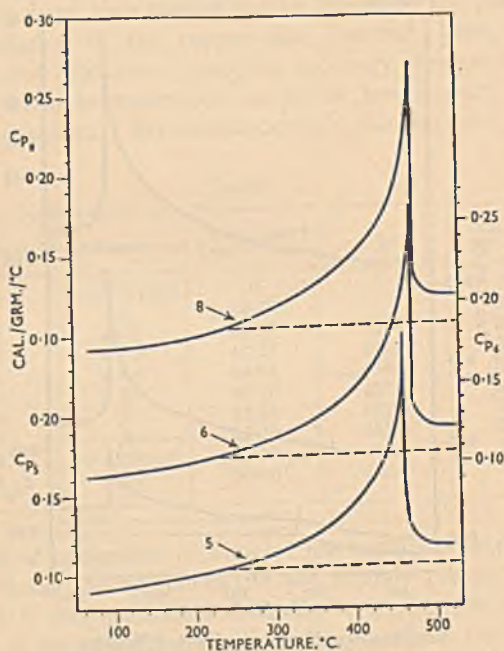


FIG. 4.—Specific Heat of β Brasses.

examined the *S.T.* curves obtained on specimen No. 6 starting from both the annealed and quenched states. Below 250° C. the curves coincided to within 1.5 per cent., whilst above this temperature the agreement was slightly better. The curve for the quenched alloy was the lower, but the difference is of the same order as the experimental error and any retardation of the transformation produced by quenching must have been very small. The measurements on the quenched alloy were started 3 hrs. after the quenching operation, and this represented the minimum time in which the apparatus could be assembled and evacuated.

(c) Energy Content Differences.

It is clear from the *S.T.* curves that the critical temperature is below 500°C. in every case, so that 500°C. may be taken as an upper limit to the transformation. The lower limit is rather indeterminate.

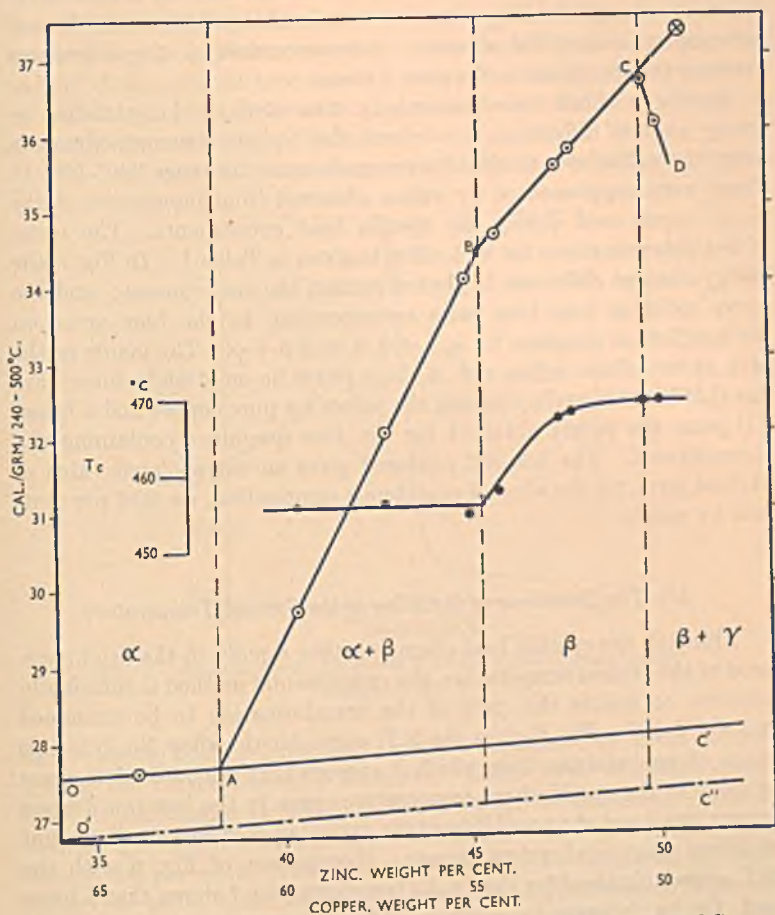


FIG. 5.—Difference in Energy Content of Brasses Between 240° – 500°C.

Detailed examination of the *S.T.* curves shows that all the specimens have practically the same specific heat at 240°C. (0.104–0.107), and the β brasses (5–9) have the same specific heat at 100°C. , viz. 0.094. It follows, therefore, that the difference in energy content at 240° and 100°C. is practically the same for all the brasses in the β phase, and

any differences which exist between the various specimens in the phase are confined to the temperature interval 240° – 500° C. Direct energy content measurements could have been made from 20° to 500° C., but this would have meant diluting the energy corresponding to the interesting part of the *S.T.* curve (from 240° to 500° C.) with a fairly constant amount of energy due to the interval from 20° to 240° C. and reducing somewhat the accuracy of measurement of the differences between the specimens in the pure β phase.

As the authors were particularly interested in the variation in energy content differences throughout the β phase, the measurements using the voltameter method ⁶ were made over the range 240° – 500° C. These were supplemented by values obtained from integration of the power input used during the specific heat experiments. The mean of 2–4 determinations for each alloy is given in Table I. In Fig. 5 the energy content difference is plotted against the zinc content; and the curve splits up into four parts corresponding to the four areas on the equilibrium diagram, *i.e.* α , $\alpha + \beta$, β , and $\beta + \gamma$. The points in the $(\alpha + \beta)$ two-phase region and in the β phase lie on straight lines; the line *OAC'* is obtained by joining the points for pure copper and α brass, *CD* joins the points obtained for the two specimens containing the γ constituent. The line *BC* produced gives an extrapolated value of 37.3 cal./gram. for the alloy of equiatomic composition, *i.e.* 50.7 per cent. zinc by weight.

(d) *The Behaviour of the Alloy at the Critical Temperature.*

Although the specific heat changes rather rapidly in the neighbourhood of the critical temperature, the experimental method is sufficiently sensitive to enable this part of the transformation to be examined in some detail. Fig. 6 gives the *S.T.* curve for the alloy No. 8 in this range of temperature, from which it appears that the rate of increase of slope of the specific heat–temperature curve in the last few degrees is very small and the possibility of the evolution of even a small amount of latent heat is therefore remote. (Comparison of Fig. 6 with the *S.T.* curves obtained for the Cu_3Au transformation ⁶ shows that β brass and Cu_3Au behave in quite a different manner at the critical temperature.)

The maximum specific heat observed for specimens 6, 7, and 8 was about the same and equal to 0.27 cal./gram./ $^{\circ}$ C., so that it is unlikely that the behaviour of the alloy CuZn (50.7 per cent. zinc) would be greatly different at the critical temperature. Any slight temperature gradients in the specimen or sluggishness in the transformation will

tend to flatten the peak of the curve so that 0.27 cal./gram./° C. must be regarded as a minimum value for the maximum specific heat.

(e) Accuracy of the Experimental Results.

Owing to the fact that the critical temperature is higher in β brass than in the alloy Cu_3Au and that an increased heating rate was used, the accuracy is somewhat less than in the Cu_3Au transformation. Up to 500° C. the specific heat measurements are considered to be correct to within ± 2 per cent.; at temperatures below 400° C. the error is probably not more than ± 1 per cent.

The heat content measurements made by the voltameter method

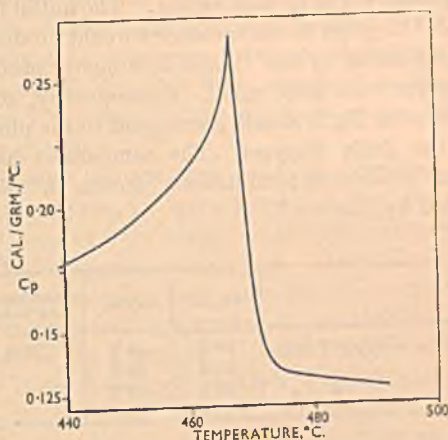


FIG. 6.—Specific Heat of β Brass Near the Critical Temperature. Specimen No. 8.

were lower by about 0.3 per cent. than those obtained by direct integration of the corresponding *S.T.* curve. Either type of measurement could be reproduced to within ± 0.4 per cent. for consecutive experiments. The relative error in the results plotted in Fig. 5 is not higher than ± 0.2 per cent. The absolute error may be estimated by comparing the result obtained by this method for pure copper with the value obtained by Jaeger and his associates. Their value for pure copper for the difference in energy content over the temperature range 240°–500° C. is 26.07 cal., with an error not greater than ± 0.1 per cent. The authors' results were :

Direct determinations (voltameter)	26.18	26.20 cal.
Integration of <i>S.T.</i> curve	26.20	26.25 „

the final value of 26.20 given in Table I being the mean. From this comparison it appears that the absolute error is within the limits $\pm 1.5-0.5$ per cent.

IV. COMPARISON WITH PREVIOUS WORK.

(a) *The Equilibrium Diagram.*

The energy content-composition curve, Fig. 5, cannot be claimed to contribute any very reliable information regarding the position of the phase boundaries in the copper-zinc system, since the measurements cover a range of temperature throughout which the limiting composition of the phases varies to some extent. The initial heat-treatment of 100 hrs. at 450°C. given to the specimens would produce equilibrium conditions corresponding to 450°C. and it is highly probable that any subsequent changes were quite small. Consequently, the intersection of the various lines on Fig. 5 should correspond to the phase boundaries at 450°C. on the CuZn diagram. The comparison has been made using the most reliable determinations shown in the equilibrium diagram compiled by Hansen.⁸

	Fig. 5.	Gayler.	Genders and Bailey.	Bauer and Hansen.
$a/(a+\beta)$ boundary. Zinc, per cent.	38.3	38.7	38.9	
$(a+\beta)/\beta$ " " "	45.4	45.8		45.1
$\beta/(\beta+\gamma)$ " " "	49.6	49.7		49.7

The general agreement is good, and indicates that the precautions taken to eliminate errors due to loss in zinc have proved effective.

(b) *Effect of Composition on the Critical Temperature.*

The critical temperature is plotted against composition in Fig. 5, the temperatures chosen being those at which the specific heat first begins to diminish rapidly. This point can be very readily observed during the specific heat measurements and is about 1°C. higher than the temperature corresponding to the maximum specific heat. Haughton and Griffiths,⁹ from resistance-temperature curves, give the critical temperature as 453°C. in the $\alpha + \beta$ region and 470°C. in the $\beta + \gamma$ region. Their curve is similar in shape to the one in Fig. 5, so that the general agreement may be considered good.

(c) *The Experiments of Steinwehr and Schulze.*^{10 *}

Apart from the original experiments of one of the present authors, the investigation of Steinwehr and Schulze appears to be the only one attempting to determine quantitatively the heat evolved during the β - β' transformation. The experimental method consisted in taking a cooling curve on a large specimen (20 kg. in weight) which was very heavily lagged. The specimen was heated to various steady temperatures by means of a Nichrome coil and the power input determined. It was then allowed to cool freely from about 550° C. and a temperature-time curve taken. The logarithm of the temperature was plotted against the time and the curve obtained was found to split up into two straight lines with an intermediate section corresponding to the interval in which the transformation occurred. The retardation in cooling, in minutes, was estimated from this curve and the excess energy given out during this time calculated as the product of the power necessary to maintain the specimen at the mean temperature multiplied by the time.

Steinwehr and Schulze examined two brasses, one containing 56.46 per cent. copper, *i.e.* an $\alpha + \beta$ brass, and the other containing 49.8 per cent. copper; the energy of the transformation was found to be 1.81 and 2.48 cal./gram., respectively. On the basis of certain values for the phase boundaries, they calculate the energy/gram. of pure β as 3.0 cal./gram. from both specimens and conclude that it is independent of composition in the β phase. This conclusion is scarcely justified in view of the large dispersion in their experimental results for each specimen, ± 20 per cent. Further, the relative amounts of the two phases obtained by calculation are very sensitive to small changes in the precise values chosen for the phase boundaries.

The experimental method suffers from the same defect as the

* In a recent paper by Moser¹⁴ some further results on a β brass containing 48.2 per cent. zinc are reported. The work was carried out using a different method from that used by us, although the true specific heat as distinct from the mean specific heat was measured directly. His specific heat-temperature curve is in very good agreement with our results. For the total energy content from 20° to 650° C. a value of 74.2 cal./gram. is obtained. Using Moser's results for the specific heat from 20° to 240° C. and 500° to 650° C. we find that the energy content difference from 240° to 500° C. for his specimen is 35.6 cal./gram.

For the energy content difference from 20° to 650° C. Ruer and Kremers¹⁵ give 74.5 cal./gram. This result was obtained by direct calorimetric measurement on an alloy containing 48.2 per cent. zinc. Using Moser's values for the specific heat above 500° C. this leads to an energy content difference of 35.9 cal./gram. from 240° to 500° C.

Our result obtained from Fig. 5 is 35.95 cal./gram. with an estimated maximum error of ± 1.5 and -0.5 per cent. Both results are well within these limits.

Finally, the maximum value of the specific heat found by Moser is about 0.26 cal./gram. at the critical temperature; this is in good agreement with our value of 0.27 cal./gram. bearing in mind the difficulties associated with the investigation of this part of the curve.

standard cooling curve method applied to β brass : it gives the impression that the transformation takes place over a much smaller temperature interval than is actually the case. For example their experimental results indicate that the transformation ends on cooling above $400^{\circ}\text{C}.$; comparison with the *S.T.* curves in Fig. 4 show that this is not the case. The experimental method of Steinwehr and Schulze is strictly applicable only to the cases in which the transformation occurs over a limited temperature interval and where the specific heat of the alloy both above and below the temperature of the transformation varies only slightly with temperature. Their value of 3 cal./gram. is much smaller than that of 10 cal./gram. obtained in the present authors' experiments. (See next section.)

(d) *Experiments of Sykes.*³

In a previous paper dealing with thermal methods for investigating transformations of the β brass type, one of the present authors published a *S.T.* curve for a β brass containing 49.06 per cent. zinc. The total energy of the transformation calculated from this curve by Bragg and Williams is in satisfactory agreement with the value found in the present investigation. (See next section.) The *S.T.* curve is in excellent agreement with Fig. 7 at temperatures up to $450^{\circ}\text{C}.$; above this temperature the original curve is higher by an amount greater than the experimental error claimed in the present paper. This discrepancy is to be ascribed to experimental errors present in the original work which have been eliminated by the improved technique and apparatus now employed.

V. COMPARISON WITH THE THEORETICAL WORK.

The transformation has been investigated theoretically on the basis of two different assumptions : Bragg and Williams^{2, 4} assume that the energy of a given structure is determined by the average degree of order throughout the whole structure, *i.e.* by the long distance or superlattice order. The whole of the change in energy and entropy is to be found therefore below the critical temperature since superlattice order disappears at this point on heating. Bethe,⁵ on the other hand, assumed that interaction occurred only between nearest neighbours and showed that, whilst superlattice order disappears at the critical temperature, a certain amount of local order exists above this temperature since a tendency for unlike atoms to be neighbours still persists. Local order only disappears completely at very high temperatures; consequently an abnormally high specific heat should exist above the critical temperature. As both theories deal quantitatively with certain features of the transformation which have been investigated experimentally a comparison is possible.

(a) *The Specific Heat-Temperature Curve.*

The *S.T.* curve, Fig. 7(a), specimen 8, is, as has already been mentioned, the best approximation to the *S.T.* curve for the hypothetical alloy CuZn which can be realized experimentally. It contains the effects of the atomic rearrangement process superimposed on the normal (Dulong and Petit) *S.T.* curve, and it is necessary to make an estimate of the latter in order to obtain results which can be compared with those obtained theoretically.

It may be assumed, to a first approximation at any rate, that the

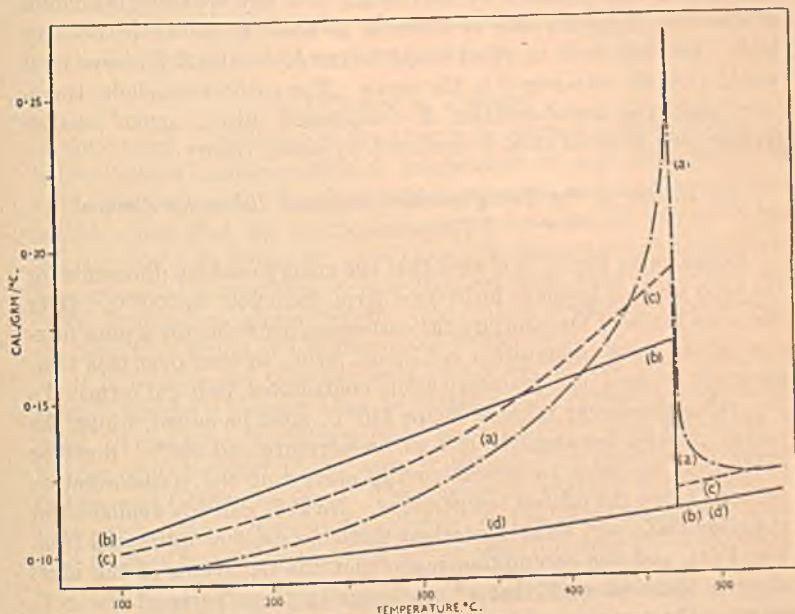


FIG. 7.—Specific Heat Curves (Theoretical).

specific heat of an alloy in the absence of any transformation is equal to the specific heat of a mixture of copper and zinc of the same composition. According to Jaeger¹¹ the specific heats of pure copper and pure zinc are given by the equations:

$$\begin{aligned} \text{Copper } C_p &= 0.092597 + 0.20832 \times 10^{-4} t; \quad t = \text{temperature in } ^\circ\text{C.} \\ \text{Zinc } C_p &= 0.093335 - 0.778 \times 10^{-6} t + 0.12708 \times 10^{-6} t^2 \end{aligned}$$

The *S.T.* curve for a mixture having the same composition as specimen 8 is given by Fig. 7(d); the actual curve follows 7(a). The two curves coincide at 160° C. and are practically the same down to 100° C., suggesting that the transformation ceases to affect the specific heat appreciably below 160° C.

The *S.T.* curves derived theoretically according to Bragg and Williams and Bethe are given in Fig. 7 (b) and (c). Bethe's curve is strictly applicable to an alloy having a simple cubic lattice. For a body-centred lattice the curve will have a slightly lower maximum.* The change in specific heat at the critical temperature is very much larger than that given by either Fig. 7 (b) or (c), which suggests that the disappearance of order at the critical temperature takes place much more rapidly than either theory predicts. At lower temperatures the experimental curve lies below the theoretical curves. It is unlikely that this effect is produced by the freezing in of any appreciable amount of disorder, since the rate of diffusion in brass is known to be very high. Further, such an effect could be traced on the *S.T.* curve as it would give rise to a step † in the curve. The authors conclude, therefore, that the transformation is compressed into a much smaller temperature interval than is predicted by either theory.

(b) *Energy of the Transformation Released Below the Critical Temperature.*

Referring to Fig. 5, it is seen that the energy content difference for the alloy CuZn is found to be 37.3 cal./gram. from 240° to 500° C. Over the same range of temperature the corresponding value for a pure mixture of the same composition is 27.3 cal./gram., so that over this temperature interval the transformation contributes 10.0 cal./gram. To this value the energy released below 240° C. must be added, whilst the energy released between the critical temperature and 500° C. must be subtracted in order to determine the energy of the transformation released below the critical temperature. No *S.T.* curve is available for the alloy CuZn and these corrections therefore must be estimated from Fig. 7 (a), and the assumption made that the behaviour of the ideal alloy is identical with that of specimens in these parts of the *S.T.* curve. The two corrections are quite small, i.e. + 0.32 cal./gram. and - 0.48 cal./gram., so that the final value for the energy released by the transformation below the critical temperature is 9.8 cal./gram. The theoretical results are 11.4 cal./gram. according to Bragg and Williams and 10.9 cal./gram. according to Bethe, and the agreement is therefore quite good.

It is possible, however, that this agreement is to some extent fortuitous. Referring to Fig. 5, line *O'C''* represents the change in energy content difference with zinc content assuming the alloys to have the same specific heat as mixtures of the same composition. It falls well

* In comparing the curves it should be remembered that the transformation energy in CuZn is about 8 per cent. higher than in specimen No. 8.

† Cf. *S.T.* curves for Cu₃Au.¹²

below the experimental point for the α brass, and suggests that $O'C''$ gives too low an estimate for the normal heat content. For example, if the experimental values for pure copper and α brass are extrapolated linearly into the β phase (line OAC'), the normal energy content difference for CuZn is given as 28.05 cal./gram. so that the energy of the transformation below the critical temperature is reduced to 8.75 cal./gram. As has already been pointed out, the $S.T.$ curve for α brass is anomalous. Further, the use of line OAC' automatically assumes that the transformation ends at about 240°C. , whereas the $S.T.$ curves show no peculiarity in this region. These considerations throw considerable doubt on the validity of this second method of estimation and we think the first method more reasonable.

(c) Change in Entropy.

According to Williams¹³ the change in entropy accompanying an order-disorder transformation is independent of any assumptions as to the precise mechanism of the ordering process, and should provide a reliable check that the phenomenon under consideration is due to the formation of a superlattice. The change in entropy below the critical temperature for specimen 8 is 0.0145 cal./gram., and the value for CuZn is therefore about 0.0157. The values predicted theoretically are 0.0214 by Bragg and Williams and 0.0198 by Bethe.

If it be assumed that the total energy of 10.9 cal./gram. given by Bethe's theory is correct, then according to the present experimental work 1.1 cal./gram is still available below 160°C. This will make a further contribution* to the entropy change lying between the limits 0.0025 and 0.0050 cal./gram. The change in entropy is therefore in reasonably good agreement with theory, and substantiates the opinion that the β - β' transformation is in fact an order-disorder transformation.

(d) Specific Heat above the Critical Temperature.

Referring to Fig. 7, it is seen that the experimental curve (a) is slightly higher than the $S.T.$ curve (d) above the critical temperature. The difference in specific heat given by Bethe⁵ is about 0.008 cal./gram. for the simple cubic lattice; for the body-centred lattice it will be slightly lower. Within the limits of experimental error this prediction is verified.

(e) Effect of Concentration on the Critical Temperature.

The critical temperature at which long distance order sets in on cooling is affected by the relative concentration of the two types of

* The value of 0.0025 cal./gram. is obtained by assuming all the energy is released at 160°C. , i.e. 430°K. , whereas the value of 0.005 cal./gram. corresponds to its release at 210°K. The true value should lie between these two values.

atom being a maximum for the equiatomic alloy.⁴ The variation with concentration is given by the equation :

$$T_c = T_c^\circ (1 - 4\delta^2) \quad \delta = (\tfrac{1}{2} - c),$$

where T_c° is the critical temperature for the alloy CuZn and c is the concentration of one constituent (zinc).

For an alloy containing 45.7 per cent. zinc $\delta = 0.05$ and therefore

$$T_c^\circ - T_c = \frac{T_c}{100} = 7.4^\circ \text{C.}$$

Experimentally, a difference of 12°C. is found. The theoretical result is thus of the right order, and the expression gives a curve (parabolic) of the right shape.

(f) *Effect of Concentration on the Energy of the Transformation.*

Once the composition of the alloy is changed from that corresponding to equiatomic proportions the energy of the transformation will diminish. The magnitude of this effect has been calculated by Easthope* using Bethe's theory, who obtained the result :

$$E = K c \left(c - \frac{1}{z} \right)$$

where E is the energy released below the critical temperature, c the concentration, z the number of nearest neighbours (eight for CuZn), and K a constant.† The ratio of the energies for the alloy at the extremity of the β phase poor in zinc ($c = 0.45$) and the alloy CuZn is 0.78 according to this equation. The experimental result is 0.75 so that the agreement is again quite good.

VI. CONCLUSIONS.

Comparison of these results with those obtained for the alloy Cu_3Au ¹² shows that in both cases an excess specific heat exists above the critical temperature, so that this feature of the order-disorder transformation may be considered as established. The Bethe theory also gives the better agreement as regards total energy and entropy change. Consequently, the assumption that interaction occurs only between nearest neighbours must be considered more probable than the more general assumption of Bragg and Williams. In both cases the energy predicted by Bethe's theory is about 10 per cent. higher than the value found experimentally, and is not sufficiently compressed into the temperature interval within 200°C. of the critical temperature.

In particular, the theoretical $S.T.$ curves are a very poor approxi-

* Private communication.

† K is a function of the energy of interaction between neighbouring atoms and also depends on the type of structure.

mation to the actual curves. Their shape is fixed by the assumptions made as to the precise nature of the ordering force and, as Williams has pointed out, slight modifications are likely to make large changes in the *S.T.* curve at the critical temperature. It is not surprising, therefore, that this feature of the transformation is the least satisfactory, since it is unlikely that the form of the ordering force is as simple as Bethe assumes. Further theoretical improvements must be chiefly concerned in the evaluation of the correct *S.T.* curve.

CuZn and Cu₃Au are probably amongst the simplest examples of order-disorder transformations which exist, and are the only cases which have been examined experimentally in order to determine whether they obey the various theoretical predictions. It is highly probable, that the majority of such transformations will be more complicated (e.g. MgCd, CuAu, &c.) so that any detailed generalization is best avoided until a large number of different transformations have been studied.

VII. ACKNOWLEDGMENTS.

The zinc used in these experiments was kindly supplied by Mr. Stanley Robson of the National Smelting Company, Ltd., Avonmouth.

The authors are indebted to the Department of Scientific and Industrial Research for the grant made to one of them (H. W.).

The authors' thanks are also due to the Metropolitan-Vickers Electrical Company, Ltd., for kindly providing the necessary facilities for this work, and in particular they are indebted to Mr. A. P. M. Fleming, C.B.E., Director of the Metropolitan-Vickers Electrical Company, Ltd., and Manager of the Research Department, for his personal interest in the investigation.

The authors thank Professor W. L. Bragg, F.R.S., for his kind and continued interest.

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DISCUSSION.

DR. C. H. DESCH,* F.R.S. (Vice-President): There is nothing to say by way of criticism of this paper, because the old problem of the transformation in β -brass was cleared up when Dr. Sykes published his earlier work. This paper, however, gives the finishing touch and the last proof which was necessary, and also provides an important quantitative treatment. Not only has the problem been solved for β -brass, but a firm foundation has been laid for the study of these transformations in general.

Professor F. C. THOMPSON,† M.Sc., D.Met. (Member): I should like to reiterate what Dr. Desch has said, that the very fact that there has been no discussion of this paper may be taken as an indication of the high opinion which has been formed of the authors' work.

The AUTHORS (*in reply*): Since the paper was written two interesting communications have appeared which deal specifically with the β - β' transformation in brass, and a brief summary of their contents may be of interest.

Jones and Sykes,‡ using the $K\alpha$ radiation of zinc, have obtained X-ray powder diagrams of β -brass which show superlattice lines, thus producing direct evidence of an ordered structure in the alloy at room temperature.

Bethe, in his original treatment of the order-disorder transformation in a body-centred lattice, assumed that interaction occurred only between an atom and its nearest neighbours. In any final theory the possible effect of higher interactions should be taken into account. Recently Chang § has worked out the effect of interaction between next nearest neighbouring atoms, and has shown that, provided that a reasonable value is assumed for this second interaction energy, an $S.T.$ curve is obtained which is in much better agreement with the experimental results. In particular, the specific heat attains a much higher maximum at the critical temperature and decreases more rapidly with diminishing temperature than in the case for the $S.T.$ curve (Fig. 7 (c)) given by Bethe.

CORRESPONDENCE.

DR. HELMUT MOSER ||: This paper interests me very much, since I have recently determined the true specific heat of a definite β -brass by a somewhat different method. The very close agreement between my result and that of the authors shows that the technique of calorimetric measurements at high temperatures has now reached such a degree of precision as to enable us to form satisfactory conclusions on the correctness of theoretical relations. There can be no further doubt that the frequently-used cooling method is unsuitable for quantitative measurements when the material undergoes a transformation extending over a wide temperature range.

The anomaly in the C_p curve of $\alpha + \beta$ brass at about 210° C. found by the authors, and not yet satisfactorily explained, appears to me to be very remarkable, since it seems to bear no relation to the true transformation as it occurs also in α -brass which undergoes no transformation. On the basis of observations previously made on certain irregularities in the property-temperature curves of gold-copper alloys and of nickel, I originally expressed the opinion that a similar anomaly should be found in β -brass but, like the authors, I have failed to find it.

* Superintendent, Department of Metallurgy and Metallurgical Chemistry, National Physical Laboratory, Teddington.

† Professor of Metallurgy, Manchester University.

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|| Reg. Rat. an der Physikalisch-Technischen Reichsanstalt, Berlin-Charlottenberg, Germany.

ALLOYS OF MAGNESIUM. PART VI.—THE 777 CONSTITUTION OF THE MAGNESIUM- RICH ALLOYS OF MAGNESIUM AND CALCIUM.*

By J. L. HAUGHTON,† D.Sc., MEMBER.

SYNOPSIS.

The constitution of magnesium-rich alloys of magnesium and calcium has been re-determined. The eutectic point occurs at 16.2 per cent. calcium and at 517° C. Magnesium dissolves about 1.8 per cent. calcium at the eutectic temperature and about 0.5 per cent. at 250° C.

INTRODUCTION.

THIS report is Part VI of the investigation of the constitution and mechanical properties of magnesium alloys which is being conducted at the National Physical Laboratory under the direction of Dr. C. H. Desch, F.R.S., for the Metallurgy Research Board.^{1. 2 3. 4. 5}

It has been shown recently⁶ that additions of small amounts of calcium cause an improvement in the mechanical properties of some magnesium alloys at high temperatures; they also reduce the tendency of magnesium and its alloys to burn, and appreciably reduce the amount of scale formed during annealing. The present work has been carried out, in connection with the investigation of the mechanical properties, to check the existing equilibrium diagram, and has been extended to alloys containing up to 26 per cent. calcium in order to determine accurately the composition of the eutectic.

PREVIOUS WORK.

The complete system was investigated in 1911 by N. Baar,⁷ whose diagram up to 26 per cent. calcium is given in Fig. 1. Further work was carried out by R. Paris⁸ in 1933, as a preliminary to an investigation into the ternary system magnesium-calcium-zinc. Paris, however, did not publish a diagram, but stated that his results differed slightly from those of Baar, in particular with reference to the maximum in the

* Manuscript received February 10, 1937.

† Principal Scientific Officer, Metallurgy Department, National Physical Laboratory, Teddington.

liquidus which he found at the 50:50 alloy, indicating a compound containing less calcium than the Mg_2Ca , given by Baar. This part of the diagram, however, is outside the range dealt with in the present report.

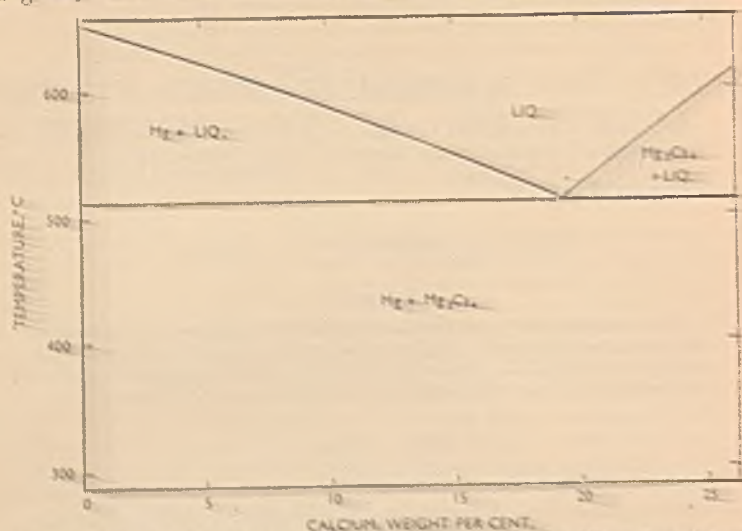


FIG. 1.—Equilibrium Diagram of the Magnesium-Calcium Alloys Containing up to 26 Per Cent. Calcium. (Baar.)

PRESENT WORK.

Preparation of the Alloys.

The magnesium used was from the same source as that mentioned in the previous reports. It contained as impurities: aluminium 0.018; iron 0.020; silicon 0.013 per cent. For the solid solubility determination, resublimed metal was used.¹

The calcium was purchased from Messrs. Hopkins and Williams, and contained as impurities: silicon 0.06; iron 0.29 per cent.; copper trace.

The magnesium was melted in stainless steel crucibles under a flux of the composition used in the work on magnesium-nickel alloys,² and the calcium was added to it, in the form of borings. In a few instances specimens were made by mixing together weighed quantities of other alloys.

It was found that large, and quite unpredictable, losses of metal occurred. Generally, the calcium loss was the greater, but in some cases a larger quantity of magnesium was lost. This loss also continued during the taking of the thermal curves, making it very difficult to decide the actual compositions of the alloys at the moment at which the curves were taken. In the early part of the work the procedure adopted

was the same as that for the magnesium-silver alloys,⁵ i.e. the thermal curve crucible was filled from the pot in which the alloy was made, and the remainder of the liquid was poured into chill moulds; after the thermal curves were taken the metal from the crucible was remelted and poured into chill moulds, from which a sample for analysis was taken by cutting a slice right through the ingot. It was hoped in this way to get a more truly average sample of the metal than would be obtained by taking drillings from the ingot in the crucible. When the variable loss in calcium was observed, however, it was realized that serious errors might be introduced in remelting the metal in the crucible. To check this an alloy was made to contain 18 per cent. calcium and cast into a thermal-curve crucible and into a chill mould. A sample (A) was taken from the chill mould, and then a pair of heating and cooling curves were taken. Drillings (B) were then removed from the pot, and the metal was melted and cast into a chill mould from which a sample (C) was cut. The results of analyses were:

Sample A	.	.	14.42	} Calcium Per Cent.
B	.	.	14.70	
C	.	.	12.89	

A similar experiment on an alloy made up to contain 10 per cent. calcium gave on analysis:

Sample A	.	.	8.49	} Calcium Per Cent.
B	.	.	8.31	
C	.	.	6.82	

It is obvious that a large loss of calcium takes place in melting the metal out of the crucible, and it was considered wiser to risk trouble due to segregation and to obtain the sample for analysis by taking drillings from the actual ingot in the crucible after the curves had been taken. That the risk of errors from segregation was small was shown by sectioning a thermal curve ingot from top to bottom, and examining it under the microscope, which showed that the change in structure from inside to outside, or from the top to the bottom, was small.

To the difficulties already mentioned must be added the fact that the estimation of small amounts of calcium in magnesium is not easy. Mr. W. H. Withey, B.A., of the Chemical Division of this Laboratory, has worked out a new method for this purpose.⁹

Thermal Analysis.

Owing to the low densities of magnesium and calcium, it was considered unlikely that errors due to segregation would occur, and most of the thermal curves were taken in the gradient furnace. Seven curves, however, were taken in the stirring apparatus,¹⁰ and these agreed well

with those taken in the gradient furnace, though the observed arrests were somewhat sharper. As stated above, microscopic examination of a sectioned ingot suggested that segregation was small.

Thermal curves were taken on 33 alloys, but only 27 of these have been used in establishing the diagram. The remainder were either

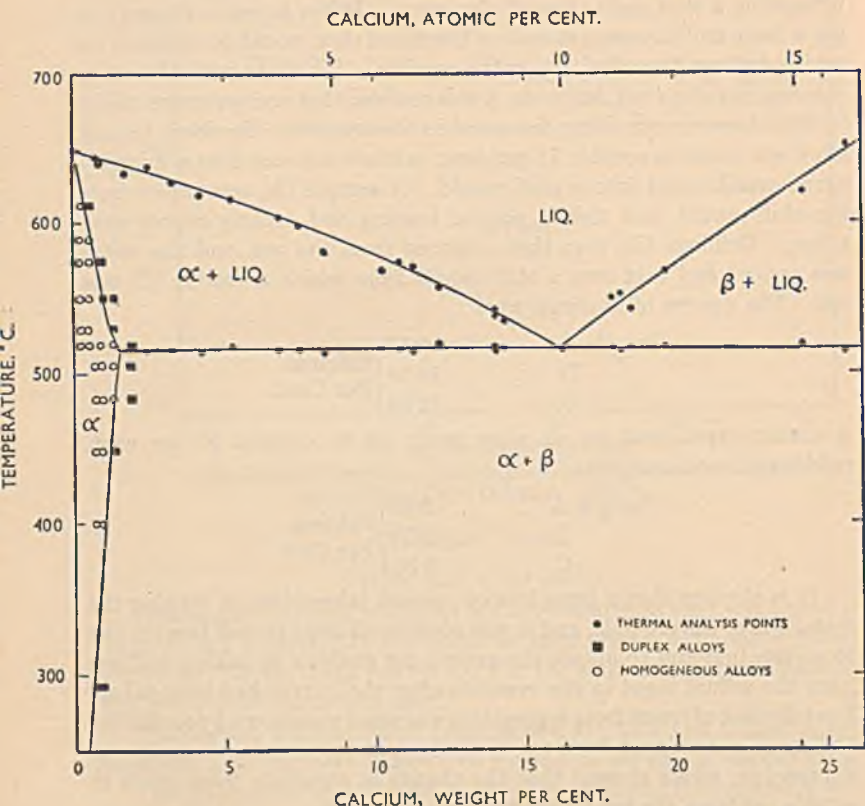


FIG. 2.—Equilibrium Diagram of the Magnesium-Calcium Alloys Containing up to 26 Per Cent. Calcium. (Haughton.)

poor curves or gave points which were obviously incorrect, though the cause of the inaccuracy was not known. The alloys as a whole gave unsatisfactory arrests, and this, with the continuous change in composition of the alloy and the difficulty in analysis, has made difficult the determination of this apparently simple diagram.

The impossibility of preparing alloys to a required composition, together with the other difficulties referred to above, accounts for the fact that 33 alloys were made to determine a simple liquidus curve



3



4

FIG. 3.—16.3% Ca. $\times 500$.
FIG. 4.—10% Ca. $\times 150$.



over a range of 26 per cent. The curves were taken on Payne's automatic potentiometer.¹¹

Microscopical Examination.

The method of polishing the specimens was the same as for the magnesium alloys previously studied. In general, they were etched in 4 per cent. nitric acid in alcohol, though in a few cases a much weaker solution was used.

The specimens used for the determination of the solidus and of solid solubility were annealed in sealed tubes of Pyrex glass *in vacuo*, in hydrogen, and in argon. The earlier specimens were annealed *in vacuo* and were perfectly satisfactory. Later, however, when a new Pyrex tube of larger diameter was used, marked sublimation of the alloys took place, the tube becoming lined with a dark blue deposit, presumably Mg_2Si , at temperatures considerably below that at which successful annealings had been carried out previously. The tubes were then filled with hydrogen or with argon in such quantity that they were at about atmospheric pressure at the temperature of annealing. Even this did not completely prevent sublimation. Success was obtained, however, on using a piece of tube similar to the original one and filled with argon. The reason for this is obscure, but is being investigated.

The diagram obtained is given in Fig. 2.

The Equilibrium Diagram.

(a) *The Liquidus.*—Except for alterations introduced by the change in composition of the eutectic, the liquidus found differs little from that given by Baar.

(b) *The Eutectic.*—The eutectic temperature ($517^\circ \pm 1^\circ \text{C.}$) is in very good agreement with that found by Baar, who gave it as 514°C. The eutectic composition found in the two investigations is, however, very different: Baar gave it as 19 per cent. calcium, while the present investigation shows it to be 16.2 per cent. The determination of the composition was rendered difficult by the fact that the errors in the thermal and chemical analyses introduced a certain amount of uncertainty into the location of the position of the liquidus. The error in composition of the eutectic as determined from the intersection of the liquidus curves is unlikely to be greater than ± 0.5 per cent.; the probability of its being so great as this is reduced by the fact that micrographic examination of the chill-cast 16.27 per cent. alloy suggested that it was pure, or very nearly pure, eutectic. Fig. 3 (Plate XVIII) is a photograph of this alloy, while Fig. 4 shows an alloy containing 10 per cent. calcium.

(c) *Solubility Limits*.—The solubility limits were determined by the microscopic examination of annealed and quenched specimens. Magnesium dissolves about 1·8 per cent. of calcium at the eutectic temperature; at 250° C. the solubility has decreased to about 0·5 per cent.

SUMMARY.

The equilibrium diagram of alloys of magnesium with up to 26 per cent. of calcium has been determined. The alloys form a simple eutectiferous series between magnesium and a compound whose composition has not been determined, but which is given by Baar as Mg_4Ca_3 . The liquidus and eutectic temperatures are in fair agreement with those of previous workers, but the eutectic composition is found to occur at 16·2 per cent., whereas Baar gave it as 19 per cent. No previous determination of solid solubility had been made, but the present work shows the solubility limit to occur at 1·8 per cent. calcium at the eutectic temperature, and about 0·5 per cent. at 250° C.

ACKNOWLEDGMENTS.

The author wishes to express his indebtedness to Dr. C. H. Desch, F.R.S., Superintendent of the Metallurgy Department, under whose direction the work was undertaken, and to the members of the Chemical Division of the Department for carrying out the very difficult chemical analyses of the alloys. His thanks are also due to Mr. R. Spencer, who took some of the thermal curves in the early stages of the work, and particularly to Mr. E. C. Ellwood who carried out the greater part of the experimental work.

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THE CONSTITUTION OF THE NICKEL-ALUMINIUM SYSTEM.*

778

By W. O. ALEXANDER,† Ph.D., MEMBER, and N. B. VAUGHAN,‡
M.Sc., MEMBER.

SYNOPSIS.

The system nickel-aluminium has been studied by thermal and micrographic methods, and a hitherto unsuspected phase is found to exist, containing 84.5-87 per cent. nickel, and probably corresponding to the intermetallic compound Ni_2Al (86.7 per cent. nickel). Otherwise the diagram remains substantially as determined by Gwyer, except that the compound described by Gwyer as NiAl is shown to be Ni_2Al_3 .

A change in solubility of nickel in NiAl causes alloys with 80-85 per cent. nickel to exhibit a suppressed structure when quenched from temperatures exceeding 1150°C ., and to undergo hardness changes on heat-treatment similar to those which occur in the suppressed β phase of the copper-aluminium system.

Some preliminary observations suggest that the nickel-rich alloys may possess desirable heat-resisting properties.

INTRODUCTION.

MICROGRAPHIC evidence obtained in the course of an investigation of the constitution of the nickel-copper-rich aluminium-nickel-copper alloys, pointed to the existence of a phase which could not be identified by reference to the only published diagram for nickel-aluminium alloys, due to Gwyer.¹ A re-examination of these alloys was therefore rendered necessary.

The only other published work on the constitution of this system until very recently was that of Fink and Willey,² who made a detailed investigation of the alloys containing up to 18 per cent. nickel. They determined accurately the eutectic composition and temperature and the changes with temperature of the solid solubility of nickel in aluminium. Just as the present paper was completed, however, Bradley and Taylor³ published the results of an X-ray study of the phases present at room temperature, together with a few results obtained from quenched specimens.

* Manuscript received April 9, 1937. Presented at the Annual Autumn Meeting, Sheffield, September 7, 1937.

† William Gibbins Fellow, Metallurgical Department, University of Birmingham.

‡ Investigator, British Non-Ferrous Metals Research Association, London; Late Research Student, Metallurgical Department, University of Birmingham.

PRELIMINARY WORK.

Through the interest of Dr. L. B. Pfeil, several nickel-rich nickel-aluminium alloys were prepared in a small high-frequency induction furnace in the laboratories of The Mond Nickel Company, Ltd.

Examination of the microstructures of slowly-cooled and heat-treated specimens lead to the tentative modification of Gwyer's diagram by the introduction of an additional phase, which has been termed θ , for ease of reference in discussing the constitution of aluminium-nickel-copper alloys, which is to be the subject of a subsequent paper. The authors have preferred to name this phase θ , rather than β or γ , because its space lattice and electron-atom ratio do not correspond with those usually now associated with the phases denoted by the latter symbols. The phase in this series of alloys which has the typical β features is the compound NiAl .

The range of existence of the θ phase field appeared to be from 85.5 to 88 per cent. nickel, for alloys with compositions lying between these limits underwent no change in structure on slow cooling from 1400°C . It was noted that a compound having the formula Ni_3Al would contain 86.7 per cent. nickel. An X-ray spectrogram showed that the θ phase has a face-centred cubic lattice with a superlattice, a fact that has been confirmed independently by Bradley and Taylor,³ who also agree with the suggested formula.

EXPERIMENTAL WORK.

As a result of the above observations it was decided to proceed to a fuller investigation of the nickel-aluminium system. Alloys covering the entire range of compositions were therefore made up, aluminium of 99.89 per cent. purity and Mond Nickel shot of an equal degree of purity being used.

Alloys containing up to 20 per cent. nickel were prepared in an electric resistance furnace and cooling curves were taken on samples of them which were remelted and cooled in a gradient furnace. A Chromel-Alumel couple was employed, which had been calibrated against the usual pure metals and the copper-silver eutectic, and it was estimated that the accuracy of temperature measurement was $\pm 0.25^{\circ}\text{C}$.

All the alloys containing more than 20 per cent. nickel were made in a high-frequency induction furnace, through which a continuous stream of dry, oxygen-free nitrogen was passed. Sillimanite crucibles, coated internally with a white Alundum cement, were found suitable for containing the melt. The volume of alloy was kept approximately constant and, since considerable changes in density occur over the range

of alloys investigated, the weight of a melt varied from 100 gm. for aluminium-rich alloys to 300 gm. for nickel-rich alloys. The loss on melting was of the order of 1 per cent. of the total weight.

Cooling curves were taken of the alloys as they cooled in the furnace immediately after synthesis, the temperature being measured with a platinum/platinum-rhodium couple which was protected by a silica sheath coated at the end with Alundum cement. Determinations of the melting points of pure copper and pure nickel with this couple showed close agreement with a standard calibration curve which was available, and of which use was consequently made. The accuracy of the temperatures obtained is estimated as $\pm 2^\circ \text{C.}$ at 1400°C. and $\pm 1^\circ \text{C.}$ at 1100°C. A Carpenter-Stansfield potentiometer was used throughout, and all cooling curves were recorded as inverse rate curves on a Rosenhain plotting chronograph.

The observation of Gwyer and earlier workers (*e.g.* Guillet), that large evolutions of heat occur on synthesizing alloys containing 40–85 per cent. nickel, was confirmed. If nickel shot be stirred into aluminium at 800°C. sufficient heat is generated to increase the temperature of the melt to 1500°C. for a brief time.

Analysis of a few representative alloys showed that in most cases the nickel content was slightly less than the calculated value, but the discrepancy was not large enough to make it necessary for every alloy to be analyzed and in constructing the equilibrium diagram the nominal values have been used.

The methods of analysis were as follow: A 0.5 gm. sample was dissolved in sulphuric acid. An aliquot portion of solution was taken and, after addition of tartaric acid to keep the aluminium in solution, was made faintly ammoniacal. Gravimetric determination of nickel by the usual dimethylglyoxime method or volumetric estimation could then be made. In the latter case excess of a standard potassium cyanide solution was run in and the excess titrated with standard silver nitrate solution, potassium iodide serving as indicator.

The results of the analysis of a few alloys by these methods are given in Table I. Spectrographic analysis of one or two alloys showed that the only impurities present to the extent of more than a trace were iron and silicon, which were of the order of 0.05 and 0.10 per cent., respectively.

RESULTS OF THERMAL ANALYSIS.

The thermal arrests obtained from the cooling curves are given in Table II and in the diagrams, Figs. 1 and 2. The results for alloys containing between 0 and 68.5 per cent. nickel, where a maximum occurs in the liquidus curve, corresponding to the compound NiAl ,

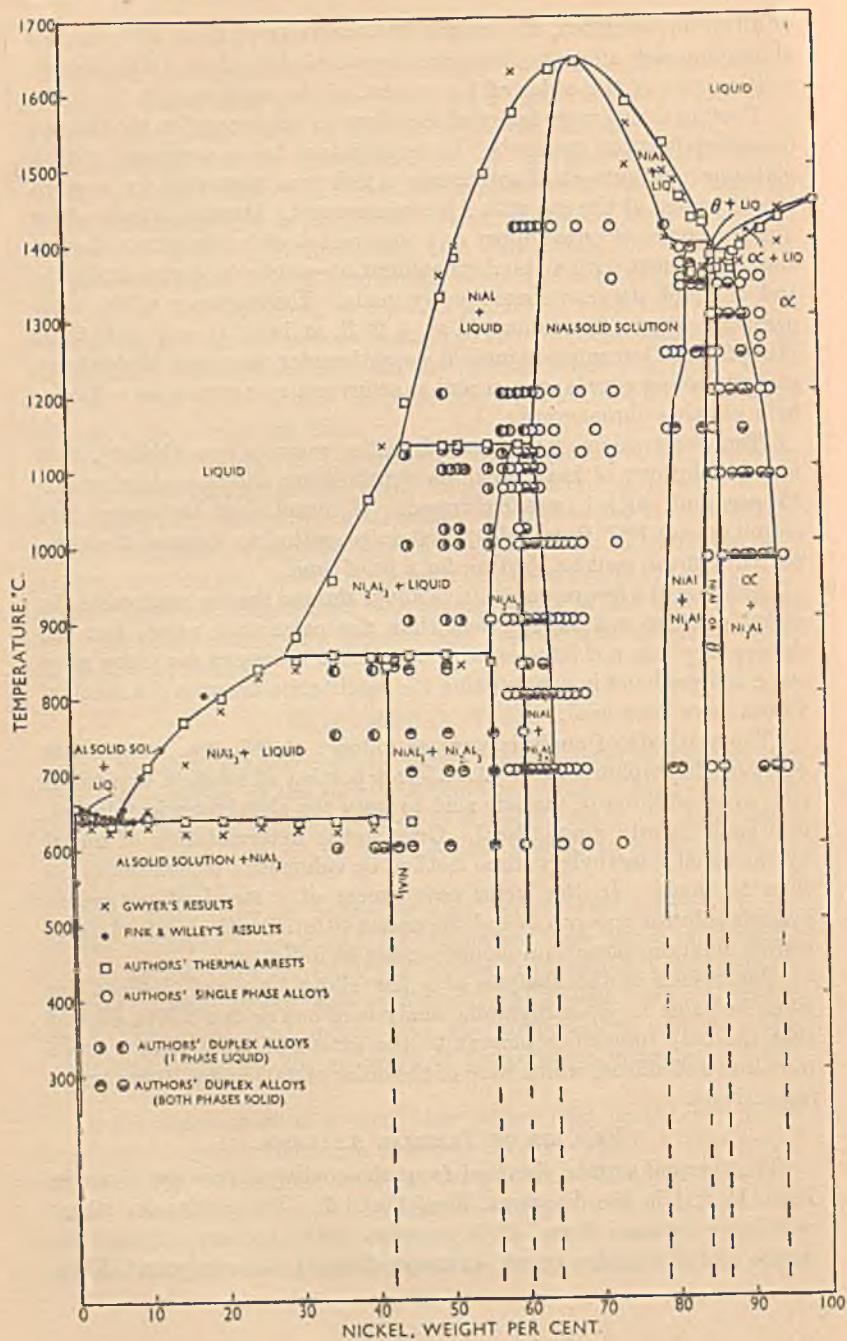


FIG. 1.

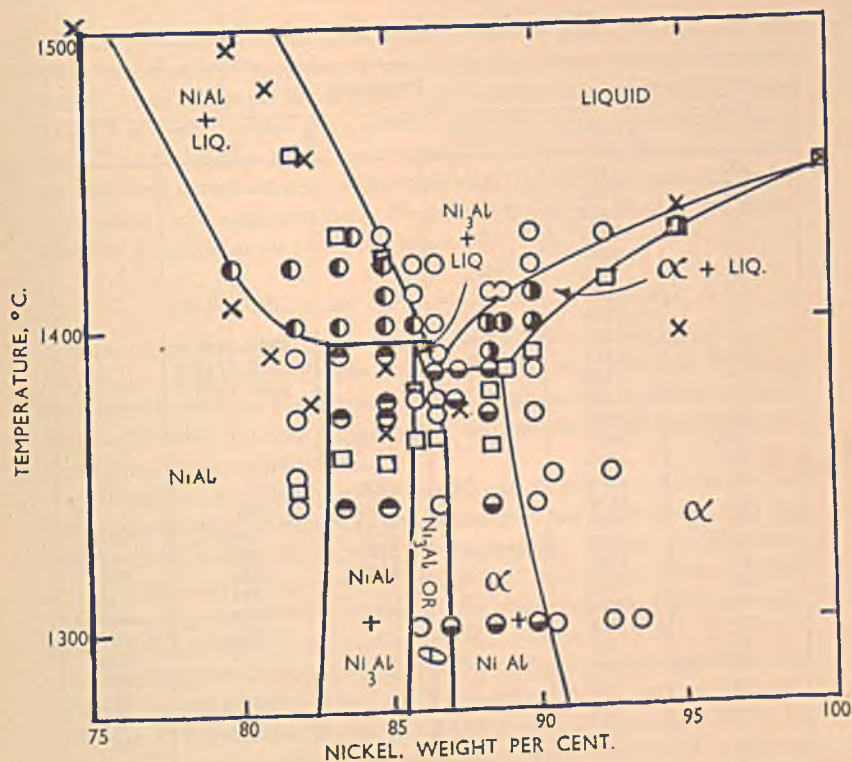


FIG. 2.

TABLE I.

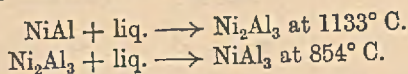
Nickel, Per Cent.	
Nominal.	By Analysis.
90.5	90.60
86.7	86.65
80.0	79.92
75.0	74.75
60.0	59.85
40.0	39.90

TABLE II.—Cooling Curve Arrests.

Nominal Composition, Nickel, Per Cent.	Temperature, ° C.				
	Liquidus.	Solidus.	1.	2.	3.
100	1452				
95	1431				
92.5	1414				
90	1391				
89	1384				
88.5	1378	1360			
86.7	1363				
86	1379	1362			
85	1424	1354		1320-1167	
83.5	1431	1357		1305-1145	
82	1458	1347		1248-1190	
80	1531				
75	1586				
68.5	1638				
65	1629				
60	1574		1133		
56	1493		1134	845	
52	1385		1133	854	635
50	1329		1133	853	
45	1191		1133	857	636
40	1062			853	636
35	956			856	636
30	881			850	634
25	838				638
20	800				638
15	772				642
10	710				642
5					632
0	659				

In alloys containing less than 60 per cent. nickel, the temperatures given in columns 1-3 refer to: (1) peritectic reaction: $\text{NiAl} + \text{liq.} \rightarrow \text{Ni}_2\text{Al}_3$; (2) peritectic reaction: $\text{Ni}_2\text{Al}_3 + \text{liq.} \rightarrow \text{NiAl}_3$; (3) Al-NiAl_3 eutectic.

support in general those of Gwyer and of Fink and Willey, which are also included in Fig. 1. The peritectic reactions were found to occur at the following constant temperatures:



That the peritectic reactions did not proceed to completion at the rate of cooling obtaining in the high-frequency furnace, was apparent from the eutectic arrest given by the 45 per cent. nickel alloy.

No evidence was found in alloys containing 0-40 per cent. nickel of the arrest at about 550° C. which was observed by Gwyer, and which, it must be concluded, was in some way connected with the impurities present in the materials used.

The liquidus curve fell both from pure nickel and from the 68.5 per cent. nickel alloy, reaching a minimum at a temperature of about 1362° C. and a composition of 86.7 per cent. nickel. Alloys containing 82–88.5 per cent. nickel gave arrests near this minimum temperature, and, in addition, those alloys containing 82–85 per cent. nickel exhibited an extended arrest between 1320° and 1150° C. of a type indicative of a separation from solid solution. No investigation has been made of the effect of aluminium on the Curie point of nickel.

MICROSTRUCTURES OF SLOWLY-COOLED ALLOYS.

Specimens cut from the cooling curve ingots were examined microscopically. The most suitable etching reagents were found to be dilute hydrofluoric acid for the aluminium-rich alloys and a mixture of nitric and acetic acids in water, glycerine, or acetone for all alloys containing more than 20 per cent. nickel.

Alloys with compositions between 80 and 95 per cent. nickel proved very difficult to prepare as they were extremely hard and tough, and the only method of securing suitable microspecimens was by grinding with a high-speed abrading disc. The greatest combined hardness and toughness appeared to be possessed by the alloy containing 86.7 per cent. nickel, the hardness of which was 270 V.P.N. (see Table III, p. 258).

The alloys containing more than 92.5 per cent. nickel exhibited the cored structure typical of cast solid solutions. Alloys having between 87.5 and 92.5 per cent. nickel presented a similar appearance (Fig. 5, Plate XIX), but in these cases the darker areas were found at higher magnifications to possess a duplex structure of α and θ having a fine cellular form, as shown in Fig. 6. The 86.7 per cent. nickel alloy was quite homogeneous, and thus the existence of the θ phase was confirmed.

In alloys containing less than 86.7 per cent. nickel, primary dendrites of the NiAl phase appeared (Fig. 7) which down to 82 per cent. nickel bore a suppressed structure, while some θ which had separated was also visible (Fig. 9, Plate XX). The matrices of all these alloys consisted of uniform θ . No trace could be seen of the eutectic, to the existence of which the minimum in the liquidus curve pointed.

In the range 55–80 per cent. nickel all the alloys appeared homogeneous and it was not possible at this stage to differentiate between NiAl and Ni_2Al_3 (see later). It has been decided, on the authors' own evidence and that of Bradley and Taylor,³ to refer throughout the paper to Ni_2Al_3 for the compound which Gwyer assumed to be NiAl_2 . This phase is characterized by a blue-grey colour and by a lack of intergranular cohesion, so that alloys largely or wholly composed of this constituent tend to crumble. The difficulty which this latter property

offered to the preparation of microspecimens was overcome by mounting the powdered alloys in Bakelite. The authors do not agree with Bradley and Taylor that Ni_2Al_3 is readily attacked by water; specimens left for days in water appeared quite unchanged.

Alloys containing between 35 and 53 per cent. nickel, in the un-etched state were seen to consist of the blue-grey Ni_2Al_3 phase and the brilliant white NiAl_3 phase. The latter, when etched with dilute hydrofluoric acid, became blue, brown, or black, according to the duration of attack. The 35 per cent. nickel alloy (Fig. 14, Plate XX) contained some Ni_2Al_3 , present as a result of the incompleteness of the peritectic reaction: $\text{Ni}_2\text{Al}_3 + \text{liq.} \rightarrow \text{NiAl}_3$.

Between 5 and 30 per cent. nickel the alloys consisted of primary NiAl_3 dendrites and NiAl_3 -aluminium eutectic. The 5 per cent. nickel alloy showed eutectic with a trace of primary aluminium.

DETERMINATION OF THE SOLIDUS.

The solidus curves were determined from the microscopic examination of numerous small specimens which had been cut from the cooling curve ingots and subjected to various heat-treatments. These heat-treatments were given at intervals of 5° in the region between 80 and 90 per cent. nickel, and the results are incorporated in Figs. 1 and 2. Incidentally, it was revealed in the course of this work that some of these alloys, when they solidified, were undercooled to the extent of 20°C. , a result, probably, of the very rapid cooling which takes place in the high-frequency induction furnace at these high temperatures.

No special precautions were taken against surface deterioration during the heat-treatment, as it was found that all these alloys are extremely resistant to heat. As the specimens were treated in batches, however, each one was lightly covered with a wash of Alundum cement to prevent those containing liquid at the high temperature from running together.

For treatments above 1100°C. , a platinum-wound resistance furnace was used, periods of the order of 2 hrs. at 1400°C. and 3 hrs. at 1300°C. proving to be sufficient to ensure the attainment of equilibrium. Since these times were comparatively short, the temperature could be controlled manually to within $\pm 2^\circ \text{C.}$ of the desired figure. Annealings at temperatures below 1100°C. were carried out in Kanthal-wound furnaces, supplied with current through a voltage regulator which maintained the temperature constant to within $\pm 2^\circ \text{C.}$ over periods of several days.

It was found possible, by quenching specimens, to reveal the eutectic which had been believed to exist near the nickel end of the diagram

(Fig. 8, Plate XIX) and to place its temperature at $1385^{\circ} \pm 2^{\circ} \text{C.}$ and its composition very close to 86.7 per cent. nickel. The observation that the alloy of this composition consists entirely of θ when slowly cooled, or quenched from below 1375°C. , is explained by the increase of solubility of nickel in θ that occurs between 1385° and 1370°C. and which results in the disappearance of what little α has separated in the eutectic.

At the eutectic temperature the limit of the α phase field was estimated to be 89 per cent. nickel, and that of the θ phase field as 86.4 ± 0.2 per cent. nickel.

The peritectic reaction of NiAl with liquid to give θ appears to take place at $1395^{\circ} \pm 2^{\circ} \text{C.}$, for whereas at 1400°C. the alloys containing 86, 85, 83.5, and 82 per cent. nickel consisted of NiAl solid solution and liquid, at 1390°C. they were all solid. The first alloy was composed wholly of θ , the second and third of NiAl solid solution and θ , and the last of NiAl solid solution bearing a suppressed structure, such as is shown in Fig. 12 (Plate XX). The NiAl phase extends to about 83 per cent. nickel at the peritectic temperature.

On the other side of the maximum which occurs in the liquidus at 1638°C. and 68.5 per cent. nickel, the solidus falls steeply to 1133°C. at 61.0 per cent. nickel, where NiAl solid solution of this composition reacts with liquid containing 44.4 per cent. nickel to produce a new phase having 59.5 ± 0.3 per cent. nickel.

That the alloys containing 44–60 per cent. nickel did not undercool when they first solidified, was shown by heating curves and by the micrographic work, both of which confirmed the reaction temperature given by the cooling curves. The alloys containing 51, 52, and 53 per cent. nickel, when annealed at 1100°C. , proved to consist of compound and liquid in approximately equal quantities, whereas one phase only was present in the 59 and 60 per cent. nickel alloys. The composition of the origin of this phase thus affords substantial grounds for attributing to the phase the formula Ni_2Al_3 (59.18 per cent. nickel) and for rejecting NiAl_2 (52.12 per cent. nickel).

The solidus curve again falls sharply from 59.5 per cent. nickel to the temperature of the next peritectic reaction (851°C.), in which Ni_2Al_3 solid solution containing 55 per cent. nickel reacts with liquid having 28.4 per cent. nickel to give another compound, NiAl_3 , at about 41–42 per cent. nickel. The composition of this phase cannot be given more closely because the single phase alloy proved very difficult to produce. The alloys in this region are not forgeable, and although some were chill-cast in order to obtain a fine structure before reheating, traces of the compound Ni_2Al_3 persisted even after slow cooling past the

peritectic temperature and annealing at 850° C. for 4 days. Theoretically, NiAl_2 contains 42.06 per cent. nickel.

So far as could be judged from the traces of liquid present in quenched alloys, the solidus line falls vertically from 854° to 539° C.

The composition (5.7 per cent. nickel) and temperature (539° C.) of the aluminium- NiAl_2 eutectic determined by Fink and Willey are incorporated in Fig. 1. The authors' evidence is in agreement with their results.

THE LIMITS OF SOLID SOLUBILITY OF THE VARIOUS PHASES.

The limits of the different phase fields were determined from the microscopic examination of numerous slowly-cooled and heat-treated specimens, cut, as before, from the cooling curve ingots. The results obtained are indicated by a system of dots in Figs. 1 and 2.

The α Phase.

On very slow furnace cooling θ separated from alloys containing 92.5 and 90.6 per cent. nickel, in the manner shown in Fig. 3 (Plate XIX). The 90 per cent. nickel alloy when quenched from 1340° C. or above consisted of uniform α solid solution, some of the grains being twinned, while after annealing at 956° C. for 2 days it became duplex, as shown in Fig. 4. The alloy with 88.5 per cent. nickel when quenched from 1340° or 1375° C. did not differ in appearance from the same alloy as slowly cooled, except that the cellular structure (Fig. 6) was very much finer in the quenched specimen, and was only just resolvable into α and θ at a magnification of 500. Another feature of this fine duplex structure is its extreme stability, for even prolonged soaking at high temperatures failed to produce perceptible aggregation of the two constituents.

The evidence indicated that the solubility of aluminium in nickel decreases from 11 per cent. at 1385° C. to 6 per cent. at 980° C. and is not less than 5 per cent. at 700° C.

The θ Phase.

There is a slight increase of 0.3 per cent. in the solubility of nickel in Ni_3Al between the eutectic temperature and 1360° C., sufficient, as has already been stated, to cause the disappearance of all α in the eutectic. Below 1360° C. the phase boundary appears to be vertical down to room temperature, at a composition of 86.7 per cent. nickel.

On the other side of the phase field, the solubility of aluminium in Ni_2Al shows a small increase, the boundary line sloping uniformly from 86 per cent. nickel at 1395° C. to 84.5 per cent. nickel at 980° C. and thereafter becoming vertical.

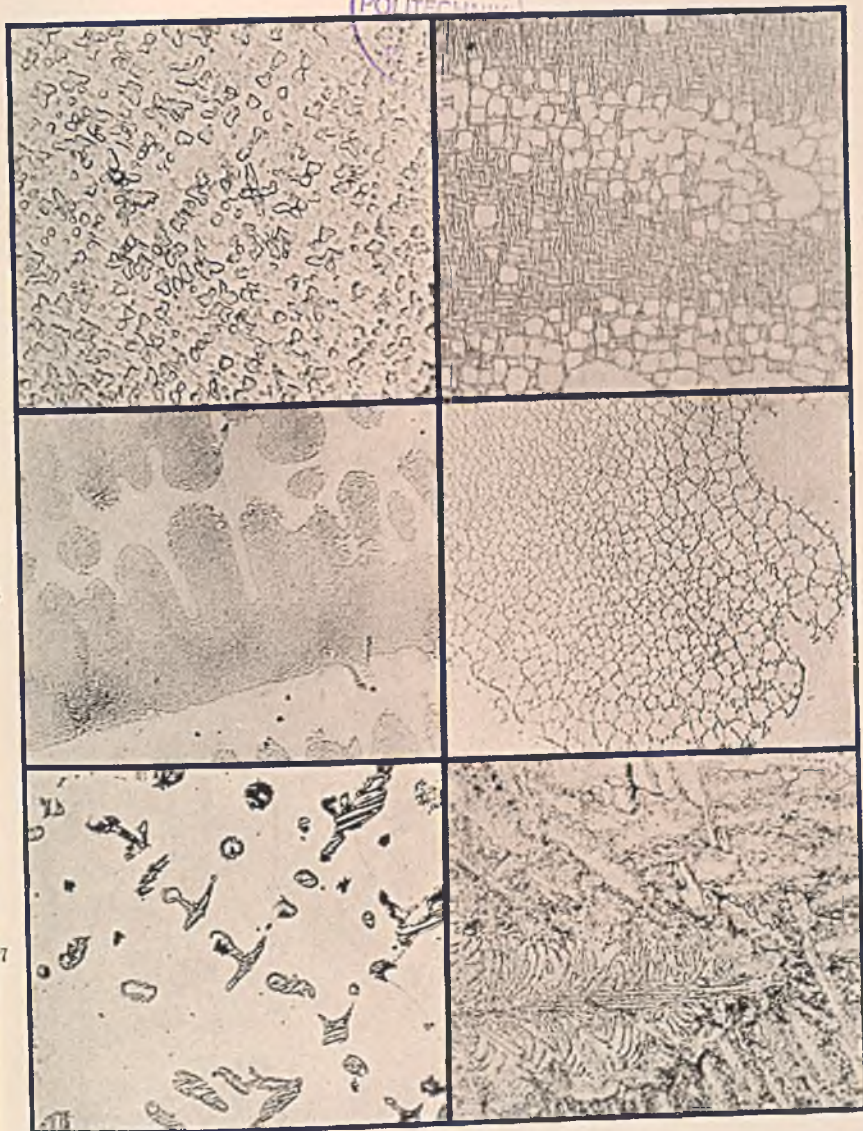


FIG. 3.—90.6% Ni Alloy. Slowly-Cooled from 1280° to 950° C. Then Water-Quenched. $\alpha + \theta$. $\times 1300$.

FIG. 4.—90% Ni Alloy. Annealed at 956° C. for 2 Days. Then Water-Quenched. $\alpha + \theta$. $\times 500$.

FIG. 5.—88.5% Ni Alloy. As Solidified. $\alpha + \theta$. $\times 60$.

FIG. 6.—Same as Fig. 5. $\times 400$.

FIG. 7.—86% Ni Alloy. As Solidified. $\text{NiAl} + \theta$. $\times 60$.

FIG. 8.—86.7% Ni Alloy. Slowly-Cooled from 1400° to 1385° C. during 4 Hrs. Then Water-Quenched. $\alpha + \theta$ Eutectic. $\times 250$.

All Specimens Etched in a Mixture of Nitric and Acetic Acids.

[To face p. 253.]

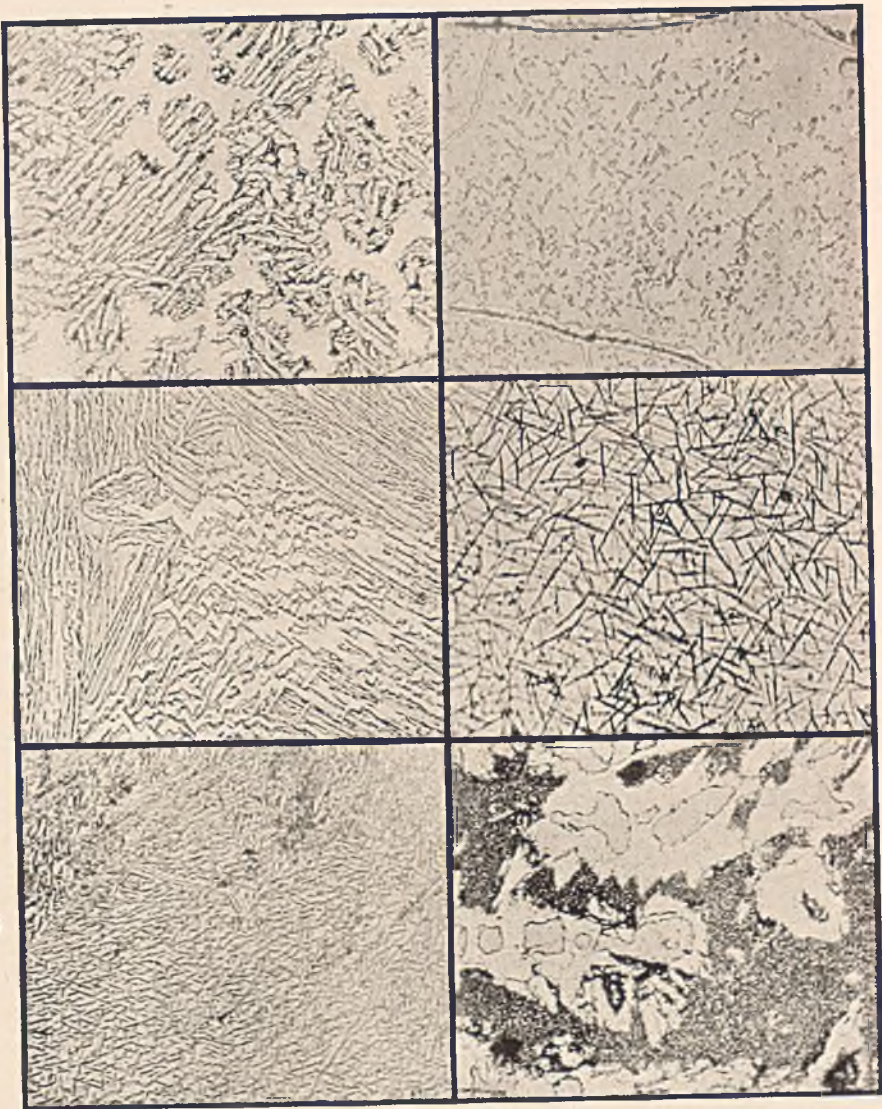


FIG. 9.—83.5% Ni Alloy. As Solidified. $\text{NiAl} + \theta$. $\times 60$.

FIG. 10.—82% Ni Alloy. Annealed at 956°C . for 2 Days, then Water-Quenched. $\text{NiAl} + \theta$. $\times 200$.

FIG. 11.—84% Ni Alloy. Water-Quenched after 5 Hrs. at 1390°C . Suppressed NiAl Structure. $\times 600$.

FIG. 12.—82% Ni Alloy. Water-Quenched after 5 Hrs. at 1390°C . Suppressed NiAl Structure. $\times 600$.

FIG. 13.—62% Ni Alloy. Water-Quenched after 6 Days at 800°C . $\text{NiAl} + \text{Ni}_2\text{Al}_3$. $\times 250$.

FIG. 14.—35% Ni Alloy. As Solidified. $\text{Ni}_2\text{Al}_3 + \text{NiAl}_3 + \text{NiAl}_2 - \text{Al}$ Eutectic. $\times 150$.

All Specimens Etched in a Mixture of Nitric and Acetic Acids except 35% Ni alloy, which is unetched.

The NiAl Phase.

When quenched or rapidly cooled from above 1150° C., alloys containing 80–86 per cent. nickel exhibited a variety of suppressed structures, which changed with decrease of nickel content from a form having parallel markings to others which are shown in Figs. 11 and 12 (Plate XX). Slow cooling, however, resulted in the separation of a considerable quantity of θ , so that the NiAl solid solution lost its suppressed structure and appeared as shown in Fig. 10.

Since the suppressed structures disappeared with either a decrease of nickel content below 80 per cent. or a decrease of quenching temperature below 1150° C., and, further, since alloys containing 65–80 per cent. nickel were structureless and quite homogeneous at all temperatures below the solidus, it was concluded that the suppressed structures were associated with the retention on quenching of θ in solution in the NiAl phase, and not with a eutectoid decomposition or phase modification, such as may often be found in the β phases of other alloy systems, to which, in some respects, NiAl bears a resemblance. (See sections, Preliminary Work, p. 248 and Hardness Measurements, p. 258.) As already mentioned, thermal evidence of a considerable change in solid solubility between 1320° and 1150° C. was given by the cooling curves.

The limit of the NiAl phase field at various temperatures is approximately : 83 per cent. nickel at 1395° C. ; 82.8 per cent. nickel at 1300° C. ; 80.6 per cent. nickel at 1150° C. ; and 79.2 per cent. nickel at 900° C.

Microscopic examination afforded no grounds for supposing that any appreciable change occurs in the limits of solid solubility of the α , θ , and NiAl phases between 700° C. and room temperature.

The determination of both boundary lines of the two-phase field NiAl + Ni_2Al_3 proved very difficult. With decrease of nickel content from 68.5 to 56 per cent., the alloys change progressively in colour from a blue-grey to a pale purple, and unetched specimens failed to show under the microscope any difference in colour by which the two phases might be distinguished. The only reagent to differentiate between NiAl and Ni_2Al_3 was a mixture of nitric and acetic acids in acetone, which, after about 3 minutes, etched the boundaries of the constituents as shown in Fig. 13 (Plate XX). It then became possible to show that the boundary line of the NiAl phase falls uniformly from 61 per cent. nickel at 1133° C. to 64.2 per cent. Ni at 850° C. and that the solubility of aluminium in NiAl then remains unchanged down to room temperature.

The Ni₂Al₃ Phase.

The Ni₂Al₃ phase field has a uniform width and exists over the range 56–60 per cent. nickel, the nickel-rich boundary falling vertically from 1133° C. and the aluminium-rich boundary from 854° C.

The NiAl₃ Phase.

In view of the extreme difficulty experienced in trying to obtain the single phase alloy, it seems reasonable to suppose that NiAl₃ has a very limited capacity for dissolving either aluminium or nickel.

The Aluminium-Rich Solid Solution.

No work has been done by the authors on the solubility of nickel in aluminium, but Fink and Willey report that it decreases from 0.05 per cent. at the eutectic temperature to 0.002 per cent. at 450° C.

HARDNESS MEASUREMENTS.

Because of the pronounced hardness and toughness which characterize the nickel-rich alloys, and the solid solubility changes which occur in them, it was thought of interest to carry out a few hardness determinations. A Vickers Diamond Indenter was used, with a 50 kg. load. The results are given in Table III.

TABLE III.—*Hardness Determinations.*

Nominal Composition, Nickel, Per Cent.	V.P.N.* 50 Kg. Load.			
	As Slowly Cooled.	As Quenched from 1250° C. after 5 Hrs.	Reheated.	
			17 Hrs. 690° C.	+ 20 Hrs. 710° C.
95	101	102	98.5	96.3
92.5	232	152	246	242
90	238	239	267	288
88.5	253	233	241	231
86.7	270	238	164	178
86	292	238	217	227
85	324	521	470	394
83.5	285	571	499	431
80	318	234	409	464

* V.P.N. = Diamond Pyramid Hardness.

In the as-cooled alloys there is an increase in hardness with decrease of nickel content, from 101 V.P.N. for the 95 per cent. nickel alloy to 324 V.P.N. for the 85 per cent. nickel alloy.

When quenched from 1250° C., the 92.5 per cent. nickel alloy is

softer than it is in the as-cooled state, as might be expected since at the higher temperature it consists entirely of α solid solution. Reheating for 17 hrs. at 690°C . followed by water quenching, leads to an increase in hardness, since it permits the precipitation of θ from solution. This is likewise the cause of the slight increase in hardness which occurs on reheating the 90 per cent. nickel alloy.

The changes in hardness which occur on heat-treating the 86.7 and 86.0 per cent. nickel alloys are interesting, and, since there is no micrographic change, may be the result of a disorder to order rearrangement of the atoms which takes place on reheating.

Hardness changes in the opposite direction are found in the alloys containing 85 and 83.5 per cent. nickel, which, as-cooled, contain over 50 per cent. of NiAl solid solution bearing the suppressed structure. Maximum hardness is developed in the fully quenched specimens, and subsequent reheating leads to a softening, as occurs in the suppressed β phase of the copper-aluminium system.

The 80 per cent. nickel alloy as quenched from 1250°C . shows little suppressed structure though some separation of Ni_3Al occurs on reheating to 690°C . accompanied by an increase in hardness from 234 to 409 V.P.N.

In view of their marked heat-resistance and their maintained hardness at 700°C . (as evidenced by the figures in col. 5, Table III) these alloys would appear to merit further attention. The alloy containing 80 per cent. nickel and 20 per cent. aluminium has, in fact, been made the subject of a patent⁴ on account of its high resistance to oxidation and scaling at elevated temperatures. Another patent⁵ covers alloys containing 9-15 per cent. aluminium.

CONCLUSIONS.

The work carried out on alloys containing up to 68.5 per cent. nickel supports the constitutional diagram advanced by Gwyer, except that the phase called by him NiAl_2 is suggested to be Ni_2Al_3 .

A new phase, θ , having a narrow range of existence, has been found between the nickel-rich α solid solution and the NiAl solid solution phase fields. It has a face-centred cubic lattice, with superlattice, and probably corresponds to the intermetallic compound Ni_3Al . This phase is formed as the result of a peritectic reaction which occurs at 1395°C . between NiAl solid solution and liquid and it yields a eutectic with α solid solution at 1385°C .

The nickel-rich alloys in general possess considerable heat-resistance and hardness, the latter quality being capable of modification by heat-treatment.

ACKNOWLEDGMENTS.

The authors wish to thank Professor D. Hanson, D.Sc., for his guidance and interest. The thanks of one of the authors (W. O. A.) are due to The Mond Nickel Company, Ltd., for the alloys mentioned in the preliminary work, and to Messrs. I.C.I. Metals, Ltd., for monetary assistance in the early stages of the research.

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- ⁵ Herneus Vacuum-Schmelze A.G. and W. Rohn, E.P. 342,868, 1930.

DISCUSSION.

(Condensed.)

MR. VAUGHAN (in introducing the paper) said: A month or so before the present paper appeared, Bradley and Taylor published the results of an X-ray investigation of the phases existing in the nickel-aluminium system and of their limits at room temperature. We are in complete accord with the sequence of phases they give, and the agreement with the phase limits is also quite good if it be remembered that our own work was carried out at high temperatures and that the figures given in the paper are therefore estimates.

But where we are at variance with Bradley and Taylor is in respect of the newly-discovered θ phase—called by them the α' phase. From results obtained on quenched powder specimens, they concluded that above 1100° C. the α' phase is continuous with the α phase and that the $\alpha + \alpha'$ phase field takes the form of a closed loop. Our own evidence gives no support at all to this theory and hence, for the moment, the two diagrams are unfortunately irreconcilable.

Dr. A. G. C. GWYER, B.Sc.* (Member): This review of work, carried out thirty years ago, is of considerable interest because it shows the importance of reviewing these equilibrium diagrams at intervals of time. I should be interested, on theoretical grounds, if someone would repeat the cobalt diagram, which was very similar in general outline to the nickel diagram.

Since the days of the early investigations, our interests being mainly concerned with the higher aluminium end, in the work which has been carried out in my laboratory we have used the super-purity aluminium, 99.99 per cent., and the highest purity nickel, and the only revision we have made is in the eutectic, which we have fixed between 6.30 and 6.40 per cent.

We did not in those days pay very much attention to the points in the solidus, and, in fact, we could not do so as our apparatus was not sufficiently sensitive. I do not question, therefore, that the compound which I gave as NiAl_2 is, as the authors state, Ni_2Al_3 .

* Chief Metallurgist, The British Aluminium Company, Ltd., Warrington.

These remarks are mainly concerned with the historical side of the matter, but I would mention that one reaction which has always bothered us is that which I found at 550° C. The arrests which I found at 550° C. in the nickel system, and at just about the same temperature in the cobalt system, seemed probably due to something in the aluminium.

I have not re-investigated the higher end of the system, but the region between 82 and 90 per cent., to which the authors refer, seems to be of very considerable importance, in view of the great differences in hardness. I took no measurements in the early days, but I did observe these differences when preparing sections for micro-examination. It would be an advantage if the authors and Dr. Bradley could get together and come to an agreement. The advantages and accuracy of the X-ray method, as compared with the thermal and microscopic, cannot be ignored, and a joint effort would probably result in the removal of such discrepancies as now remain.

[Dr. Gwyer, the President, Dr. W. H. Hatfield, Member, and Mr. A. J. Murphy, M.Sc., Member, here made some interesting observations on the high degree of accuracy that was obtained in the early days of the study of equilibrium diagrams with the comparatively simple apparatus then available.]

Mr. A. J. MURPHY,* M.Sc. (Member): This paper illustrates the great value of the high-frequency induction furnace in work on the nickel-rich alloys of very high melting point. When Austin and I were working on these alloys some 15 years ago, in the absence of a high-frequency furnace or other external means of attaining temperatures of 1700° C., we made use of the intense evolution of heat on adding aluminium to molten nickel (mentioned by the authors on p. 249) to increase the temperature of the melt sufficiently to allow the liquidus to be determined by cooling curves in the neighbourhood of the NiAl phase.

The form of the liquidus of the copper-nickel-aluminium system would not lead one to suspect the existence of the new θ phase which the authors have discovered, in view of the pronounced ridge in the ternary constitution model running across from NiAl to the copper-aluminium β phase. It will be most interesting to see how this new phase fits into the space model depicting the solid constitution.

Mr. VAUGHAN (*in reply*): Dr. Gwyer seems to place rather more confidence in the results obtained by the X-ray method than in those obtained by the more conventional technique. We are ready to acknowledge that, so far as the determination of the limits of the phases at room temperature is concerned, the X-ray method is likely to be the more accurate one. X-ray results obtained from specimens consisting of quenched powders are, however, rather a different matter. If Dr. Gwyer reads very carefully the paper by Bradley and Taylor, we think that he will find that they are not too confident of their conclusion that above 1100° C. the α and α' phases are continuous. As they say, it all depends on the fact that "The gradual approach of the lines of the α and the α' phases"—what we call θ they call α' —"as the quenching temperature is increased shows that the two-phase region is gradually closing. The final photograph of the powder quenched from 1100° C. shows scarcely any trace of Ni₃Al superlattice lines, which are present in all the other photographs;" but then they continue: "Some faint lines occur, but these may be due to impurities introduced during quenching, or possibly there is another high temperature phase which has almost disappeared during quenching." We submit, therefore, that Bradley and Taylor should adduce additional evidence in favour of their theory; in the meantime we prefer to adhere to

* Chief Metallurgist, J. Stone & Company, Ltd., Deptford.

the conclusions set out in the paper, since, from our microspecimens, we found no evidence whatever that the $\alpha + \alpha'$ phase field is in the form of a closed loop.

Mr. Murphy referred to the disturbing influence of the θ phase we have introduced, on the ternary copper-nickel-aluminium system. As was pointed out at the beginning of this paper, Dr. Alexander's investigation of the ternary system showed that there must be some such phase, and the *actual establishment of the existence of this phase* was really the object of the present investigation. When the second part of Dr. Alexander's work is published, Mr. Murphy will see that it is possible to fit in this phase quite readily.

CORRESPONDENCE.

DR. A. J. BRADLEY,* D.Sc. (Member), and Dr. A. TAYLOR*: The phase diagram proposed by the authors is in excellent agreement with that suggested by ourselves,† the only important difference being the nomenclature and range of the phase which includes the composition Ni_2Al . We termed the phase α' ; the present authors use θ . Recent experiments which we have carried out on ternary alloys containing iron, in addition to aluminium and nickel, show the advantage of using the same letter for the two phases.

We have found that the addition of iron to the nickel-aluminium alloys gradually closes the gap between the α and the Ni_2Al phase. This is possible because there is only one type of space-lattice (face-centred cubic) common to the two phases. In the ternary system, the miscibility gap no longer corresponds to a change from a random structure to a superlattice, as in the binary system. The change from disorder to order takes place before the break, and the Ni_2Al type of structure is found on either side of the miscibility gap. In this case the ordered structure is merely a portion of the α -phase, and not in any way separated from it.

The general slope of the α -boundary, in agreement with our evidence, indicates an increase in the solubility of aluminium in nickel at high temperatures, but the position of the α -boundary at 1100°C . does not agree with our X-ray photograph from a quenched powder. It is doubtful whether quenching from such a high temperature can be relied upon to preserve the high temperature state. Powders cool more rapidly than solid specimens, and should give a closer approximation to the original state, but they are liable to oxidation.

The range of the NiAl β -phase shrinks with decreasing temperature. Our evidence favours a much greater contraction on the nickel side than is indicated by the authors. After slow-cooling, we found the boundary to be at 76.5 per cent. of nickel, which is about 2 per cent. less than the minimum value given here. The other boundaries agree excellently.

The authors state that Ni_2Al_3 is not attacked by water. This is due to their use of a solid specimen. In our experiments we left powdered Ni_2Al_3 standing under cold water for several days. There was a gradual evolution of gas (probably hydrogen).

The AUTHORS (in joint reply): In spite of our correspondents' additional evidence regarding the behaviour of the θ (or α') phase at high temperatures, we cannot help thinking that they still have no direct knowledge of what occurs in this region of the nickel-aluminium system.

It seems strange to us that Drs. Bradley and Taylor should apparently

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† Reference 3 of Alexander and Vaughan's paper.

have felt no necessity at all to confirm their results by further work employing the conventional metallurgical technique, especially in view of the doubts cast by Hume-Rothery and Reynolds,* and also by Desch, Stockdale, and Gayler in the discussion of that paper, on the advisability of using unaided X-ray methods for the determination of constitutional diagrams.

In our opinion such supplementary work would lend much greater authority to our correspondents' publications, particularly in the eyes of those metallurgists who, rightly or wrongly, still lack complete confidence in the X-ray method when employed alone for constitutional work. For, while in no way wishing to belittle the importance of the use of X-rays in metallurgy, or to deny that X-rays have been the cause of great advances in the science, we deprecate the tendency that has arisen to publish equilibrium diagrams based solely on X-ray results.

Dr. ALEXANDER (*in further reply*): In the absence of any positive proof by Drs. Bradley and Taylor of the efficacy of the practice of quenching powders from very high temperatures, I prefer the evidence obtained by fundamental metallurgical methods, which are those of the microscope and thermal analysis.

There is no doubt that needless bickering will cease when the powder-versus-lump controversy has been adequately solved. Apart from the very valuable contribution to the problem by Hume-Rothery and Reynolds,* together with the discussion thereon, little comparative observation has been made of the limitations of powder and lump specimens for X-ray work. Whether the safe procedure will be found to vary with every different phase change, or whether some principal will prove generally applicable, remains to be determined experimentally. After all, vast tonnages of metals are produced in bulk form, and it is in the behaviour of bulk samples that metallurgists are at present primarily interested. Powder metallurgy is in its infancy.

In this connection I should like to know to what linear depth from the surface, surface freedom and/or surface energy are likely to play an important part in the phase behaviour of the samples. Here, again, it must be borne in mind that the X-ray method is selective in that it only reveals phase relations as they exist at or very near to the surface of the sample.

A further point, which has not been fully appreciated, is that powders are essentially single crystals, whereas most lump samples are polycrystalline aggregates. Evidence by Wiest† and by Phillips and Brick‡ shows that a difference in phase solid solubility relationships occurs between polycrystalline aggregates and single crystals. This phenomenon has never received adequate explanation, but, if true, clearly leads to the core of the problem.

* W. Hume-Rotherby and P. W. Reynolds, *J. Inst. Metals*, 1937, 60, 303-317.

† P. Wiest, *Z. Physik*, 1932, 74, 225-253.

‡ A. Phillips and R. M. Brick, *J. Franklin Inst.*, 1933, 215, 557-577, and *Metallwirtschaft*, 1933, 12, 161-162.

THE CONSTITUTION OF TIN-RICH ANTIMONY-CADMIUM-TIN ALLOYS.*

By PROFESSOR D. HANSON, D.Sc., VICE-PRESIDENT,[†] and
W. T. PELL-WALPOLE, B.Sc., Ph.D., MEMBER.[‡]

SYNOPSIS.

The constitution of antimony-cadmium-tin alloys containing up to 43 per cent. of cadmium and 14 per cent. of antimony has been established by thermal and microscopical analyses. The results are presented as isothermal diagrams of the various surfaces, and as vertical and horizontal sections through the constitutional model. There are three ternary peritectic reactions at 227°, 209°, and 180° C., respectively. Metastable conditions occur during cooling in parts of the system, but these have been related to the stable state which is obtained by prolonged annealing of specimens.

It is shown that at 227° C. tin will dissolve 9 per cent. of antimony with 1.5 per cent. of cadmium, and at 209° C. 5.5 per cent. of antimony with 2.4 per cent. of cadmium; below 209° C. the solubilities decrease continuously to 1 per cent. of antimony with 0.7 per cent. of cadmium at 145° C., and to 0.6 per cent. of each metal at 20° C.

The solubility of antimony in the β phase of the cadmium-tin system is shown to decrease from 5.1 per cent. at 209° C. to 0.8 per cent. at 145° C. The surface of the eutectoid decomposition of β has been determined by thermal and microscopical analyses.

INTRODUCTION.

THE system antimony-cadmium-tin is one of the many ternary systems of which no systematic investigation has been made previously. The present research is an extension of that carried out on the cadmium-tin alloys, and already described. The main object of the research was to discover whether the addition of antimony to alloys of cadmium with tin would effect any further improvement in mechanical properties, especially with reference to heat-treatment. It was hoped that alloys suitable for use as bearing metals might be developed. The constitution of the alloys was determined first, to provide the necessary theoretical basis for a methodical investigation of the mechanical properties of the alloys.

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PREVIOUS WORK.

A knowledge of the component binary systems is essential to the study of a ternary system, and the previous work on the former will be considered first.

The constitution of the cadmium-tin system has been established and described previously by the present authors.^{1, 2} The diagram is reproduced in Fig. 1.

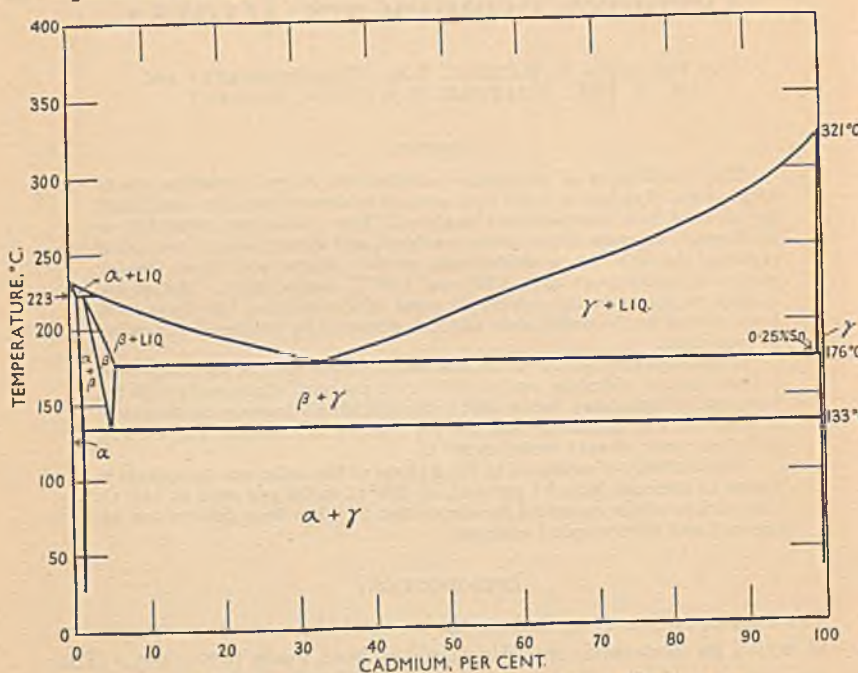


FIG. 1.—Constitutional Diagram of the Cadmium-Tin System.

Previous work on the antimony-tin system has been summarized by the authors in a paper describing a research on the constitution of the tin-rich alloys.³ During the present research on the ternary alloys, a stirring apparatus, devised for use in thermal analyses to prevent segregation, was also used to check the liquidus of the tin-rich binary alloys. With alloys containing up to 10 per cent. of antimony, the results agreed with those obtained previously (when stirring was done by hand), but for the alloys containing 12 and 14 per cent. of antimony, respectively, the results were some degrees higher and the thermal arrests were more sharply defined. The necessary corrections to the

second branch of the liquidus are incorporated in Fig. 2, which is otherwise identical with the diagram given previously.³

Since the alloys to be investigated lay principally in the tin corner of the system, it was expected that the third binary system involved, viz. antimony-cadmium, would not play an important part in the constitution of these alloys. The experimental work reveals, however, that

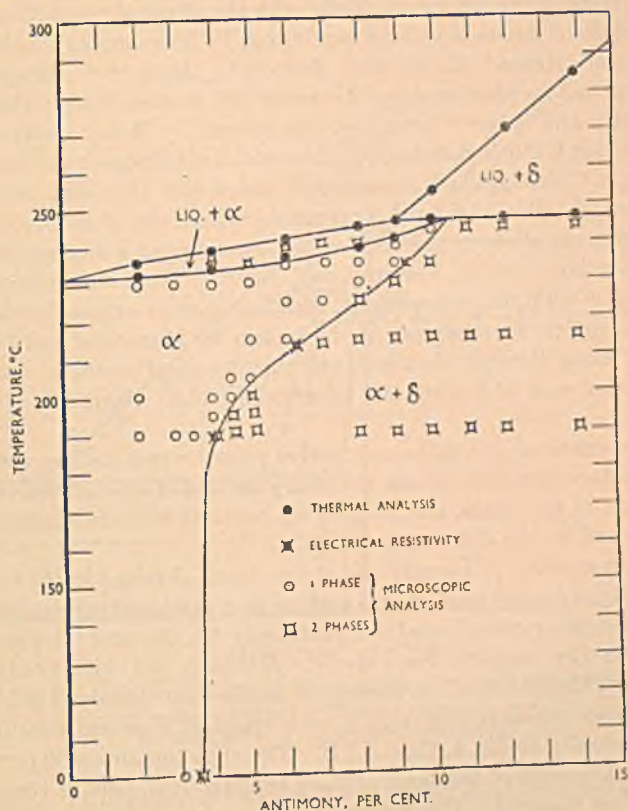


FIG. 2.

one phase of the antimony-cadmium system has a dominating influence on the form of the ternary system, hence a brief *resumé* will be given of the previous work on antimony-cadmium alloys.

The earliest systematic investigations of the antimony-cadmium alloys were carried out by Treitschke⁴ and by Kurnakow and Konstantinow.⁵ A summary of their results is given in the constitutional diagram of the system according to Desch.⁶ This indicates a stable and

a metastable liquidus with two intermediate phases, CdSb and Cd_3Sb_2 . The former does not separate from the liquid on cooling, unless inoculated with powdered CdSb .

Fischer and Pfeiderer⁷ state that CdSb is formed at 456°C. , and reacts at 410°C. , to give $\text{Cd}_3\text{Sb}_2 + \text{Sb}$, but at lower temperatures Cd_3Sb_2 decomposes and CdSb is again formed.

Investigations concerned chiefly with the physical properties of the intermediate phases have been carried out by Kremann and Lobinger,⁸ Biltz and Haase,⁹ Honda and Endo,^{10, 11} Meara,^{12, 13} Matuyama,¹⁴ Volfson and Rojdestvenskiy,¹⁹ Portevin and Bastien,²⁰ and Ölander.²¹

Halla and Adler¹⁵ examined the system by X-ray analysis and stated that CdSb is rhombic, but they could not discover the lattice of Cd_3Sb_2 . Chikashige and Yamamoto¹⁶ stated that there are two modifications of CdSb , both with hexagonal lattices, and that Cd_3Sb_2 does not exist, the alloys of this composition consisting of a mixture of CdSb and cadmium. Halla, Nowotny, and Tompa¹⁷ have since stated that the lattice of Cd_3Sb_2 is monoclinic, with four atoms to the unit cell.

A complete investigation of the system by Murakami and Shinagawa,¹⁸ using thermal, electrical, and microscopical methods, confirms the earlier work of Fischer and Pfeiderer.⁷ Their diagram is given in Fig. 3.

The existence of Cd_3Sb_2 as a stable phase over a limited range of temperature only will explain the many contradictory results as to the existence of this phase, according to the previous heat-treatment of the alloys used by the different investigators.

In an attempt to identify one of the phases obtained in the ternary alloys of the present research, the authors have examined microscopically three antimony-cadmium alloys containing 50, 60, and 80 per cent. cadmium (by weight), respectively. Although the specimens were chill-cast, the 50 : 50 alloy consists of needle-like crystals of a bluish-grey phase, which is very brittle, with traces of a second constituent at the boundaries (Fig. 4, Plate XXI). The alloy containing 60 per cent. cadmium consists of the same primary crystals with more of the inter-crystalline material. This bluish-grey phase has the appearance and characteristics of an intermetallic compound, and is presumably CdSb . The alloy containing 80 per cent. of cadmium has a primary phase, similar in colour but different in form, in a eutectic consisting of the same phase and a cadmium-rich solid solution (Fig. 5, Plate XXI). The primary constituent in this case appears to be the phase known as Cd_3Sb_2 by previous workers.

Annealing for 1 month at 200°C. , has no appreciable effect on the structure of CdSb , but the Cd_3Sb_2 in the 80 : 20 alloy appears to be under-

going decomposition (Fig. 6, Plate XXI), in accordance with the results of Fischer and Pfeleiderer,⁷ and of Murakami and Shinagawa,¹⁸ discussed previously.

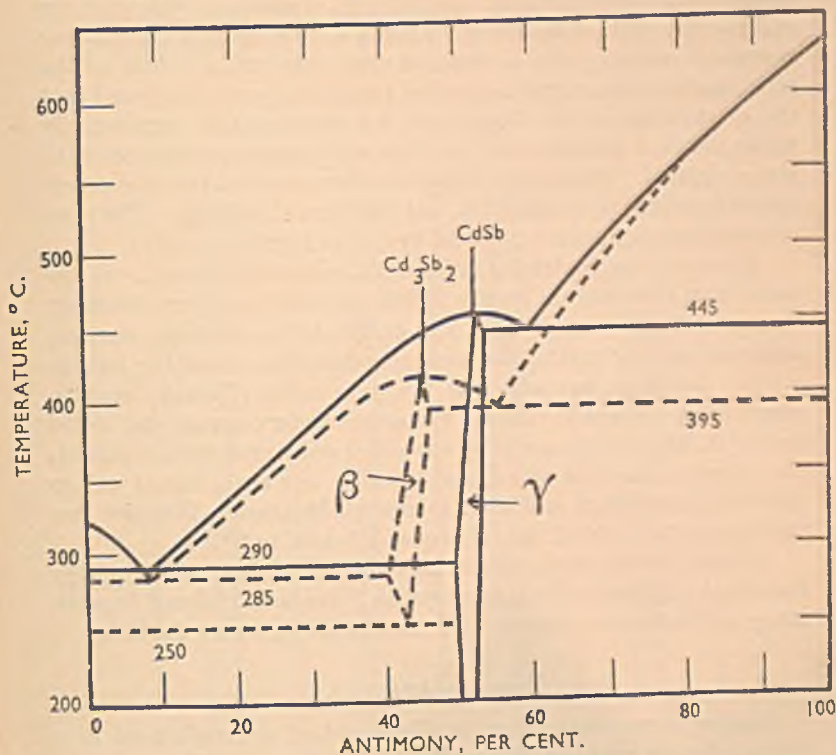


FIG. 3.—Cadmium-Antimony Diagram (Murakami and Shinagawa).
Continuous Curve = Stable System.
Broken Curve = Metastable System.

THE TERNARY SYSTEM ANTIMONY-CADMIUM-TIN.

PREVIOUS WORK.

There has been no previous systematic investigation of the ternary system, but Campbell²² reported that the microstructure of an alloy containing antimony 25, cadmium 10, tin 65 per cent., consisted of cuboids of the SbSn phase, and prisms of a pink-coloured constituent (probably one of the compounds of the antimony-cadmium system), in a cored solid solution.

Cournot²³ states that a ternary eutectic is formed.

PREPARATION AND ANALYSIS OF ALLOYS.

The portion of the ternary system which was investigated first consisted of alloys containing 1 to 8 per cent. of cadmium with additions of 1 to 9 per cent. of antimony. From a knowledge of the two binary systems it seemed probable that this small area would include all the tin-rich alloys with useful mechanical properties, but it was found that the constitution of the alloys could not be established satisfactorily unless the work were extended to alloys with higher cadmium and antimony contents. The range of alloys was then extended (at more widely spaced intervals) to antimony 14, and cadmium 43 per cent. The compositions investigated are indicated by dots in Fig. 7 (page 274).

A temper alloy, containing antimony 50 and tin 50 per cent., was prepared from Chempur tin (purity 99.992 per cent.) and pure antimony (purity 99.7 per cent.). This was analyzed for antimony content, and was used for making the antimony additions to all the ternary alloys. Cadmium was added as the pure metal (Tadanac brand—purity 99.95 per cent.). The tin was melted under charcoal and heated to 400° C., when the temper alloy was added and stirred until dissolved; the cadmium was then added, and the alloy was again stirred well to dissolve the cadmium and effect thorough admixture. The alloy was then cast at 300°–350° C. into chill moulds heated to 100° C.

A large number of the alloys, including all of those which occupy important positions in the ternary system, have been analyzed for antimony and cadmium contents. The results are shown in Table I.

THERMAL ANALYSIS.

Cooling curves were taken on alloys melted under charcoal in a Salamander pot, contained in a vertical electric furnace. Temperatures were measured with an iron-Constantan thermocouple and a Carpenter-Stansfield potentiometer, and curves were plotted on a Rosenhain chronograph.

For the group of alloys first examined (containing up to 9 per cent. antimony and 8 per cent. cadmium), stirring by hand was used to prevent severe undercooling, since this method had been found to be quite effective for similar binary cadmium-tin alloys. When it was decided to examine alloys with higher antimony and cadmium contents, it was known that at least one segregating phase would be present, viz. SbSn , which would be considerably lighter than the tin-rich liquid. The mechanical stirring device mentioned previously was then evolved. The use of this apparatus prevented appreciable segregation, and almost completely eliminated undercooling, so that duplicate results agreeing

to within 2° C. could be obtained, even in parts of the system where the liquidus is very steeply inclined, and the thermal arrest obtained is very slight. Cooling curves on several of the alloys for which hand-stirring had been used, were repeated with the mechanical stirrer. The results obtained agree to within 1° C. with those obtained previously,

TABLE I.—*Analyses of Antimony-Cadmium-Tin Alloys.*

Intended Composition.		Analysis.	
Cadmium, Per Cent.	Antimony, Per Cent.	Cadmium, Per Cent.	Antimony, Per Cent.
0.5	2.0	0.50	1.90
1.0	9.0	1.00	9.03
1.5	14.0	1.50	13.70
2.0	3.0	2.00	3.10
2.0	5.0	2.0	4.86
2.0	10.0	2.02	10.10
3.0	5.0	2.98	5.05
3.0	9.0	3.05	9.10
4.0	5.0	4.10	5.00
5.0	1.0	5.00	1.00
5.0	5.0	5.00	5.10
5.0	7.0	5.10	7.00
5.0	10.0	5.00	10.08
6.0	2.0	6.04	1.95
6.0	9.0	6.01	9.10
6.0	12.0	6.00	12.10
7.0	6.0	7.10	6.10
8.0	5.0	8.10	4.90
8.0	14.0	8.12	14.18
10.0	1.0	10.00	1.06
10.0	7.0	10.02	7.10
10.0	9.0	10.02	9.00
10.0	14.0	10.12	14.10
12.0	10.0	12.00	10.18
14.0	1.5	14.03	1.60
14.0	4.0	14.03	4.00
16.0	3.0	15.90	2.90
20.0	10.0	20.10	10.00
25.0	1.0	25.00	1.00
28.0	3.0	28.10	3.05
33.0	1.0	33.00	1.00
33.0	9.0	33.00	9.30
43.0	5.0	42.80	5.10

in all cases except in alloys of the series containing 9 per cent. of antimony. In these alloys it was found that the supposed liquidus arrests obtained by the hand-stirring were actually caused by a peritectic reaction, whilst the true liquidus arrests, which occur at a slightly higher temperature and are very slight in magnitude, had been missed completely when hand-stirring was used.

The cooling curves were continued to 100° C. in some cases, but generally were discontinued at 150° C.; in either case the alloy was then re-melted and cast into a chill mould. From the ingot obtained, a specimen 1 in. long was taken and drilled to take the bare junction of the thermocouple. These specimens were annealed for 1 month at 170° C., and cooling curves were taken from 165° C. to room temperature, in order to investigate the presence of transitions in the solid state.

The eutectoid transition of the cadmium-tin system was found to occur in the ternary alloys at a higher temperature, but for each alloy the arrest occurred at a temperature which varied according to that at which cooling commenced; the degree of undercooling at the transition was greater the lower the temperature at which cooling commenced. This factor was standardized, the time of heating being so controlled that the maximum temperature reached was 170° C.; the cooling curve was commenced when the specimen had cooled to 165° C. This method gave consistent results, but the arrest temperatures obtained are obviously arbitrary.

Heating curves were then taken on the same specimens, the rate of heating being 3° C. per minute.

MICROSCOPICAL ANALYSIS.

Microscopical examinations have been carried out on chill-cast specimens, cooling-curve ingots and on quenched heating-curve specimens. Chill-cast specimens were used for investigating the equilibrium structures of these alloys; these were annealed for 1 month at 170° C., and examined after cooling to room temperature, and after quenching from a series of temperatures at 5° C. intervals, to determine the positions of the phase boundaries and of the solidus and reaction surfaces. An annealing time of 2 days was used for all experiments subsequent to the preliminary heating at 170° C.

IDENTIFICATION OF THE PHASES.

The phases which occur in the ternary alloys examined are: (1) the ternary tin-rich solid solution α ; (2) the β phase of the cadmium-tin system, with antimony in solution; (3) a cadmium-rich solid solution (γ); (4) a hard, white phase very similar to the SbSn of binary antimony-tin alloys: this is termed δ , and not SbSn, since it dissolves a considerable amount of tin and cadmium; (5) a brittle, pale bluish-grey phase, similar to that found in the binary cadmium-antimony alloy, containing 50 per cent. antimony (Fig. 4, Plate XXI). This is probably the

compound CdSb but, since it appears to have some solubility for the other constituents, it is referred to as ϵ , in accordance with the usual method of nomenclature of solid solutions. In the group of alloys which were examined first (containing up to 9 per cent. antimony and 8 per cent. cadmium), this phase occurs only as a fine separation, and in an etched section this is so much like the white δ precipitate that it was not recognized as a separate phase until it was observed as a primary constituent in alloys with higher cadmium content. In the latter state its form renders it unmistakable.

Considerable difficulty was experienced in etching the specimens satisfactorily when three phases were present. A solution of 2 per cent. nitric acid in alcohol stains the whole of the tin-rich matrix black, whether α or β or both phases are present, but does not attack the δ or the ϵ . A solution of ferric chloride etches γ black and stains β brown, but does not give a very satisfactory etch if α , β and ϵ are present together. Dilute potassium dichromate solution gives the most satisfactory etch if the ($\alpha + \gamma$) eutectoid is present. None of these reagents distinguishes δ from ϵ , but it was found that a solution of potassium ferricyanide in caustic soda will stain ϵ brown, whilst not affecting δ . The etching scheme described below was then devised for annealed and quenched specimens.

The specimen was etched in ferric chloride solution; if β was shown to be present as well as α , then only one of the other phases δ or ϵ could be present. Preliminary experiments showed that ϵ was the other possible constituent; hence a subsequent etch in 2 per cent. alcoholic nitric acid would reveal if ϵ were present. In alloys which contain no β , a subsequent etch in the same reagent reveals the presence of ϵ or δ , but does not distinguish between them. Without repolishing such a specimen, it then was etched for 2 minutes in the ferricyanide reagent; if ϵ was present it was stained brown or blue, whilst δ was not attacked. The alloys containing ($\beta + \gamma$) ($\beta + \epsilon$) or ($\beta + \gamma + \epsilon$) gave no difficulty in etching. Slowly cooled specimens and specimens quenched from temperatures below the eutectoid transition contain eutectoid ($\alpha + \gamma$) in the place of β . The presence of eutectoid was detected by etching with potassium dichromate solution, after which the methods given above were used to detect and distinguish between ϵ and δ .

DISCUSSION OF RESULTS.

The results of thermal curves are given in detail in the Appendix, and are incorporated in the isothermal diagrams (Figs. 8-12) and in the vertical sections through the constitutional model (Figs. 13-30).

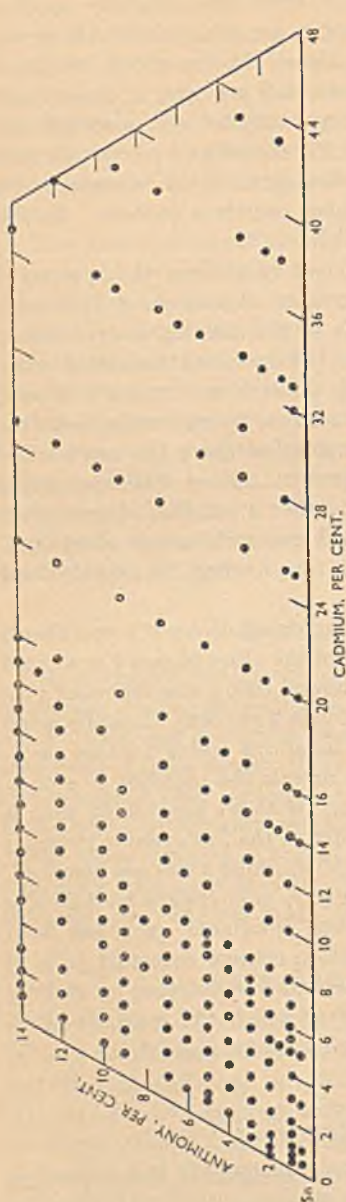


FIG. 7.—Positions of Alloys Investigated.

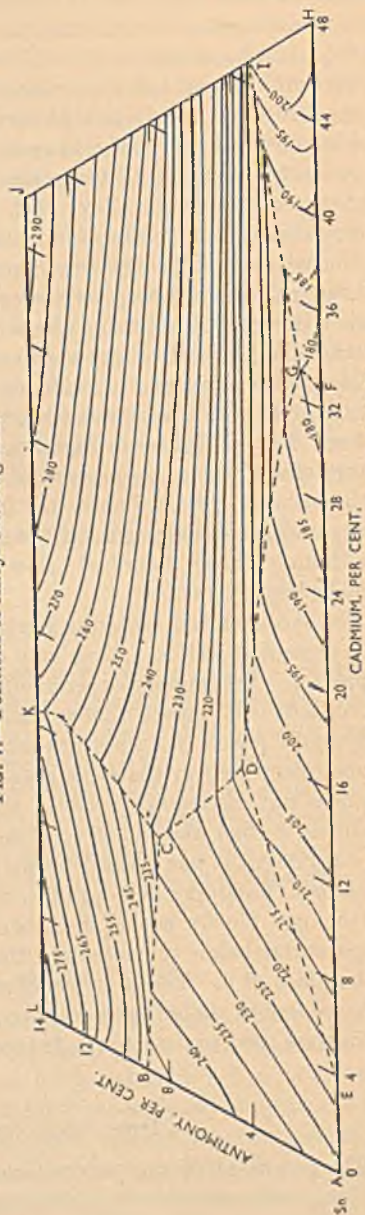


FIG. 8.—The Liquidus Surface (Temperatures in $^{\circ}\text{C}.$).

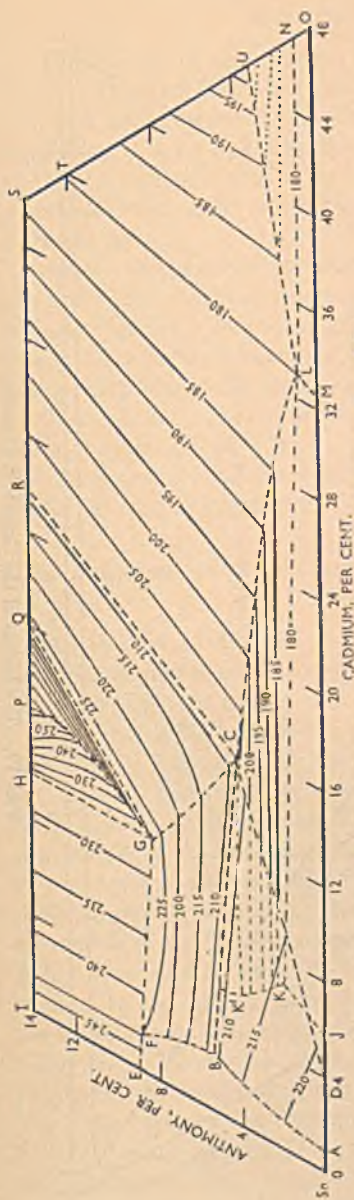


FIG. 9.—Surfaces of Secondary Separation (Isotherms in °C.).



FIG. 10.—The Boundaries of the Ternary Reaction Planes.

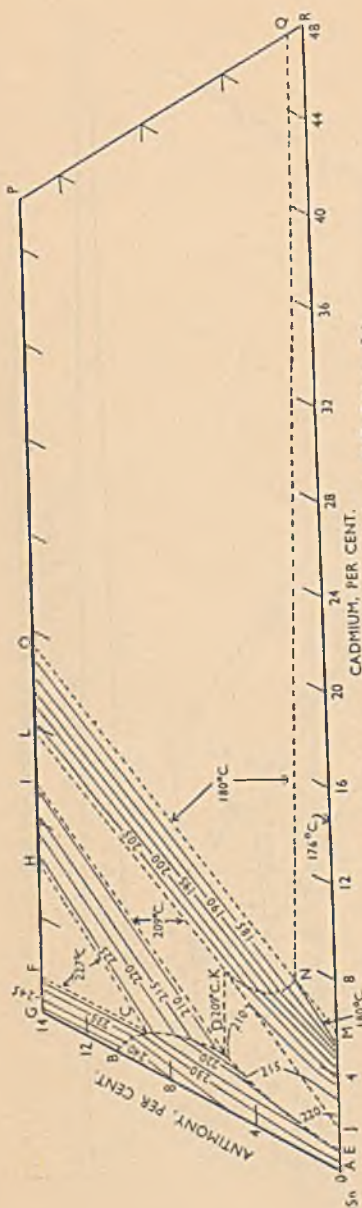


FIG. 11.—The Solidus Surface (Isothermals at 5° C. Intervals).

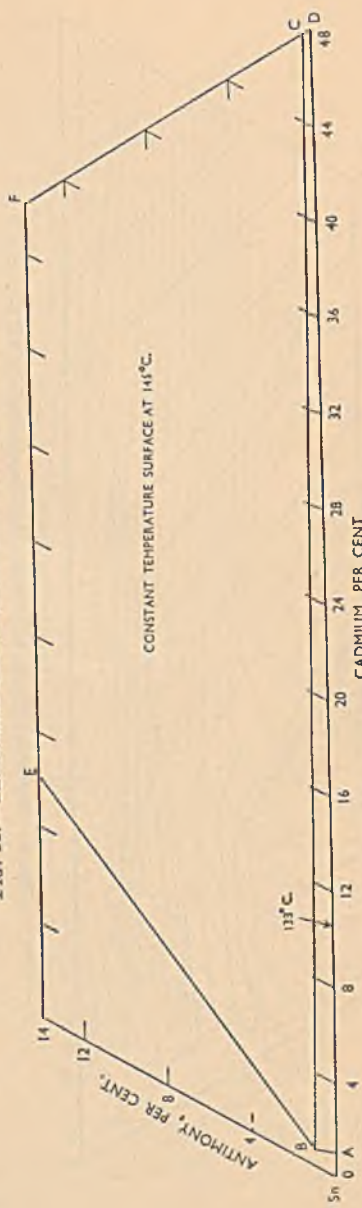


FIG. 12.—The Limits of the Eutectoid Transition.

THE LIQUIDUS SURFACE.

The ternary liquidus surface is shown as an isothermal diagram in Fig. 8. There are five areas corresponding to the separation of the phases α , β , γ , δ , and ϵ , respectively. The area $ABCDE$ represents the primary separation of α tin-rich solid solution, $DEFG$ that of the solid solution β , $FGIH$ a portion of that of the γ cadmium-rich solid solution, $CDGIJK$ a portion of that of the ϵ (CdSb) phase, and $BCKL$ a portion of that of the δ (SbSn) phase.

Along the groove BC the reaction $\delta + L = \alpha$ takes place, and along the groove ED the reaction $\alpha + L = \beta$. Along FG the binary complex $\beta + \gamma$ separates. The other grooves have no corresponding reactions in any of the binary systems; along CK ϵ plus δ separate simultaneously, along DG , β plus ϵ , and along GI γ plus ϵ .

The points C , D , and G are invariant points, corresponding to the ternary reactions $(L + \delta = \alpha + \epsilon)$, $(L + \alpha = \beta + \epsilon)$ and $(L + \epsilon = \gamma + \beta)$, respectively. The microstructures of chill-cast, and of slowly-cooled, alloys, which confirm these separations, are described later.

THE SURFACES OF SECONDARY SEPARATION AND THE PERITECTIC REACTIONS.

An isothermal diagram of the surfaces of the peritectic reactions and of secondary separation is shown in Fig. 9, which has been constructed from the combined results of thermal and microscopical examinations.

The area $ABCD$ represents the depressed binary peritectic reaction $\alpha + L = \beta$, and $EFGHI$ the depressed binary peritectic reaction $\delta + L = \alpha$; these surfaces were built from thermal results. An additional surface of the reaction $(\delta + L = \alpha)$ falls almost vertically from the line FG to the isothermal at 227°C . This cannot be shown clearly in the present diagram, but it can be seen in the vertical sections (Figs. 23 and 24, page 293). The areas $JKLM$ and $MLNO$ represent the separation of the binary complex $(\beta + \gamma)$ on either side of the groove ML . This surface rises in temperature with increasing antimony content to the ternary point L . The areas GHP and GPQ represent the simultaneous separation of δ and ϵ , respectively, on either side of the valley GP . These surfaces are very steep, but in several alloys arrest points were obtained (on cooling curves) corresponding to this separation. G is the invariant point corresponding to the ternary peritectic reaction $\delta + \text{Liq.} = \epsilon + \alpha$, at 227°C ., and FG , GQ are boundaries of the horizontal surface. The areas $BCGF$ and $CGQR$ represent the separation of $(\alpha + \epsilon)$ from the liquid, on either side of the valley CG . Within the area $CGQR$ the alloys gave strong arrests, corresponding to this separa-

tion on cooling curves, but in the area *BCGF* no thermal evidence of this separation was obtained, and the surface has been constructed entirely from microscopical examinations. The intersection of the binary surfaces ($\alpha + L + \beta$) and ($\alpha + L + \epsilon$) in the line *BC* produces a ternary peritectic reaction $\alpha + L = \beta + \epsilon$ at 209° C., the point *B* being the composition of the α , *K'* of the β , and *C* of the liquid which takes part in this reaction. The lines *BC* and *CR* are portions of the boundaries of the horizontal plane concerned.

The areas *CRSTL* and *K'KLC* represent a portion of the surface of separation of the complex ($\epsilon + \beta$). The area *KK'LC* lies partly beneath the surface of the reaction $\alpha + L = \beta$, but the details of this portion may be seen in the vertical sections (Figs. 14-16, pages 284-285). Within this area the surface is very steeply inclined, and no thermal arrests were obtained corresponding to the separation of ($\epsilon + \beta$); the results were obtained by microscopical examinations. In the area *CRSTL*, cooling curves gave well-marked arrests, corresponding to this separation. The groove *KL* is part of one boundary of the horizontal plane at 180° C. with β of composition *K* in equilibrium with liquid of composition *L*. The valley *LT* lies in this horizontal plane.

The areas *TLU* and *NLU* are parts of the surfaces on which the complex ($\epsilon + \gamma$) separates from the liquid, on either side of the valley *LU*. Within the area *TLU* strong arrests were obtained on cooling curves, but no arrests were obtained with alloys in the area *LUN*, this part of the surface being very steep. The line *LN* is a further portion of the boundary of the horizontal plane at 180° C.

THE CONSTANT TEMPERATURE REACTIONS AND SURFACES.

The limits of the constant temperature reaction surfaces are shown in Fig. 10.

The area *ABCD* represents a portion of a ternary reaction $\delta + L = \alpha + \epsilon$ at 227° C. The reacting α (point *A*) contains 1.5 per cent. cadmium, 9 per cent. antimony; the liquid (*D*) contains 10 per cent. cadmium, 8.2 per cent. antimony. The compositions of the other reacting phases, δ and ϵ , cannot be stated accurately, since they lie outside the portion of the system examined. From the direction of the line *AB*, it appears that the δ taking part in this reaction will contain at least 1.5 per cent. of cadmium.

This reaction does not occur on cooling, except in those alloys which already contain ϵ when the temperature 227° C. is reached. The metastable structures which result from this suppression are described later. The reaction is marked by a very strong arrest at 227° C. on the heating

curves of annealed solid specimens. The temperature of the reaction, and the positions of the bounding lines, have been confirmed by microscopical examination.

The area *EFGHI* represents a portion of the ternary reaction $\alpha + \text{Liquid} = \beta + \epsilon$. The composition of the α of this reaction (point *E*) is cadmium 2.4 per cent., antimony 5.5 per cent.; the β (point *F*) contains 5.5 per cent. of cadmium, 5.1 per cent. of antimony, and the liquid (point *G*) contains 15.4 per cent. cadmium, 4.3 per cent. of antimony. These compositions appear to lie in a straight line (*EFG*), so that the ϵ phase has little or no part in the reaction, but its presence requires a constant temperature until one of the reacting phases has disappeared. The results of cooling curves are again of little use in determining the temperature and limits of this horizontal plane, since the separation of secondary ϵ is completely or partially suppressed in alloys containing less than 7 per cent. of antimony, and the reaction $\alpha + L = \beta$ continues to decrease in temperature, producing a metastable position of the ternary surface at $203^\circ \pm 2^\circ \text{C}$. Alloys with higher antimony content give constant temperature arrests at $205^\circ \pm 2^\circ \text{C}$. Heating curves did not give satisfactory results in many cases, since the rate of heating ($2\text{--}3^\circ \text{C}$. per minute) is too rapid for equilibrium to be maintained, and the alloy commences to melt before 209°C . is reached, owing to the presence of β , containing more cadmium than is required for equilibrium. Microscopical examination of annealed and quenched specimens shows that the equilibrium temperature of the reaction is 209°C . The positions of the boundaries *EG*, *EI* have also been determined microscopically.

The area *JKLMN* is a portion of the horizontal plane at 180°C . with β , γ , and ϵ in equilibrium with the liquid, in the reaction $\epsilon + \text{Liq.} = \beta + \gamma$. The reacting β contains 7 per cent. cadmium, 2 per cent. antimony (point *J*), and liquid (point *K*) contains 33 per cent. cadmium, 1 per cent. antimony. The compositions of ϵ and γ cannot be stated accurately, but the γ must be very nearly pure cadmium. Again, ϵ appears to play very little part in the reaction since the β , liquid, and γ compositions must lie very nearly in a straight line.

The arrests on cooling curves corresponding to this reaction are very sharp and prolonged, but in alloys near to the boundary *JN* the temperature is suppressed to $176^\circ\text{--}178^\circ \text{C}$. In alloys near the boundary *JKL*, a further slight arrest is obtained on cooling curves at $173^\circ\text{--}175^\circ \text{C}$. This is probably caused by the reaction at 180°C . not proceeding to completion owing to lack of equilibrium; the liquid is not completely absorbed and the temperature decreases, the liquid composition moving along the valley *LM* (Fig. 9) to the cadmium-tin binary eutectic point,

when the temperature must remain constant until the alloy has completely solidified.

The boundaries *JKL*, *JN* have been determined from microscopical examinations.

THE SOLIDUS SURFACES.

An isothermal diagram of the solidus surfaces is given in Fig. 11, which is constructed chiefly from the results of heating curves and microscopical examination of quenched specimens.

The area *ABCDE* represents the solidification of the ternary α solid solution; *BCFG* is the solidus surface of the peritectic reaction $\delta + L = \alpha$. *CFH* is a portion of the constant temperature surface at 227°C ., and corresponds to the solidification of $\alpha + \delta + \epsilon$. The area *DCHI* represents the solidification of $\alpha + \epsilon$. The surfaces discussed so far were determined from the results of heating curves, confirmed by microscopical analyses. The remaining surfaces were built from microscopical results only, except the area *NOPQ*, which was determined from cooling curve results and microscopical examinations.

The area *DEJK* is the solidus surface of the depressed binary peritectic reaction $\alpha + L = \beta$. *JKNM* represents the solidification of the β solid solution, and *KNOL* that of the complex ($\beta + \epsilon$). In the area *DKLI*, $\alpha + \beta + \epsilon$ solidify at 209°C .

MNQR represents the solidus surface of the binary complex ($\beta + \gamma$). This is almost identical with the secondary separation surface of these alloys, since the temperature range of solidification is so small that it could not be determined microscopically. A range of solidification is shown in vertical sections to satisfy theoretical requirements.

The area *NOPQ* is a portion of the constant temperature reaction plane at 180°C ., beneath which the alloys consist entirely of $\beta + \gamma + \epsilon$.

THE EUTECTOID DECOMPOSITION OF β .

There is only one transition in the solid state, corresponding to the eutectoid decomposition of the β solid solution to form ($\alpha + \gamma$). The area over which this transition occurs is marked *ABEFCD* in Fig. 12.

The transition increases in temperature from 133°C ., at the cadmium-face, to 145°C ., when 0.8 per cent. of antimony is present. Within this area (*ABCD*) the β must be presumed to decompose over a slight range of temperature, but this could not be detected microscopically. Within the area *BEFC*, the decomposition of β takes place in the presence of ϵ , and for equilibrium conditions the temperature of the transition must be constant in this area. Owing to lack of equilibrium, the eutectoid arrests on heating and cooling curves do not occur at

constant temperature until considerably more than 0.8 per cent. of antimony is present, but microscopical examinations of annealed specimens confirm that the temperature of the transition is $145^{\circ} \pm 1^{\circ}$ C. within the area *BEFC*; this temperature is approximately the mean of the temperatures obtained on cooling and heating curves (see Appendix).

Additional slight arrests occur at 160° – 170° C. on heating curves of alloys which contain α plus β . These are very similar to arrests obtained previously,² with the corresponding binary cadmium-tin alloys, and are probably caused by the changing solubility of tin in β .

MICROSTRUCTURES.

1. *Chill-Cast and Slowly-Cooled Alloys (Cooling-Curve Ingots).*

The microstructures of chill-cast alloys and of the cooling-curve ingots confirm the types of primary and secondary separations discussed previously, and will be described with reference to Fig. 9.

Alloys in the area *ABFE* consist of a cored α -solid solution similar to that of the corresponding binary antimony-tin alloys (Fig. 31, Plate XXII). In the area *ABCD* the alloys contain primary α with a narrow fringe of peritectic β , formed at the reaction $\alpha + \text{Liq.} = \beta$, and traces of binary complex $\beta + \gamma$ (Fig. 32). The latter is metastable in the alloys with lower cadmium contents, and becomes absorbed on annealing. The separation of secondary ϵ is suppressed in alloys in the area *KK'C*, except when they are cooled very slowly.

In the area *BCGF* the primary α is surrounded by the complex $\alpha + \beta + \epsilon$, and traces of the tertiary complex $\beta + \gamma + \epsilon$. The amount of the latter increases with increasing cadmium content (Fig. 33).

Owing to lack of perfect equilibrium, even in cooling curve ingots, which are cooled very slowly, no alloys consist entirely of β . In the area *JKLM* the alloys consist of primary β grains in a network of the $\beta + \gamma$ complex (Fig. 34), while those in the area *CKL* contain β with secondary ($\epsilon + \beta$) and the tertiary complex ($\beta + \gamma + \epsilon$) (Fig. 35).

Alloys whose compositions lie along the valley *LM* consist entirely of the binary complex ($\beta + \gamma$), and are very similar to the cadmium-tin eutectic alloy (Fig. 36). The alloy C_{33}S_1 has actually the composition of the ternary point *L* and there is no ϵ present after solidification.

Within the area *EFGHI* the structures of the chill-cast alloys containing up to 1.5 per cent. of cadmium are very similar to the corresponding antimony-tin binary alloys (Fig. 37, Plate XXIII). With more than 2 per cent. of cadmium the primary δ crystals are less perfectly developed, and are surrounded by the complex ($\alpha + \beta + \epsilon$)

with traces of the very fine tertiary complex ($\beta + \epsilon + \gamma$) (Fig. 38). These structures are metastable, owing to the suppression of the ternary reaction at 227° C. ($\delta + \text{Liq.} = \alpha + \epsilon$) on cooling. Annealing these alloys for a very short time causes an apparent breakdown in the δ crystals, to form ϵ plus α . This probably takes place as the reaction $\delta + \gamma = \epsilon + \alpha$. The breakdown structure appears first as a fringe around the δ crystals, and on continued annealing proceeds towards the interior (Fig. 39), when the particles of α and of ϵ begin to coalesce. In alloys with higher cadmium contents, the whole of the δ is absorbed (Fig. 40), but in alloys with less cadmium there is a residual core of δ within the ϵ fringe (Fig. 41).

Alloys within the area *GHPQ* consist essentially of primary crystals either of ϵ or of δ with secondary ($\epsilon + \delta$) complex in a tin-rich matrix with a small amount of tertiary complex ($\beta + \gamma + \epsilon$) at the grain boundaries (Fig. 42).

In the area *CGQR*, alloys with more than 10 per cent. cadmium contain primary ϵ , with secondary $\alpha + \epsilon$ in a matrix of ($\alpha + \beta + \epsilon$) with traces of the fine complex ($\beta + \gamma + \epsilon$). In alloys with less than 10 per cent. antimony, the separation of primary ϵ is suppressed on chill-casting, and metastable δ separates. Subsequent annealing causes the reaction $\delta + \gamma = \epsilon + \alpha$ to occur in the solid state, and equilibrium is restored (Figs. 43 and 44, Plate XXIV).

Alloys in the area *CLTSR* separate primary ϵ needles, secondary ($\epsilon + \beta$) and tertiary ($\epsilon + \beta + \gamma$) (Fig. 45). Alloys whose compositions lie along the valley *LT* consist of primary ϵ needles in a matrix of tertiary complex $\beta + \gamma + \epsilon$ (Fig. 46). There is no secondary separation in these alloys.

Alloys in the area *LUT* consist of primary ϵ needles, secondary ($\epsilon + \gamma$) and tertiary ($\epsilon + \beta + \gamma$) (Fig. 47).

In the area *LUN* the primary separation is the cadmium-rich phase γ ; the γ crystals are surrounded by secondary ($\gamma + \epsilon$) and tertiary ($\gamma + \epsilon + \beta$), and in the area *LMON* the primary γ crystals exist with the binary complex ($\beta + \gamma$) (Fig. 48). Along the valley *LU* the alloys consist entirely of the secondary separation ($\epsilon + \gamma$) in a matrix of the tertiary complex ($\epsilon + \beta + \gamma$).

Microstructures of Annealed Alloys: the Constitution in the Solid State.

The equilibrium relations in the solid state have been determined by microscopical examination of annealed specimens. The results are incorporated in the vertical sections (Figs. 13-30), but since such diagrams cannot be interpreted quantitatively, with respect to the Phase Rule, some typical isothermal (horizontal) sections

Vertical Sections through the Constitutional Model.

Code :

- Thermal arrest.
- 1 phase present.
- + 2 phases present.
- × 3 phases present.
- 4 phases present.

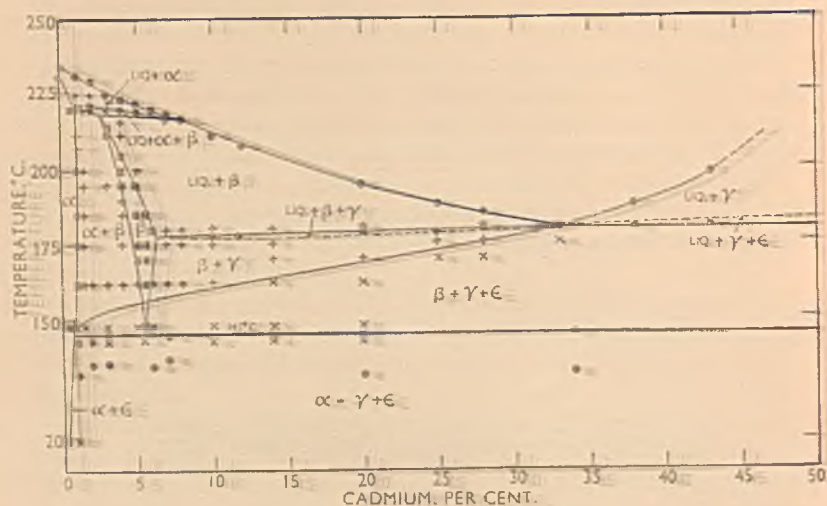


Fig. 13.—Section at 1 Per Cent. Antimony.

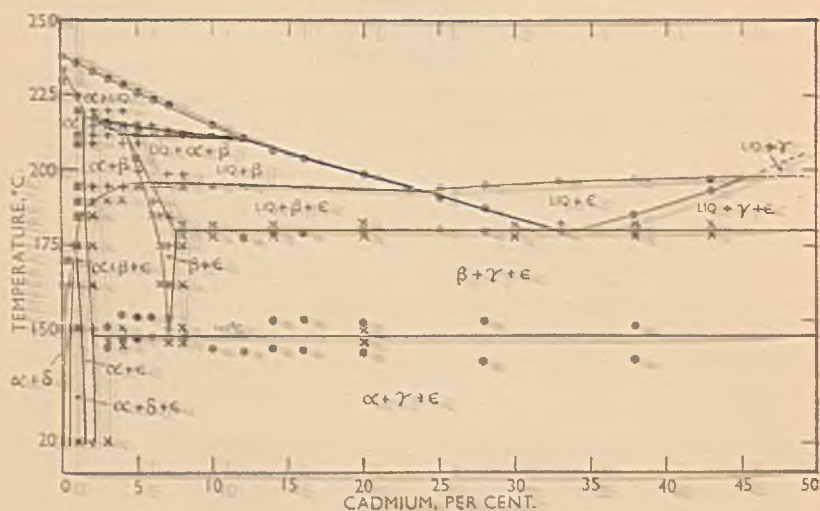


Fig. 15.—Section at 3 Per Cent. Antimony.

are given in Figs. 49-56 (pages 298-301). In these diagrams, a region in which three phases co-exist is bounded by a triangle the apices of which represent the compositions of these phases.

The horizontal section at 175° C. will be described first, since all the phases are present at this temperature.

Within the area *ABCDE* (Fig. 49, page 298) the alloys consist entirely of homogeneous α , and in the area *DEFG* of α plus δ (SbSn); the δ is present as a fine solid separation only, in alloys containing less

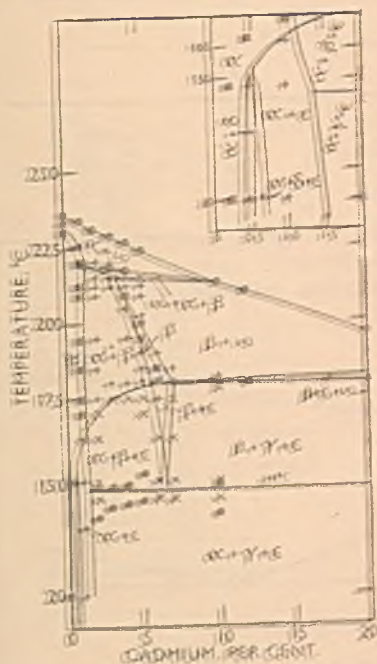


FIG. 14.—Section at 2 Per Cent. Antimony.



FIG. 16.—Section at 4 Per Cent. Antimony.

than 9 per cent. antimony (Fig. 58, Plate XXV), but in alloys with higher antimony content the primary δ outcrops are also present. These alloys are structurally identical with the corresponding binary antimony-tin alloys.

The triangular area *DGH* represents a portion of the three-phase field ($\alpha + \delta + \epsilon$) (Figs. 41 and 57). In alloys containing less than 9 per cent. of antimony, the ϵ is present only as a fine solid separation, and as such is extremely difficult to distinguish from δ (Fig. 59). The

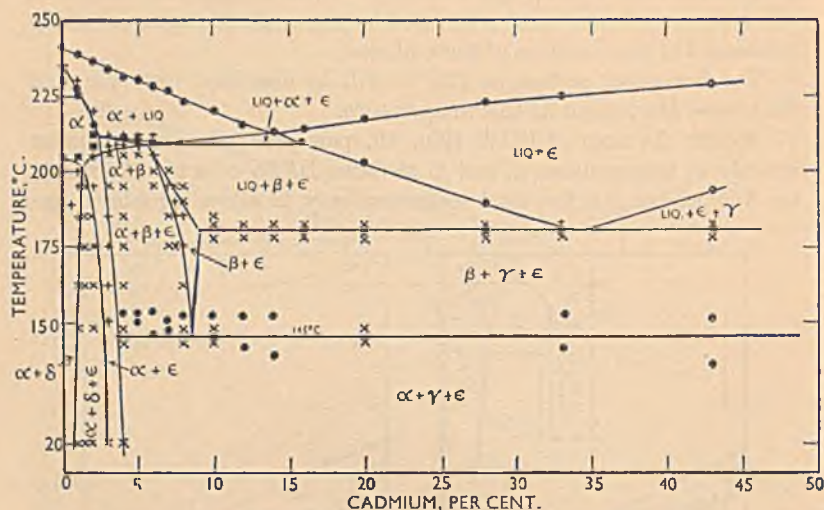


FIG. 17.—Section at 5 Per Cent. Antimony.

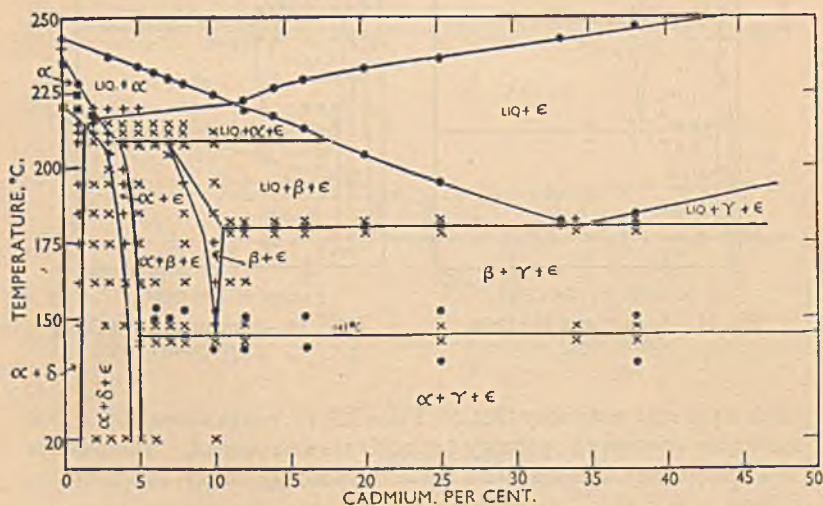


FIG. 18.—Section at 7 Per Cent. Antimony.

composition of the α present in these alloys is given by the point *D* (cadmium 1.1, antimony 3.5 per cent.).

The elongated phase field *CDHI* consists of alloys containing α plus ϵ . A typical microstructure is given in Fig. 40 (Plate XXIII).

Within the area *JKML* the alloys consist entirely of β . This is structurally identical with the β of the cadmium-tin binary alloys described previously, having a "martensitic" sub-structure, which indicates that the solid solution is not perfectly preserved by quenching. A typical microstructure is given in Fig. 60 (Plate XXV).

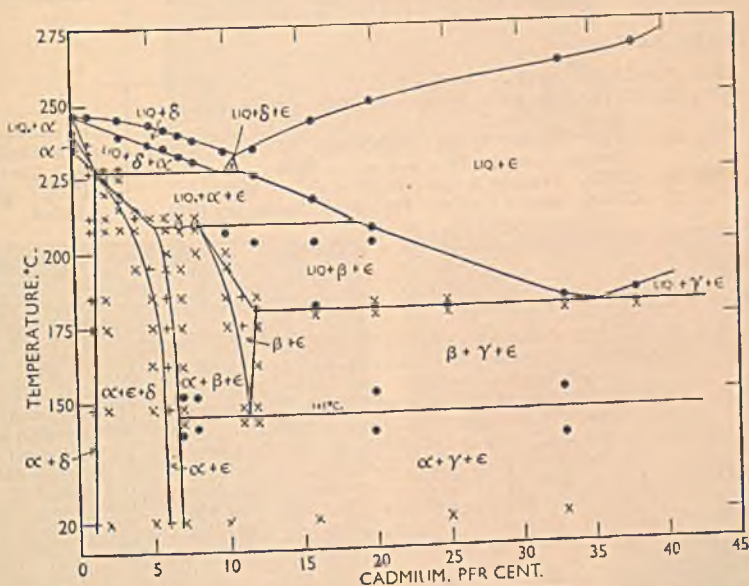


FIG. 19.—Section at 9 Per Cent. Antimony.

The area *BCLJ* represents the two-phase field ($\alpha + \beta$). The composition of the α in alloys of this field varies along *BC*, and that of β along *JL*. The microstructures are again similar to those of ($\alpha + \beta$) cadmium-tin alloys (Fig. 61, Plate XXV).

The area *CLNI* is a portion of a very elongated triangular three-phase field, consisting of α of composition *C* (cadmium 1.1, antimony 2.2 per cent.), plus β of composition *L* (5.6 per cent. cadmium, 1.7 per cent. antimony), plus ϵ (Fig. 62). In the area *LMON*, alloys consist of ($\beta + \epsilon$) (Fig. 44, Plate XXIV), and in the area *KMQR* of $\beta + \gamma$ (Fig. 63, Plate XXVI).

The area *MOPQ* is a portion of a triangular three-phase field

DESCRIPTIONS OF PHOTOMICROGRAPHS

PLATE XXI.

- | | |
|---|---|
| FIG. 4.—C50S50. Chill-Cast. CdSb + Traces of Cadmium-Rich Material. $\times 50$. | } Etched in 2
Per Cent.
HNO ₃ in
Alcohol. |
| FIG. 5.—C80S20. Chill-Cast. Primary Cd ₃ Sb ₂ + Eutectic. $\times 50$. | |
| FIG. 6.—C80S20. Annealed 1 Month at 200° C. Decomposition of Cd ₃ Sb ₂ . Probably to Cd + CdSb. $\times 50$. | |

PLATE XXII.

- | | |
|---|--|
| FIG. 31.—C1S1. Cored α . $\times 50$. | } Chill-Cast.
Etched in 2
Per Cent.
HNO ₃ in
Alcohol. |
| FIG. 32.—C7S5. Primary α , Peritectic β , Traces of ($\beta + \gamma$) Complex. $\times 250$. | |
| FIG. 33.—C3S9. Primary Cored α , Secondary ($\alpha + \epsilon$) Traces of Ternary Complex ($\beta + \gamma + \epsilon$). $\times 250$. | |
| FIG. 34.—C20S1. Primary β , Complex ($\beta + \gamma$). $\times 200$. | |
| FIG. 35.—C16S5. Slowly Cooled. Primary β , Secondary ($\beta + \epsilon$) + Tertiary Complex. $\times 800$. | |
| FIG. 36.—C33S1. Slowly Cooled. ($\beta + \gamma$) Complex. $\times 200$. | |

PLATE XXIII.

- | | |
|---|--|
| FIG. 37.—C1S10. Primary δ Cuboids (Light) in α (Dark). $\times 200$. | } Chill-Cast.
Etched in 2
Per Cent.
HNO ₃ in
Alcohol. |
| FIG. 38.—C8S12. Metastable δ (White) in α . Network of ($\beta + \gamma + \epsilon$) Complex. $\times 250$. | |
| FIG. 39.—C8S12. Annealed 1 Day at 170° C. Breakdown of Metastable δ (White) to $\alpha + \epsilon$. $\times 1500$. | |
| FIG. 40.—As Fig. 39. Annealed 1 Month at 175° C., Quenched. α (Dark) + ϵ (Light). $\times 200$. | |
| FIG. 41.—C2S10. Annealed at 175° C., Quenched. Grey ϵ Around White δ Cuboids in α Matrix. Unetched. $\times 250$. | |
| FIG. 42.—C12S14. Primary δ Cuboids, Secondary ϵ Needles + δ Cuboids in Tin-Rich Matrix. $\times 250$. | |

PLATE XXIV.

- | | |
|---|--|
| FIG. 43.—C12S10. Metastable δ (White) in α (Dark). Traces of Stable ϵ (Grey) in ($\beta + \epsilon$) Complex. $\times 200$. | } Chill-Cast.
Etched in 2
Per Cent.
HNO ₃ in
Alcohol. |
| FIG. 44.—C12S10. Annealed at 175° C., Quenched. $\beta + \epsilon$ (Light). $\times 200$. | |
| FIG. 45.—C20S14. Primary ϵ (White), Secondary ($\beta + \epsilon$), Tertiary ($\epsilon + \beta + \gamma$). $\times 100$. | |
| FIG. 46.—C36S12. Primary ϵ Needles in Fine Tertiary Complex ($\epsilon + \beta + \gamma$). $\times 100$. | |
| FIG. 47.—C43S5. Primary ϵ (White) Needles, Secondary ($\epsilon + \gamma$) in Matrix of ($\epsilon + \beta + \gamma$). $\times 100$. | |
| FIG. 48.—C48S1. Primary γ (Dark) in ($\beta + \gamma$) Complex. $\times 200$. | |

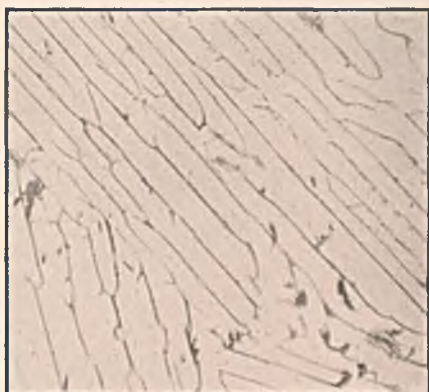


FIG. 4.

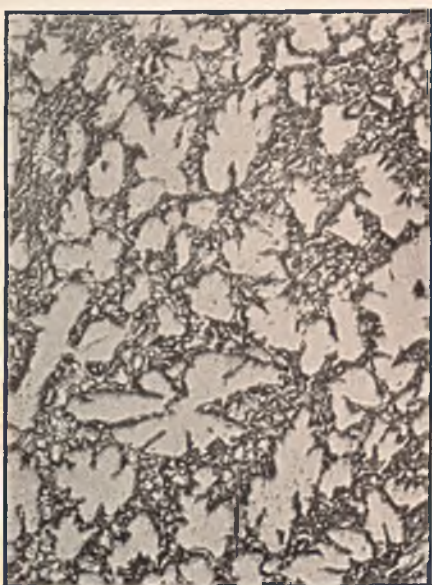


FIG. 5.

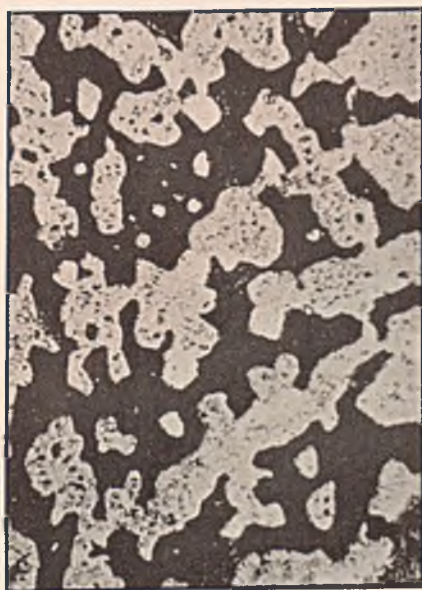


FIG. 6.

FIGS. 4-6.—For descriptions, see p. 288.

[To face p. 288.]

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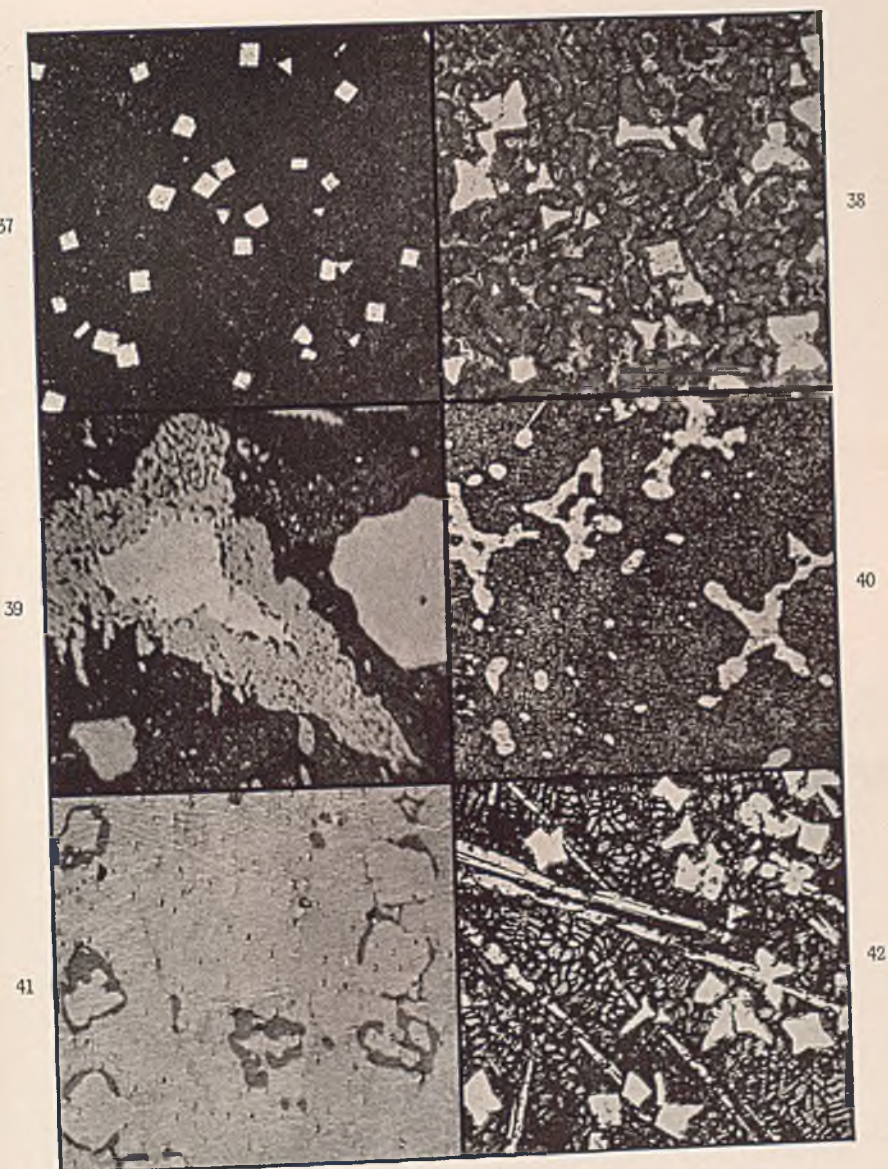
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35

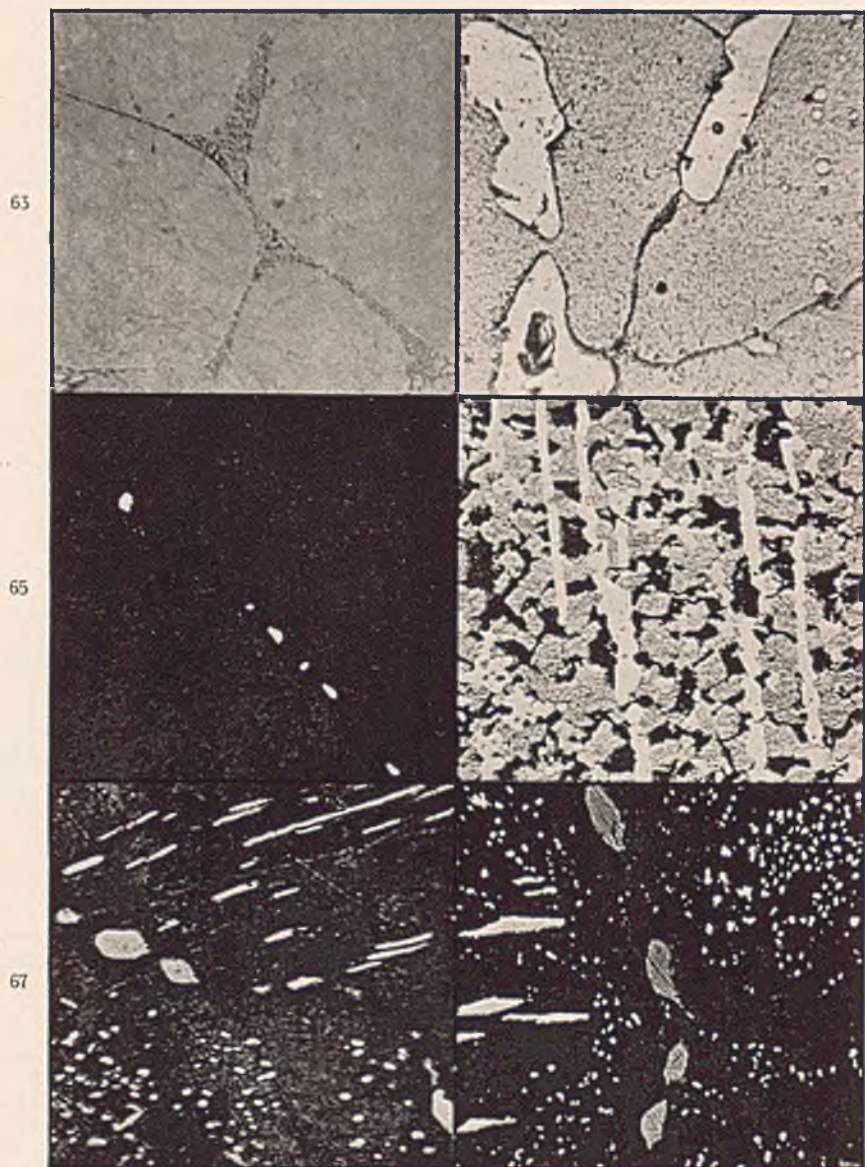


FIGS. 31-36.—For descriptions, see p. 288.

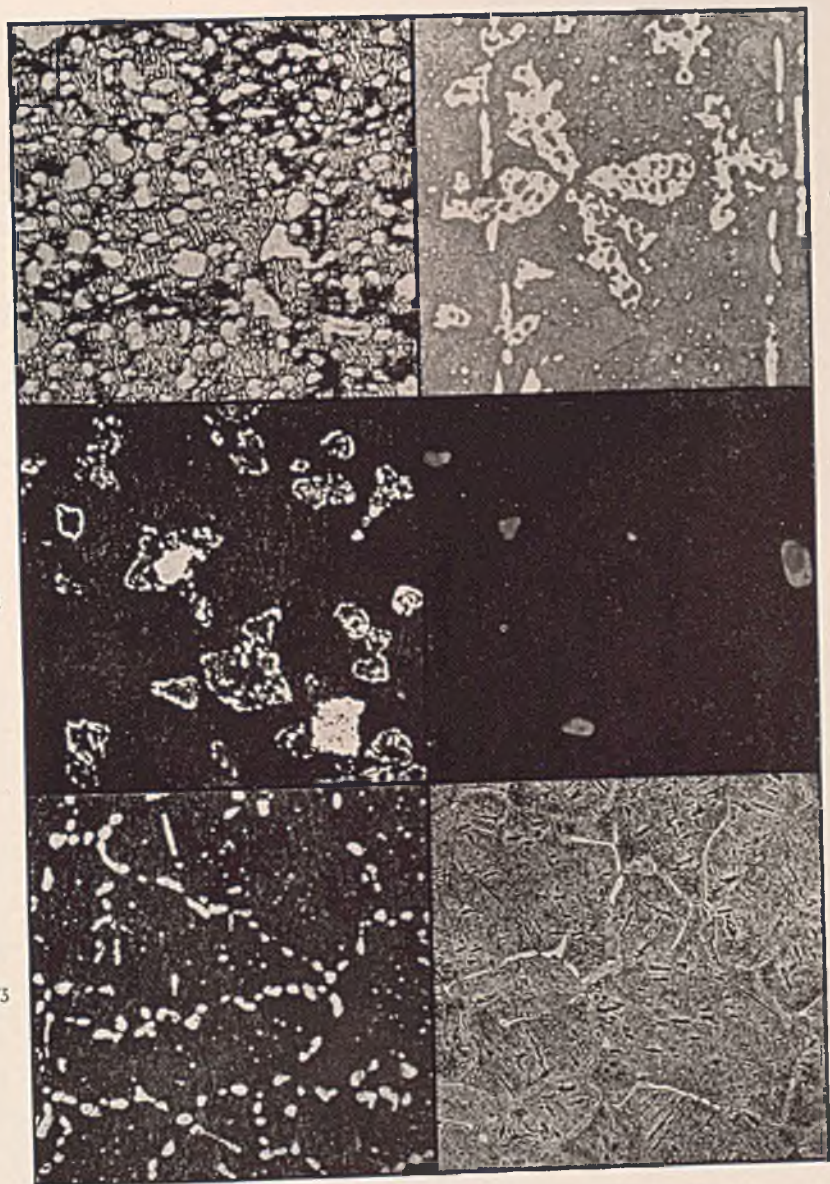


FIGS. 37-42.—For descriptions, see p. 238.



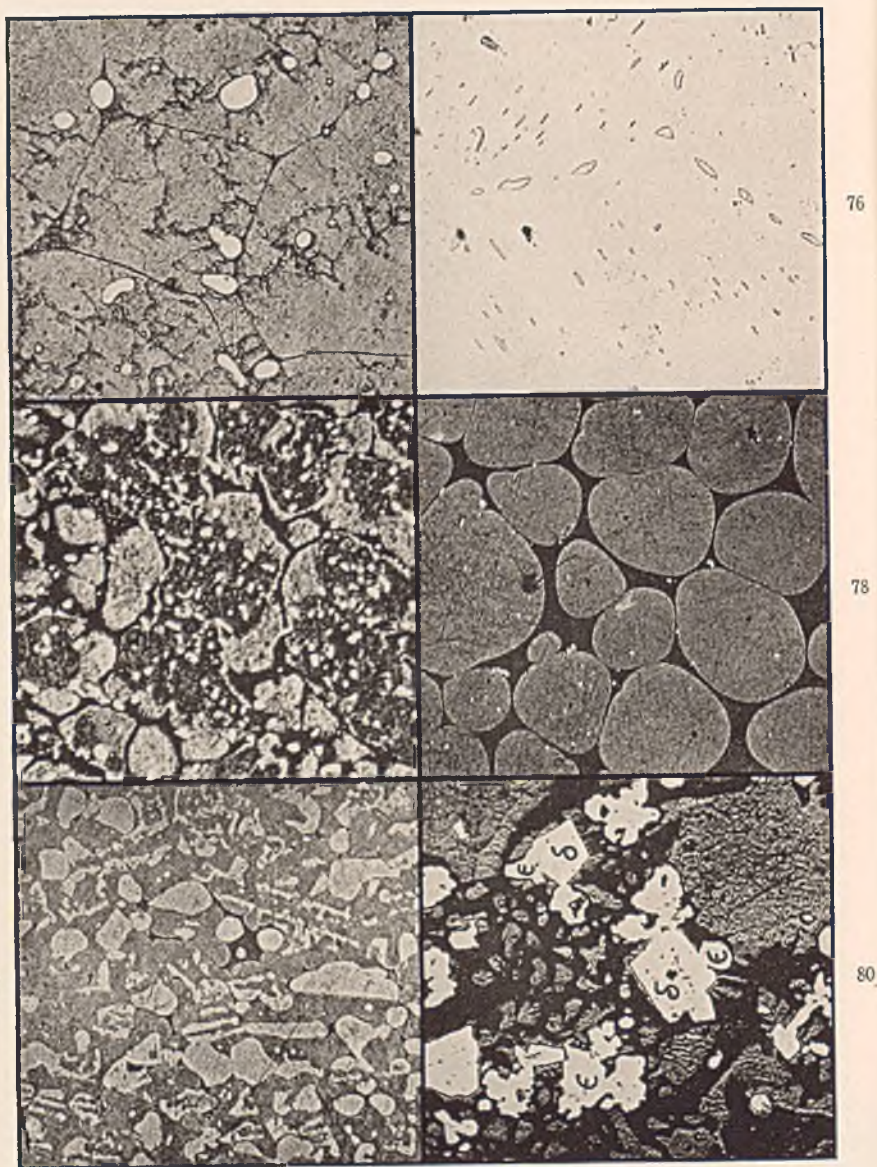


FIGS. 63-68.— For descriptions, see p. 289.



FIGS. 69-74.— For descriptions, see p. 289.





FIGS. 75-80.—For descriptions, see p. 289.

DESCRIPTIONS OF PHOTOMICROGRAPHS

ETCHING REAGENTS

- (A) 2 Per Cent. HNO_3 in Alcohol.
- (B) As in A, also in Alkaline Potassium Ferricyanide.
- (C) Acid Ferric Chloride.

PLATE XXV.

- FIG. 57.—C8S14. Quenched from 175° C. Etched in B. α (Dark), ϵ (Grey), δ (Light). $\times 300$.
- FIG. 58.—C1S7. Quenched from 175° C. Etched in A. α + Precipitate of δ . $\times 1500$.
- FIG. 59.—C5S9. Quenched from 175° C. Etched in B. Precipitates of ϵ (Grey) and δ (White) in α (Dark). $\times 600$.
- FIG. 60.—C5S1. Quenched from 175° C. Etched in A. β only. $\times 400$.
- FIG. 61.—C3S1. Quenched from 175° C. Etched in C. α (Light) + β (Dark). $\times 150$.
- FIG. 62.—C10S12. Quenched from 175° C. Etched in C. α (Grey), β (Dark), ϵ (White). $\times 300$.

PLATE XXVI.

- FIG. 63.—C8S1. Quenched from 175° C. Etched in C. β + γ (Dark). $\times 500$.
- FIG. 64.—C16S12. Quenched from 175° C. Etched in C. ϵ (White) + γ (Dark) in β . $\times 100$.
- FIG. 65.—C1S2. Quenched from 162° C. Etched in A. α (Dark) + Precipitate of ϵ . $\times 600$.
- FIG. 66.—C14S14. Quenched from 162° C. Etched in C. ϵ (White) + α (Grey) + β (Dark). $\times 200$.
- FIG. 67.—C1S9. Annealed at 170° C. and at 120° C. Etched in A. Needles and Globules of δ in α . $\times 1500$.
- FIG. 68.—C3S9. Annealed at 170° C. and at 120° C. Etched in B. α (Dark) + ϵ (Grey) + δ (Light). $\times 1500$.

PLATE XXVII.

- FIG. 69.—C14S10. Annealed at 170° C. and at 120° C. Etched in $\text{K}_2\text{Cr}_2\text{O}_7$ Solution. Eutectoid (α + γ) + γ (Dark) + ϵ (Light). $\times 600$.
- FIG. 70.—C14S14. Quenched from 185° C. Etched in C. ϵ (Light) in β . $\times 200$.
- FIG. 71.—C7S12. Quenched from 185° C. Etched in B. Fringes of δ (White) Around ϵ Areas in α Matrix. $\times 200$.
- FIG. 72.—C2S9. Quenched from 195° C. Etched in B. Precipitates of δ (Light) + ϵ (Grey) in α . $\times 1500$.
- FIG. 73.—C6S10. Quenched from 195° C. Etched in A. α (Dark) + ϵ (Light). $\times 200$.
- FIG. 74.—C3S5. Quenched from 195° C. Etched in C. ϵ (Light) + Widmanstätten β (Dark) in α . $\times 300$.

PLATE XXVIII.

- FIG. 75.—C8S5. Quenched from 195° C. Etched in A. ϵ (White) + Liquid (Dark) in β . $\times 50$.
- FIG. 76.—C1S0-5. Quenched from 209° C. Etched in C. Precipitate of β in α . $\times 200$.
- FIG. 77.—C8S9. Quenched from 209° C. Etched in C. ϵ (White) + Liquid (Black) + α (Light Grey) + β . $\times 200$.
- FIG. 78.—C6S7. Quenched from 212° C. Etched in A. ϵ (Light) + Liquid (Dark) in α . $\times 50$.
- FIG. 79.—C5S4. Quenched from 212° C. Etched in C. α (Light) + Liquid (Black) + β . $\times 50$.
- FIG. 80.—C9S12. Quenched from 227° C. Etched in A. α + Liquid + ϵ + δ . $\times 200$.

($\beta + \gamma + \epsilon$), of which the β has the composition M (cadmium 6.6, antimony 1.6 per cent.). The microstructures of this area consist essentially of ϵ as a primary or secondary separation, with β plus γ (Fig. 64, Plate XXVI).

The section at 162° C. (Fig. 50, page 298) is similar in general form to that at 175° C. and contains the same phase fields. The chief differences are the lower solubilities of antimony in α and in β , and of tin and cadmium in β .

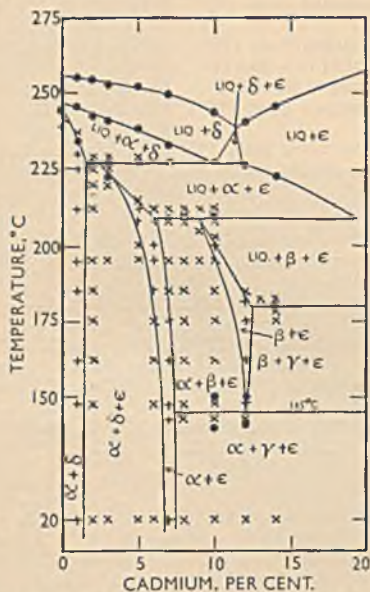


FIG. 20.—Section at 10 Per Cent. Antimony.

$ABCDE$ represents the α phase field, and $DEFG$ part of the ($\alpha + \delta$) phase field. DGH is part of the ($\alpha + \delta + \epsilon$) phase field, the α containing cadmium 0.8, and antimony 2.7 per cent. (point D). The phase field ($\alpha + \epsilon$) extends nearer to the tin corner (Fig. 65, Plate XXVI) than at 175° C. The phase fields β ($JKLM$) and $\beta + \epsilon$ ($LMON$) are appreciably narrower than at 175° C., indicating the diminishing solubility of β for both tin and cadmium. The area $BCLJ$ represents the ($\alpha + \beta$) field. The microstructures corresponding to these phase fields are similar to those described previously.

The area $CLNI$ is a part of the three-phase field $\alpha + \beta + \epsilon$, in which the α (C) contains cadmium 1.1 and antimony 1.8 per cent., and the β (L) contains cadmium 5.8 and antimony 1.2 per cent. Fig. 66 (Plate XXVI) shows a typical microstructure in which primary ϵ is present.

The area *KMPQ* is part of ($\beta + \gamma$) phase field; the structures of alloys in this field are similar to those of the corresponding cadmium-tin alloys.

The area *MORP* is a portion of the three-phase field ($\beta + \gamma + \epsilon$), in which the β (*M*) contains cadmium 6.2 and antimony 1.2 per cent.

The section at 148° C. is similar in form to that at 162° C., and will not be described in detail (Fig. 51, page 299). The phase fields β , and ($\beta + \epsilon$) are extremely narrow, since this section is only a few degrees

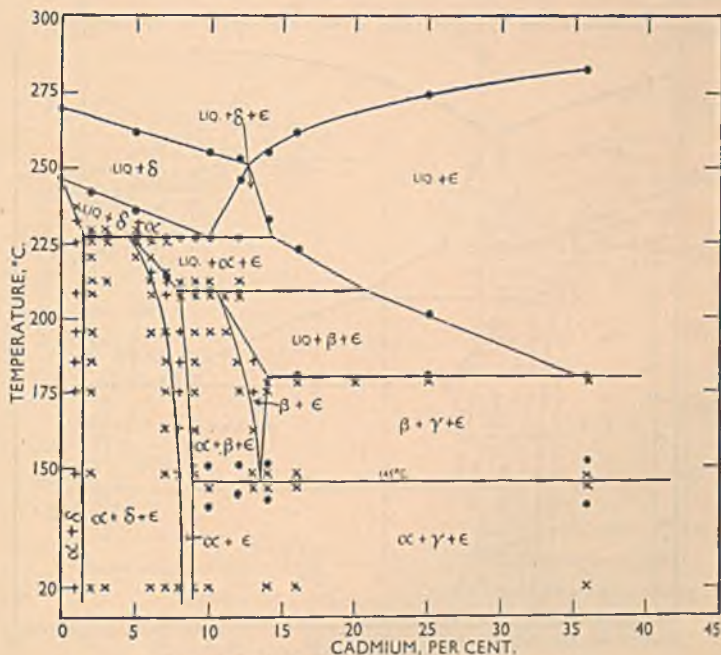


FIG. 21.—Section at 12 Per Cent. Antimony.

above the temperature of the eutectoid decomposition of β . The solubility of antimony both in α and in β shows a further decrease.

The microstructures of alloys quenched from 148° C. are similar to those described previously, but the β decomposes during quenching.

The composition of the α which is in equilibrium with $\delta + \epsilon$ at this temperature is given by the point *A* (cadmium 0.5, antimony 1.9 per cent.). In the three-phase field ($\alpha + \beta + \epsilon$), α of composition *B* (cadmium 0.7, antimony 1 per cent.) is in equilibrium with β of composition *C* (cadmium 5.4, antimony 0.8 per cent.) and with ϵ . In the

phase field ($\beta + \gamma + \epsilon$) the β contains cadmium 5.6 and antimony 0.8 per cent.

The horizontal section through the constitutional model at 20° C. is given in Fig. 52, page 299. The area *ABCDE* represents the α phase field, which has a very limited extent at this temperature. In the area *DEFG* the alloys consist of $\alpha + \delta$, with much more fine δ precipitate than at higher temperatures (Fig. 67, Plate XXVI).

The three-phase field $\alpha + \delta + \epsilon$ (*DGH*) is similar in shape to the corresponding fields in Figs. 49-51 (pages 298-299), but extends nearer

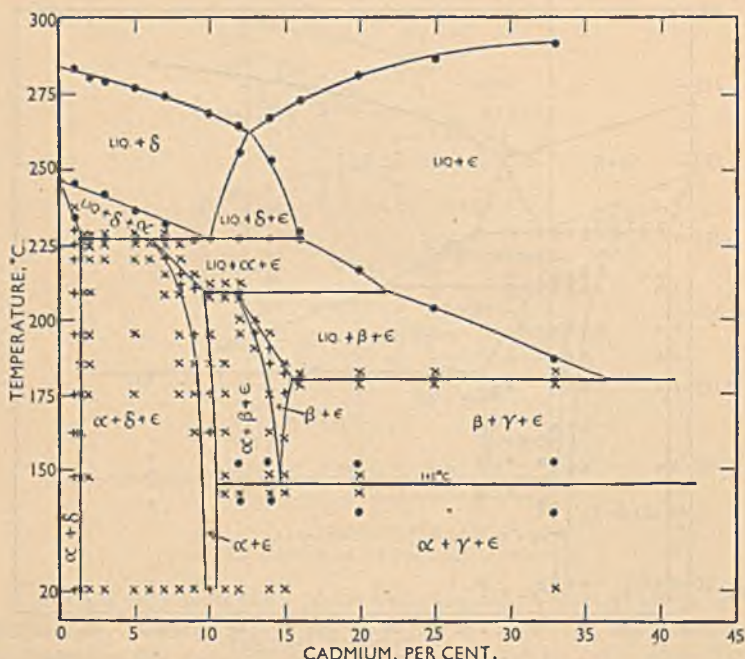


FIG. 22.—Section at 14 Per Cent. Antimony.

to the tin corner, so that more of the fine ϵ and δ precipitates are present in the microstructures (Fig. 68, Plate XXVI). The α present in all alloys within this area contains cadmium 0.5 and antimony 1.8 per cent. (point *D*). The area *CDHI* represents a part of the two-phase field ($\alpha + \epsilon$). The position of this field has moved slightly towards the right with falling temperature, and several alloys which contain $\alpha + \epsilon$ only at 175° C., now contain traces of δ .

Within the area *BCKL* the alloys consist of α plus γ . The γ (cadmium-rich solid solution) is present only as a constituent of the

eutectoid ($\alpha + \gamma$) in alloys containing up to 5.5 per cent. of cadmium, but is present both as eutectoid and as ($\beta + \gamma$) complex in alloys with higher cadmium contents. The microstructures of these alloys are very similar to those of the corresponding binary cadmium-tin alloys described previously.

The area *CIJK* is a portion of a very large three-phase field $\alpha + \gamma + \epsilon$. The α is the tin-rich solid solution containing cadmium 0.6 and anti-

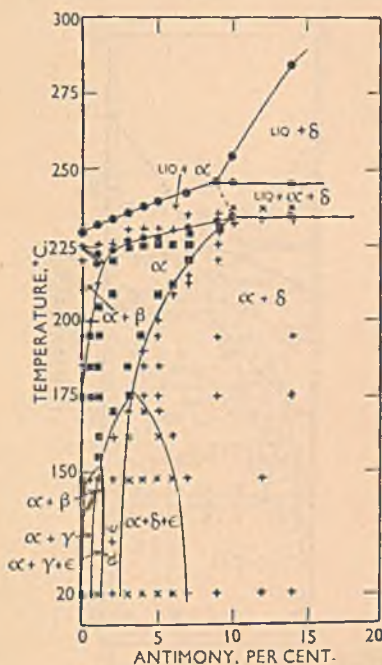


FIG. 23.—Section at 1 Per Cent. Cadmium.



FIG. 24.—Section at 3 Per Cent. Cadmium.

mony 0.6 per cent. (point *C*), γ is almost pure cadmium, and ϵ consists essentially of CdSb .

Several types of microstructure occur within this area. Along a line extending from the position $\text{C}_{5.5}\text{S}_{0.5}$ to the composition $\text{C}_{14.8}\text{S}_{14}$, the alloys consist of ϵ in a matrix of eutectoid $\alpha + \gamma$. To the left of this line alloys contain ϵ , and eutectoid with excess α , and to the right of the line they contain ϵ and eutectoid with excess γ (Fig. 69, Plate XXVII). The eutectoid ($\alpha + \gamma$) in the ternary alloys is much finer, and less clearly marked, after etching than in binary cadmium-tin alloys, but prolonged annealing coarsens this structure.

The horizontal section at 185° C. (Fig. 53, page 300) is 5° C. above the temperature of the reaction $\gamma + \beta = \epsilon + \text{Liquid}$, so that the liquid phase is present in those alloys which at 175° C. contain the $(\gamma + \beta + \epsilon)$ complex. Apart from this change, the general form of this section is similar to that at 175° C. The solubility of antimony is greater both in α and β , but the solubility of cadmium in α is slightly less; the solubility of cadmium in the β phase is appreciably lower. These

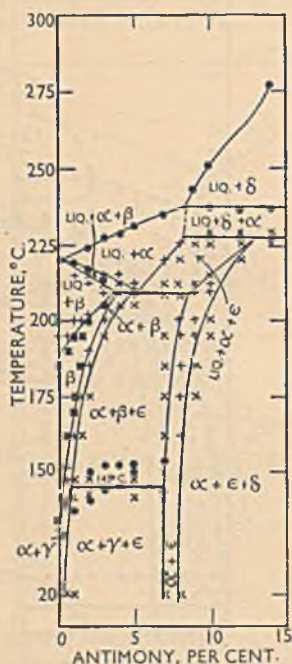


FIG. 25.—Section at 5 Per Cent. Cadmium.

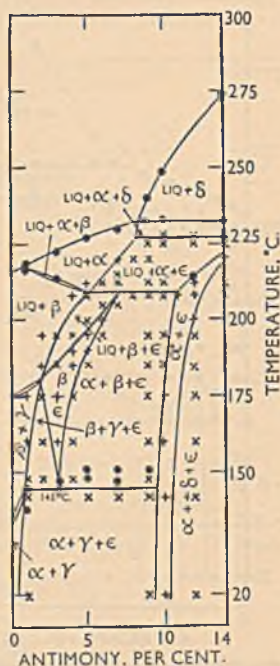


FIG. 26.—Section at 7 Per Cent. Cadmium.

changes are shown by the changed positions of the phase boundaries concerned.

The types of microstructures of alloys quenched from 185° C. (Figs. 70 and 71, Plate XXVII) are in general similar to those quenched from 175° C., but traces of a precipitate of β in α is visible in some alloys of the $(\alpha + \beta)$ and $(\alpha + \beta + \epsilon)$ regions.

In all alloys whose composition is on the right of the line *KLN* (Fig. 53, page 300) the quenched liquid phase is present.

The area *KLPO* represents a two-phase field in which β of composi-

The horizontal section at 195° C. is shown in Fig. 54, page 300. The area *ABCDE* represents the α -phase field, which extends much further into the system than at lower temperatures. The phase field $\alpha + \delta$ (*DEFG*) is similar in shape to the corresponding field at 175° C.

DGH is part of the three-phase field $\alpha + \delta + \epsilon$ in which α containing 1.1 per cent. of cadmium (4.4 per cent. of antimony) is in equilibrium with δ and ϵ . The microstructures of alloys within this field contain

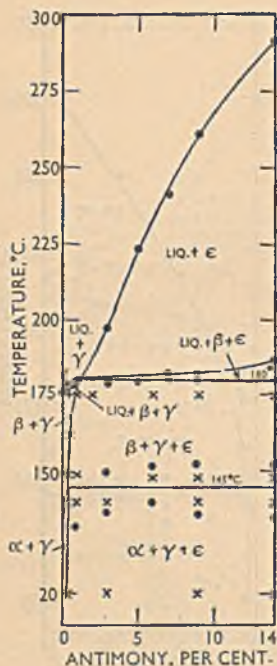


FIG. 29.—Section at 33 Per Cent. Cadmium.

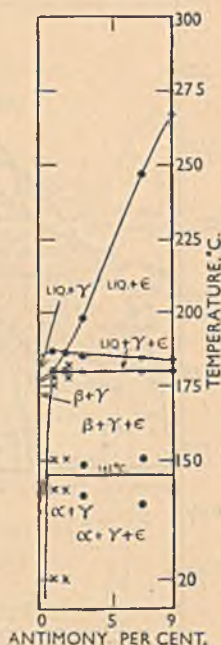


FIG. 30.—Section at 38 Per Cent. Cadmium.

much less of the fine δ and ϵ precipitates than the same alloys quenched from lower temperatures (Fig. 72, Plate XXVII).

The phase field $\alpha + \epsilon$ is nearer to the antimony-tin face, and considerably wider than at 175° C., so that several alloys which contained $\alpha + \delta + \epsilon$ at 175° C., now consist entirely of $\alpha + \epsilon$ (Fig. 73, Plate XXVII), whilst other alloys, which at 175° C. consisted entirely of $(\alpha + \epsilon)$, contain a Widmanstätten precipitate of β (Fig. 74). This structure occurs in many of the alloys of the $(\alpha + \beta + \epsilon)$ field (*CLNI*), but is less noticeable in the $\alpha + \beta$ alloys (area *BCLJ*), which are still very similar to the corresponding binary cadmium-tin alloys.

Horizontal Sections through the Constitutional Model.

Code :

- 1 phase present.
- + 2 phases present.
- 3 phases present.
- 4 phases present.

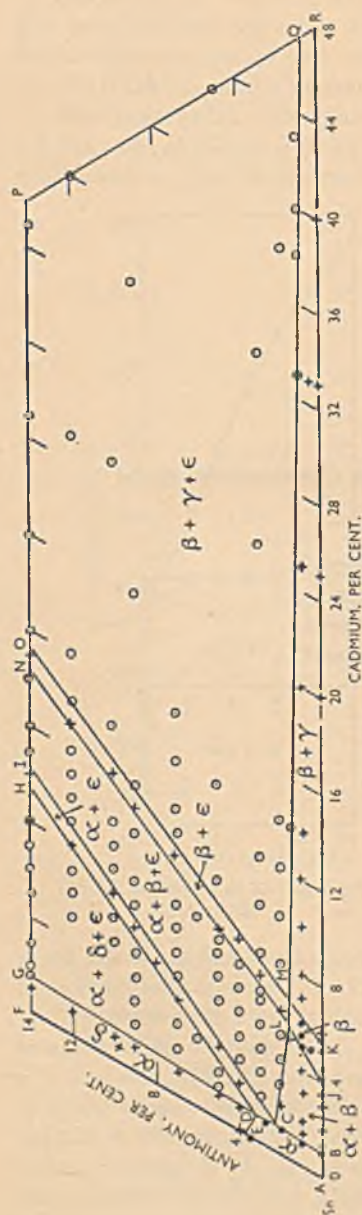


Fig. 49.—Horizontal Section at 175° C.

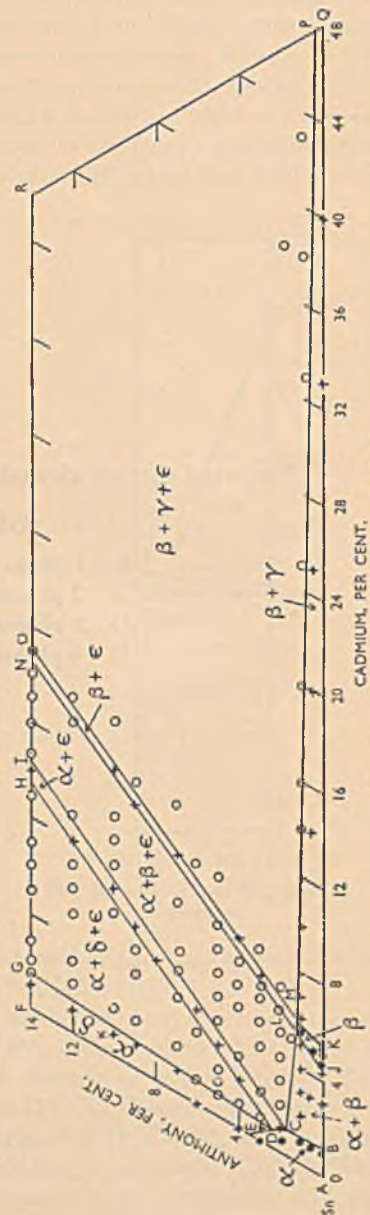


Fig. 50.—Horizontal Section at 162° C.



FIG. 51.—Horizontal Section at 148° C.



FIG. 52.—Horizontal Section at 20° C.

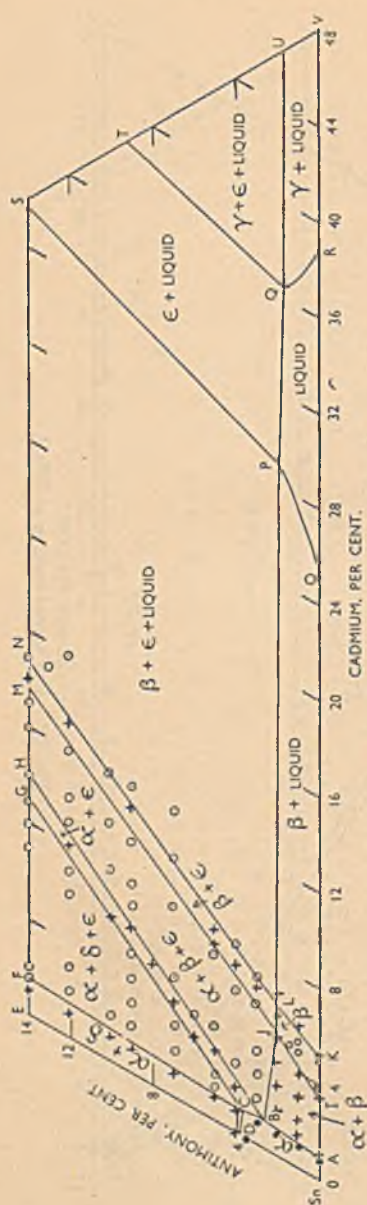


FIG. 53.—Horizontal Section at 185° C.



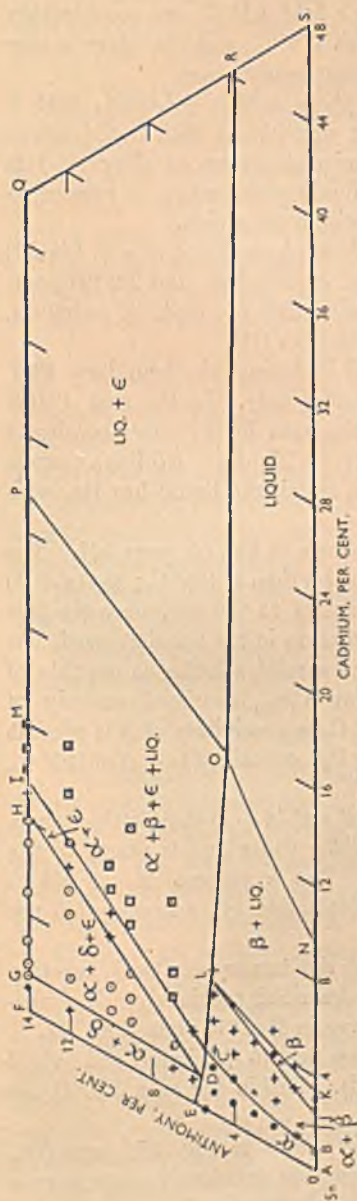


FIG. 55.—Horizontal Section at 200° C.

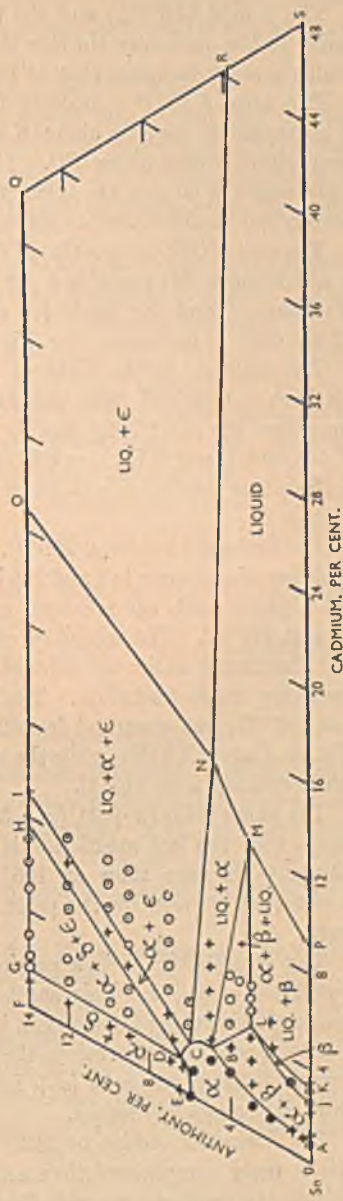


FIG. 56.—Horizontal Section at 215° C.

The β field (*JKML*) and the $\beta + \epsilon$ field *LMON* are considerably nearer to the antimony-tin face than at 175° C., and the latter in particular is much narrower than at the lower temperature.

The area *KMQP* represents the phase field $\beta + \text{Liquid}$, with β of composition varying along *KM* in equilibrium with liquid whose composition varies along *PQ*. The microstructures of alloys in this field consist of β plus the quenched liquid phase which is present as intercrystalline films, and as globules within the grains.

The area *MOTQ* is a portion of the three-phase field ($\beta + \epsilon + \text{Liquid}$) in which the β (*M*) contains 6 per cent. of cadmium, and 2.9 per cent. of antimony, and the liquid (*Q*) contains 23.2 per cent. of cadmium, 3.2 per cent. of antimony (Fig. 75, Plate XXVIII).

The diagram to the right of (and including) the boundary *PQT* has been determined from thermal curves only. In the area *PQRS* the alloys are completely liquid, in the area *RSWV* they consist of ($\gamma + \text{Liquid}$), and in the area *QTUR* of ($\epsilon + \text{Liquid}$). *RUV* is a portion of the phase field ($\gamma + \epsilon + \text{Liquid}$) in which the liquid has the composition *R*.

The horizontal section at 209° C. is shown in Fig. 55, page 301. The solubility of antimony in α and in β is greater than at 195° C.; the ($\alpha + \beta$) and β phase fields are narrower and nearer to the antimony-tin face than at 195° C. The solubility of cadmium in tin has decreased, but with increasing antimony content, the α solid solution is capable of dissolving more cadmium. The alloy $\text{C}_1\text{S}_{0.5}$ consisted entirely of α at 195° C., but quenched from 209° C., a precipitate of β is present (Fig. 76, Plate XXVIII), while the alloy C_2S_5 contained ($\alpha + \epsilon$) at 195° C., but is entirely α at 210° C.

The phase fields ($\alpha + \delta$), ($\alpha + \delta + \epsilon$) and ($\alpha + \epsilon$) show little change, except that the last mentioned is slightly wider and is nearer to the antimony-tin face than at 195° C. The α present in the alloys ($\alpha + \delta + \epsilon$) is given by the point *D* (cadmium 1.3, antimony 5.6 per cent.).

The area *CIMPOL* is a portion of the ternary peritectic reaction $\text{Liquid} + \alpha = \beta + \epsilon$. This has been described previously. A microstructure illustrating the reaction is given in Fig. 77, Plate XXVIII.

The area *KLON* represents the phase field ($\beta + \text{Liquid}$) and *OPQR* is part of the phase field ($\epsilon + \text{Liquid}$). Within the area *RSNO* the alloys are completely liquid.

The horizontal section at 212° C. is shown in Fig. 56, page 301. This is more complicated than any described previously, since it cuts through the peritectic reaction field $\alpha + \text{Liquid} = \beta$.

The area *ABCDE* represents the α phase field, *EDGF* is part of the

($\alpha + \delta$) phase field, and *DGH* is a portion of the triangular three-phase field ($\alpha + \delta + \epsilon$), in which the α contains cadmium 1.3 and antimony 6.4 per cent. (point *D*).

The area *CDHI* is a part of the ($\alpha + \epsilon$) phase field.

The area *CION* is part of a triangular three-phase field in which α containing cadmium 2.3 and antimony 6 per cent. (point *C*) is in equilibrium with liquid (*N*) containing cadmium 14.8 and antimony 4.8 per cent., and with ϵ . A microstructure quenched from this phase field is shown in Fig. 78 (Plate XXVIII).

The area *JKL* represents the β phase field, bounded on the right by the $\beta + \text{Liquid}$ field (*KLMP*), on the left by the ($\alpha + \beta$) field (*AJLB*).

The area *BLM* represents a section through the peritectic reaction $\alpha + \text{Liquid} = \beta$. The α (point *B*) contains 2.6 per cent. of cadmium and 5 per cent. of antimony, the liquid (*M*) contains 12 per cent. cadmium and 3 per cent. of antimony, and the β (*L*) contains 4.4 per cent. of cadmium and 3 per cent. of antimony. Fig. 79 (Plate XXVIII) shows a microstructure illustrating this reaction.

The area *BCNM* represents the phase field ($\alpha + \text{Liquid}$) in which α of composition varying along *BC* is in equilibrium with liquid whose composition varies along *MN*.

In the area *NOQR* the alloys consist of Liquid + ϵ , and in the area *PMNRS* the alloys are completely liquid.

The ternary reaction at 227° C., $\delta + \text{Liquid} \rightarrow \epsilon + \alpha$ is illustrated by Fig. 80 (Plate XXVIII).

SUMMARY AND CONCLUSIONS.

The constitution of antimony-cadmium-tin alloys containing up to 14 per cent. of antimony and 43 per cent. of cadmium, has been investigated by thermal and microscopical methods. A mechanical stirring apparatus was used for cooling curves to prevent segregation. The results of the thermal work are given as isothermal maps of the liquidus, secondary, and solidus surfaces.

The liquidus surface consists of five areas representing the separation of the phases α , β , γ , δ , and ϵ , respectively. The α , β and γ phases are structurally identical with those in the authors' diagram of the cadmium-tin system,² and δ consists essentially of a solid solution of cadmium in the compound *SbSn* of the antimony-tin system. The phase termed ϵ is shown to be a stable intermediate phase of the antimony-cadmium system, probably the compound *CdSb*, capable of dissolving a certain amount of tin.

The peritectic reaction at 246° C. in the antimony-tin system is depressed by the addition of cadmium. The peritectic reaction at

223° C. in the cadmium-tin system is depressed slowly by the addition of antimony, but the eutectic temperature of the cadmium-tin system is increased from 176° to 180° C. by the addition of antimony.

There are three ternary peritectic reactions, at 227°, 209°, and 180° C., respectively, but there is no ternary eutectic formed in the part of the system which has been examined.

Metastable conditions occur in certain parts of the system at normal rates of cooling, but these have been related to the stable state which is obtained by prolonged annealing of the alloys.

The results of microscopical examinations are given in typical horizontal and vertical sections through the constitutional model.

A method of etching has been developed to distinguish between the phases δ and ϵ , which are very similar in form and colour when present only as solid solubility separations.

It is shown that at 227° C., tin will dissolve 9 per cent. of antimony with 1.5 per cent. of cadmium, and at 209° C., 5.5 per cent. of antimony with 2.4 per cent. of cadmium; below 209° C. the solubilities decrease continuously to 1 per cent. of antimony with 0.7 per cent. of cadmium at 148° C. and to 0.6 per cent. of each metal at 20° C.

The solubility of antimony in the β phase of the cadmium-tin system decreased from 5.1 per cent. at 209° C. to 2 per cent. at 180° C., and to 0.8 per cent. at 145° C.

The surface of the eutectoid decomposition of β has been determined by thermal and microscopical methods. It is raised by the addition of antimony from 133° C. at the cadmium-tin face to 145° C. when 0.8 per cent. of antimony is present. With higher antimony content the decomposition takes place as an invariant transition at 145° C.

Certain features of the solid solubility relations indicate that the mechanical properties of the alloys should be amenable to heat-treatment. An investigation has been undertaken by the present authors and the results are communicated in a separate paper.

ACKNOWLEDGMENTS.

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APPENDIX.
Results of Thermal Analysis.

Composition.		Arrest Temperatures, ° C.			
		Arrests on Cooling Curves from Melt.	Arrests on Annealed Solid Specimens.		
			Cooling.	Heating.	
Cd %.	Sb %.				
1	1	231.5, 221.5	—	—	218.5
2		229.0, 221.7, 171.0	132.1	142.5, 161.5, 209.5	—
3		228.5, 220.5, 174.5, 130.7 *	136.0	142.5, 164.5, 201.0	—
4		223.5, 220.0, 174.5, 131.2 *	136.4	144.0, 173.0, 203.0	—
5		221.5, 218.5, 175.2, 131.7 *	137.2	141.0, 175.0, 195.0	—
6		219.5, 218.0, 170.0, 134.0 *	134.0	144.0, 173.5, 176.0	—
7		218.0, 216.5, 176.5	138.2	144.0, 173.5, 176.0	—
8		218.5, 176.5	—	—	—
10		211.5, 176.0	—	—	—
12		203.0, 177.0	—	—	—
20		194.5, 179.5	131.0	145.0, 176.5	—
25		188.3, 178.5	—	—	—
28		185.2, 179.0	—	—	—
33		180.0	132.0	145.0, 177.0	—
38		187.0, 179.5	—	—	—
43		198.0, 179.5	—	—	—
1	2	234.2, 219.9	—	—	224.0
2		231.0, 219.2, 171.0, 131.0 *	136.0	146.0, 162.5, 212.0	—
3		228.5, 218.0, 174.0, 134.5 *	139.0	146.0, 166.0, 201.5	—
4		226.2, 217.5, 174.2, 134.0 *	140.5	147.0, 172.0, 201.0	—
5		224.0, 216.0, 174.3, 135.0 *	141.3	150.0, 172.0, 197.0	—
10		213.0, 179.0	137.0	147.0, 170.0	—
12		209.8, 179.5	—	—	—
20		198.0, 179.5	—	—	—
1	3	235.8, 218.2	—	—	225.3
2		233.0, 217.5, 171.5, 134.5 *	—	—	214.8
3		230.5, 216.5, 174.0, 136.5 *	142.2	148.0, 168.5, 203.5	—
4		228.8, 215.0, 174.8, 137.9 *	143.8	152.0, 173.0, 200.0	—
5		227.0, 213.5, 175.3, 138.7 *	144.7	152.5, 171.2, 197.5	—
6		224.0, 214.5, 177.0	145.0	151.5, 171.5, 187.0	—
7		222.0, 213.0, 179.5	146.5	152.0, 171.8, 176.0	—
8		219.3, 212.0, 179.0	—	—	—
10		215.8, 211.5, 177.0	140.5	—	—
12		211.0, 178.0	139.5	—	—
14		207.5, 179.0	141.5	150.0, 177.0	—
16		205.0, 178.0	140.0	150.0, 176.0	—
20		199.0, 181.0, 177.5	139.5	149.0, 176.5	—
25		193.5, 191.0, 180.0	—	—	—
28		195.0, 187.0, 179.5	137.0	150.0, 176.5	—
33		197.0, 179.5	—	—	—
38		197.0, 185.0, 179.5	137.5	148.5, 178.0	—
43		197.0, 193.5, 180.0	—	—	—
1	4	237.5, 216.5	—	—	227.0
2		234.2, 215.2, 171.5, 137.5 *	—	—	214.0
3		233.0, 213.5, 173.8, 141.0 *	145.2	152.0, 166.5, 203.5	—
4		230.8, 212.5, 174.0, 141.4 *	145.5	153.5, 173.5, 200.0	—
5		229.0, 212.0, 174.5, 142.5 *	146.0	153.0, 168.5, 192.0	—
14		209.0, 205.0, 179.0	—	—	—
16		206.0, 203.5, 180.0	—	—	—
1	5	239.8, 215.0	—	—	228.0
2		236.5, 213.5, 169.5, 140.0 *	—	—	215.0
3		233.5, 211.2, 173.8, 143.3 *	—	—	204.5
4		232.2, 210.8, 174.5, 143.7 *	147.5	153.0, 174.0, 195.5	—
5		231.1, 210.8, 175.2, 144.8 *	150.0	153.5, 169.5, 191.5	—
6		229.5, 209.3, 177.0	146.0	153.5, 171.5, 191.0	—
7		227.0, 209.2, 177.5	148.0	150.5, 173.0, 185.0	—
8		223.5, 207.5, 177.0	148.5	152.0, 170.0, 176.0	—
10		219.8, 204.5, 178.0	144.5	152.0, 176.0	—
12		215.0, 200.5, 178.0	141.5	151.5, 176.5	—
14		213.5, 203.0, 178.0, 176.0	139.0	151.5, 177.0	—
16		214.0, 210.0, 180.0, 173.0	—	—	—
20		217.0, 202.5, 180.0, 176.0	—	—	—
28		223.0, 188.0, 180.0, 175.0	—	—	—
33		224.0, 180.0, 180.0	140.0	152.0, 178.0	—
43		229.0, 193.0, 179.0, 176.0	138.5	150.5	—

* Curves continued to 100° C., other curves continued only to 160° C.

APPENDIX—continued.

Composition.		Arrest Temperatures, ° C.			
		Arrests on Cooling Curves from Melt.	Arrests on Annealed Solid Specimens.		
Cd %.	Sb %.		Cooling.	Heating.	
1	7	242.5, 211.3	—	230.5	
3		236.2, 205.5, 171.2	—	206.0	
5		234.8, 204.8, 173.5, 145.0 *	146.0	164.0, 174.0, 191.5	
6		232.5, 205.2, 179.0	150.2	153.5, 170.0, 189.6	
7		230.0, 204.2, 178.0	148.5	151.0, 170.0, 190.0	
8		227.5, 201.0, 177.0	145.0	152.5, 171.5, 189.5	
10		224.0, 200.2, 177.0	140.0	152.5, 187.0	
12		222.5, 218.5, 203.0, 178.0, 173.0	139.5	150.0, 178.0	
14		227.5, 217.0, 203.0, 180.0, 172.5	140.5	—	
16		230.5, 213.0, 203.0, 181.0, 173.0	141.0	150.0	179.0
20		232.0, 204.0, 179.0, 173.0	—	—	
25		234.5, 194.5, 180.0, 173.0	135.5	151.5	177.5
33		241.5, 182.0, 180.0, 172.5	—	—	
38		247.0, 184.0, 179.0, 173.0	135.0	150.0	178.5
1	9	246.0, 208.5	—	232.3	
3		244.5, 240.5, 202.2, 172.8	—	206.5	
5		242.0, 237.0, 202.5, 175.0	—	197.0	
6		241.0, 235.0, 200.0, 176.8	—	194.5	
7		240.0, 232.5, 199.7, 177.0	139.0	151.5, 171.5, 193.0	
8		237.0, 230.0, 200.0, 178.0	141.0	152.0, 170.0, 193.0	
10		234.5, 227.0, 206.0, 180.0	—	—	
12		234.5, 225.0, 203.0, 180.0, 173.0	—	—	
16		243.5, 217.0, 202.5, 181.5, 172.5	—	—	
20		249.5, 207.0, 202.5, 179.0, 172.0, 150.0 *	138.0	151.5, 178.0	
25		255.0, 197.0, 179.0, 173.0	—	—	
33		261.0, 182.0, 179.0, 174.0	136.0	152.0, 179.0	
38		267.0, 184.0, 179.0, 174.0	—	—	
1	10	254.5, 246.0	—	234.5	
2		254.0, 242.0	—	227.5	
3		253.0, 240.5, 208.0	—	222.0, 227.5	
5		252.0, 238.0, 202.0	—	—	
7		249.5, 233.0, 204.0, 178.2	—	210.0	
10		243.5, 227.0, 208.0, 178.0, 173.0	140.0	150.0, 173.5, 197.0, 210.0	
12		240.5, 226.5, 202.0, 180.5, 173.0	142.5	151.0, 174.0, 194.0	
14		245.5, 222.5, 202.5, 180.5, 173.0	139.0	150.0, 175.0	
2	12	266.0, 241.0	—	—	
5		261.0, 236.0, 205.0	—	—	
10		255.0, 227.0, 206.0	137.0	150.0, 209.0	
12		252.5, 246.5, 227.0, 201.5, 179.0, 172.0	141.0	150.5, 176.0	
14		254.5, 232.5, 227.0, 201.5, 179.0, 172.0	139.0	151.0, 176.0, 209.0	
16		261.0, 222.5, 205.0, 181.0, 173.0	—	—	
25		274.5, 201.5, 180.0, 174.0	—	—	
36		282.5, 179.5, 172.0	136.5	151.5, 179.0	
1	14	284.0, 246.5	—	231.0	
2		281.0, 244.5	—	227.0	
3		280.0, 241.5	—	227.0	
5		277.0, 236.0, 201.5, 179.5, 173.5	—	222.0, 226.5	
7		274.0, 232.5, 203.5, 180.0, 175.0	—	215.0, 226.0	
10		268.0, 227.0, 202.5, 180.5, 173.5	—	179.0, 204.0, 209.0	
12		263.5, 226.0, 227.0, 204.0, 179.5, 172.0	140.5	152.0, 203.0, 209.0	
14		266.5, 253.0, 227.0, 206.0, 180.5, 173.0	140.5	152.0, 195.0	
16		272.0, 229.5, 227.0, 205.0, 180.0, 173.0	—	—	
20		281.0, 216.0, 207.0, 180.0, 173.5,	135.5	151.5, 177.5	
25		286.5, 204.0, 180.0, 173.0	—	—	
33		291.5, 186.5, 180.0, 172.0, 143.0 *	135.0	151.5, 177.8	
32.5	0.5	178.0, 174.0	—	—	
38	1.8	187.0, 179.0	—	—	
4	6	—	137.5	—	
5	8	—	—	208.5	
8	10	—	141.5	150.5, 210.0	
3	12	—	—	222.0	
7		—	—	214.0	
8		—	—	209.5, 227.0	
9		—	136.5	150.0, 209.0, 226.5	
1.5	14	—	—	227.5	
9		—	—	213.0, 226.0	

* Curves continued to 100° C., other curves continued only to 160° C.

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THE DETERMINATION OF ALUMINA IN THE PRESENCE OF METALLIC ALUMINIUM.*

By G. B. BROOK,† F.R.S.E., MEMBER, and A. G. WADDINGTON,‡ MEMBER.

SYNOPSIS.

The paper describes an investigation into the volatilization process for the determination of alumina in the presence of metallic aluminium, using hydrogen chloride. After reviewing the previous methods suggested for this determination, a description of a modified process and the required apparatus are given. The method has proved superior to any yet proposed for determining alumina in granulated aluminium, dross, &c., and results are given showing the application of the method to such aluminous materials.

INTRODUCTION.

THE determination of alumina in the presence of metallic aluminium has always proved a matter of considerable difficulty to the analyst. Many attempts have been made to produce a reliable method, but to the best of the authors' knowledge no really successful process has yet been described. The materials that have to be examined may vary considerably in alumina content—from aluminium dross containing about 50 per cent., aluminium skimmings with 5 to 15 per cent., to granulated aluminium containing often less than 1 per cent. alumina.

Numerous methods of a varied character have already been published as a solution to this problem. Rhodin¹ suggested the dissolution of the metallic portion with a 10 per cent. aqueous solution of sodium hydroxide with the object of obtaining the alumina as the insoluble residue, whilst another worker² employed ice-cold concentrated hydrochloric acid as the separating reagent. W. H. Withey and H. E. Millar³ tried various reagents for preferential attack on the metal, including halogens both in solution and as vapours, gaseous hydrochloric acid and fused salts. W. Ehrenberg⁴ and many others have suggested the use of cupric salts for separating the alumina from the metal, and it has also been proposed to use a gasometric method in which the volume of hydrogen evolved by dissolution of the metal is measured. F. L.

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Hahn ⁵ has worked a process in which the metal is volatilized as aluminium chloride by treatment with chlorine, but H. Lowenstein ⁶ later showed that Hahn's results were open to some doubts, owing to interaction between the molten metal and the containing boat. Takayasu Harada ⁷ employed a similar process to that of Hahn and his work may therefore be similarly criticized. G. Jander and F. Baur ⁸ designed an apparatus and method of separation of aluminium from alumina by volatilization of the metal as chloride in a stream of purified dry hydrogen chloride. Another method of almost universal application consists in converting the metal to alumina, the oxygen absorbed being the measure of the aluminium content and the alumina obtained by difference.

Since it is generally accepted that the physical properties of alumina may be varied by its mode of formation, ignition temperature, and other factors, methods employing preferential solvents for the removal of the aluminium cannot be considered as wholly reliable. Further, the determination of the aluminium content by gasometric methods or conversion to oxide and calculation of the alumina by method of difference are not to be recommended.

After a careful review of the published work cited above, the authors came to the conclusion that the process as described and worked by Jander and Baur seemed the soundest from all points of view. Although these workers employed the process for the determination of alumina in aluminium and the separation of constituents of alloys of aluminium, the process also promised considerable advantage in its application to the separation of alumina from aluminium dross, skimmings, and granulated aluminium. A very commendable feature of the process lies in the fact that the alumina is retained in its original form, and the metal content can also be determined from the condensate of the volatilized aluminium chloride.

PRELIMINARY WORK.

As early as 1925 the authors had been working on the determination of alumina in aluminium, using a volatilization process. At that time chlorine and hydrogen chloride were used as the gaseous reagents. This work indicated that chlorine was unsuitable and the results unreliable.

Withey and Millar had found in their work with chlorine that the presence of oxygen and carbon in the gas was one of the causes of unreliable results. In view of this and the experimental difficulties encountered by the authors in attempting to remove these impurities, this method was ultimately abandoned.

Earlier experiments using hydrogen chloride were also disappointing, but, even so, gave more consistent results; again, the inconsistencies were found to be, in the main, due to impurities in the hydrogen chloride, for even using the utmost care, oxygen was always present.

As an outcome of this experience, the first step was to find a practical method of eliminating the oxygen. After trying various schemes, the method as outlined by Jander and Baur was finally adopted. This consisted of mixing the hydrogen chloride with hydrogen in the proportion of 10 to 1, passing the mixed gases over platinized quartz chippings maintained at a bright heat, and then drying.

It was early found that the temperature at which the test was conducted appreciably affected the result.

The amount of sample is another matter which required consideration in view of the nature of the process, as it was essential to complete the test in a working day. When working with highly aluminous materials 1-5 gram. of sample (according to the alumina content) was quite sufficient to give weighable residues, but, owing to the heterogeneous nature of dross and skimmings and the difficulty of obtaining representative sampling, the tendency was to take much larger samples (20 gram.). Experiment soon showed that this was not feasible, for even when the volatilization tube was increased in diameter, the apparatus tended to choke with aluminium chloride and it was found impossible to keep the experiment running. Another serious difficulty encountered was the time-factor, for even using 10 gram. it was occasionally found necessary to run the test for 10 hrs.

Finally, the method to be adopted for the assessment of the alumina content of the residue had to be decided. Preliminary work showed that the residue left after volatilization (particularly in the case of granulated aluminium) was to a greater or lesser degree contaminated with iron. The method adopted at the beginning of the present investigation was to ignite the residue in the boat to 900°C. before weighing. The iron oxide was determined analytically and the alumina figure obtained by difference. Later it was decided that this method would be open to serious criticism when dealing with samples containing very small amounts of alumina. In such cases the alumina in the residue was determined directly by means of 8-hydroxyquinoline. The above refinements have all been incorporated in the following description of the process and apparatus.

DESCRIPTION OF PROCESS AND APPARATUS (see Fig. 1).

Hydrogen chloride was generated in a Kipps apparatus *A* from hydrochloric acid and sulphuric acid. The hydrochloric acid was

charged into the Kipps apparatus until the level reached the centre bulb, and the concentrated sulphuric acid was allowed to drip on to the surface from the stem of a large tap funnel, which was inserted into the centre bulb. The amount of gas generated was roughly regulated by the flow of sulphuric acid.

Hydrogen was obtained from the action of hydrochloric acid and zinc. The generator *B*, was in the form of a cylinder (a calcium chloride tower was suitable) into which the zinc was packed and had a connection

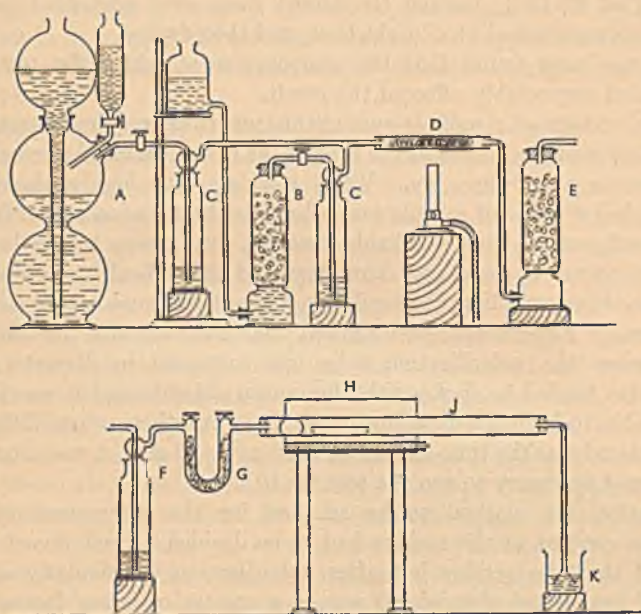


FIG. 1.

at the base for the dilute acid which was contained in a reservoir raised to a suitable level. The hydrogen chloride and the hydrogen were then passed through individual wash-bottles *C*, containing concentrated sulphuric acid, which served not only to remove a large proportion of moisture from the gases but also provided a visual indication of the rates of gas flow. The gases which were regulated approximately in the proportion of 1 part hydrogen to 10 parts hydrogen chloride, were mixed and passed into a refractory tube *D*, packed with platinized quartz chippings maintained at a bright red heat.

The use of quartz chippings (10-30 mesh) coated with platinum was finally adopted in preference to platinized asbestos, which caused

a considerable amount of trouble owing to the conversion of the magnesium compounds in the asbestos into magnesium chloride which, at the high temperature of the refractory tube, volatilized and condensed at the cool outlet. In time the tube became blocked and prevented the flow of gas, while the remaining asbestos appeared to be freed from its platinum coating and its catalytic action destroyed.

The water vapour formed by the combination of traces of oxygen with the hydrogen and the moisture still retained by the mixed gas was removed by passing the gas through three dehydrating agents :

(1) Calcium chloride packed into a cylinder *E* having an inlet tube reaching to the bottom with the gas exit at the top.

(2) Concentrated sulphuric acid contained in the gas wash bottle *F*.

(3) Anhydrous aluminium chloride packed into a U tube *G*, the upper portion of the outlet limb being packed with glass wool to act as a filter.

The dehydrated gas mixture was then passed into the reaction tube *J*, which consisted of a single piece of good resistance glass about 15 in. long and 1 in. in diameter, fitted with tubulated ground-glass stoppers at each end. The stoppers were used without any lubricant, as vaseline or any form of grease was found to be attacked by the gas. (A single piece of good glass tube fitted with rubber stoppers has been found to serve admirably so long as the ends of the tubes are maintained reasonably cool.)

The reaction portion of the tube, that is about 8 in. of its length from the gas inlet end, was maintained at a temperature of 220°–250° C. by being enclosed in a small electric heater *H*. The portion of the tube protruding beyond the heater (about 7 in.) served as the condenser for the aluminium chloride.

In passing, it may be of interest to describe another type of reaction tube used on various occasions. This consisted of two pieces of glass tube joined by means of a tapered ground joint, the reaction portion being about 8 in. long and the condensing portion about 6 in. in length. The advantages of such a tube will be obvious. After treatment of a sample it was possible to detach the condenser containing the aluminium chloride and, if it was desired to determine the metal content of the sample, the condensate could be removed and the aluminium determined as oxide.

The electric heater *H* was in the form of an asbestos-lined closed box about 8 in. long by 3½ in. square section, made in two halves, the heating element being carried in the lower half, whilst the upper

half formed a lid. Semi-circles were cut out of the end of each half so that the reaction tube lay centrally along the length of the heater.

The heating element consisted of small gauge (37 S.W.G.) Nichrome wire wound on two silica rods fixed lengthwise in the bottom half and as remote as possible from the reaction tube. Such a heater ensured a reasonably uniform heating of the reaction tube. Current from the lighting circuit (250 v.) was applied, whilst a variable resistance served to regulate the temperature.

The sample was placed in a platinum boat situated in the heated portion of the tube *J*, and a glass bulb was placed inside the tube in front of the boat to prevent aluminium chloride from condensing at the gas inlet. This platinum boat was used when the reaction temperature was 250° C. or lower. At higher temperatures quartz or porcelain boats were employed. The waste gases from the reaction tube were absorbed in water as shown at *K* on the diagram.

DESCRIPTION OF TEST.

A representative quantity of the sample was taken and placed in the boat, which in turn was inserted in the cold reaction tube, and the glass bulb placed in front of the boat. After making the necessary connections, the stream of mixed hydrogen chloride and hydrogen was started and passed through the apparatus for at least 30 minutes to sweep out the air (the platinized quartz was, of course, at a bright red heat prior to commencing the experiment). When all the air had been driven out, the heater *H* was switched on, and the resistance adjusted to give a temperature of about 250° C.

When the whole of the aluminium had reacted, the heater *H* was switched off and, after the reaction tube had cooled to just below 200° C., the boat was removed and calcined at 900° C. for 1 hr. The residue was weighed, then fused with potassium acid sulphate, the iron determined and the alumina obtained by difference. When only small quantities of residue were obtained, the alumina was determined by the 8-hydroxyquinoline method after fusion with potassium acid sulphate.

APPLICATION OF PROCESS.

It was early realized that the process was applicable to the determination of oxide in granulated aluminium, and could with advantage replace the old "total oxidation" method, which at best left much to be desired. Comparative tests by the two methods showed that the volatilization process gave appreciably lower figures owing to the presence of water, either free or combined, associated with the oxide in the samples. These lower figures were subsequently shown to be correct.

The assay of aluminium skimmings and dross by the volatilization process promised many advantages over the older method, as not only were the oxidized compounds, remaining as a residue, easily determined, but by dissolving the volatile chlorides in water, evaporating and igniting to oxide, the metallic portion was also directly determined.

(1) *Granulated Aluminium.*

Samples were selected in which the oxide had been previously determined by the "total oxidation" method. The figures given below obtained by the volatilization process represent the alumina content only and not the total non-volatile residue.

The residues were ignited at about 900° C., the ferric oxide remaining determined analytically, and the alumina content obtained by difference. The temperature of the reaction tube in this series of tests was approximately 300° C.

As will be seen, the value for the alumina content obtained by volatilization is in every case less than that given by the "total oxidation" method.

In the case of tests 9-12 the average result obtained by volatilization varies considerably from the total oxidation figure, and this variation cannot be accounted for by experimental errors inherent to either process, as might be said of Tests 1-8.

TABLE I.—*Granulated Aluminium. Comparative Results.*

Test No.	Sample No.	Alumina, Per Cent.	
		Volatilization Process.	Total Oxidation Process.
1 2	S. 6792A	0.48 0.32	1.42
3 4	S. 6792B	0.11 0.26	1.15
5 6 7	S. 6807	0.53 0.51 0.68	1.07
8	S. 6711	0.33	1.15
9 10 11 12	S. 6293B	27.8 23.0 20.2 * 19.1 *	47.0

* Tests 11 and 12 were carried out at about 450° C.

It is believed that the apparent discrepancies shown in Table I, particularly on the material rich in alumina, are due to inability to obtain a truly representative portion of the sample.

Observations of these tests showed that the granulated aluminium, although dried at 100° C. before treatment, liberated a quantity of moisture which condensed on the cooler parts of the tube before the reaction commenced. It is generally accepted that alumina cannot be completely dehydrated at ignition temperatures below 1200° C., and it was recognized, therefore, that the non-metallic portion of granulated aluminium might be hydrated. The two following tests carried out on the granulated aluminium sample S. 6293B (as used in Tests 9-12), in which both the non-volatile and volatile portions were determined, serve to confirm this assumption.

The determination of the volatile portion which represented the metallic aluminium, consisted of dissolving the condensed aluminium chloride in water, evaporating and igniting to alumina and calculating to aluminium.

TABLE II.

	Non-Volatile Residue.	Volatile Portion.	Total.	Not Accounted For.
	Al ₂ O ₃ , Per Cent.	Al, Per Cent.	Al ₂ O ₃ + Al, Per Cent.	H ₂ O, Per Cent.
1	25.64	64.95	90.69	9.31
2	23.00	66.47	89.47	10.53

Considering the figures from these two tests (Table II) it is seen that there is about 10 per cent. unaccounted for, and this amount (assuming it to be water) would give a hydrate of approximately the formula Al₂O₃.2H₂O.

An approximate determination of the water retained by this sample after drying at 100° C. was next carried out. The method adopted was to heat the sample in a porcelain boat in a glass tube to a temperature of between 600° and 700° C. (softening point of the glass), while a slow stream of dry air was passed through the tube. The moisture was then absorbed in a weighed calcium chloride tube. These approximate determinations showed :

Sample No. S. 6293B.	.	.	(1) 9.36 per cent. H ₂ O
"	"	.	(2) 8.92 "

From these figures the moisture still associated with the sample after drying at 100° C. was established as approximately 10 per cent.

The analytical figures obtained on Sample S. 6293B by the total oxidation method were then recalculated, making allowances for the

presence of 10 per cent. moisture, and the result obtained was 25.7 per cent. Al_2O_3 . This agrees approximately with the figures by volatilization.

It was apparent that the determination of alumina in granulated aluminium by the oxidation method was at fault and would give incorrect results unless the moisture content was known and the necessary allowance made for it in the calculations. The accurate determinations of such moisture, especially in samples low in alumina, would present considerable difficulty, as methods of drying such materials at a high temperature cannot be employed owing to the reactive nature of the granulated metal. The volatilization process is therefore much to be preferred for the evaluation of granulated aluminium.

At the time of carrying out the foregoing tests on granulated aluminium, it was assumed that most of the water associated with the oxide of the samples was evolved by the combined action of the dry hydrogen chloride and the temperature of the reaction tube before the reaction itself commenced. The moisture, still retained by the oxide, was believed to be associated with it in such a manner that interaction with the subsequently produced aluminium chloride did not occur. The alumina residue at the end of the treatment would still contain this moisture, which would then be removed by ignition at a high temperature.

In support of this, the powerful dehydrating properties of alumina may be cited, and the fact that the alumina residues obtained from tests invariably contained traces of moisture, serves to confirm this assumption. It was later shown, however, that some reaction does occur between the water retained by the heated alumina and the aluminium chloride, but the amount was entirely dependent on the temperature of the reaction tube. At high temperatures (about 450°C .) the amount of alumina produced by interaction of water and aluminium chloride was very small, but at lower temperatures the amount became appreciable.

Tests carried out on mixtures of aluminium hydrate (containing about 35 per cent. H_2O) and pure aluminium millings showed, that when employing a reaction temperature of about 450°C ., the alumina produced by interaction created an error of less than 5 per cent. in the final alumina determination. The bulk of the moisture appeared to be given off during the preliminary heating of the tube before the reaction commenced.

Employing a reaction temperature of about 220°C ., the error became about 80 per cent., as very little of the water was given off during the preliminary heating of the tube.

It was obvious from these tests that a reaction temperature of at least 450° C. was necessary for the accurate evaluation of materials containing alumina in a hydrated form.

(2) *Aluminium Skimmings and Dross.*

The application of the volatilization process in the analysis of aluminium skimmings and dross was very successful in so far as the determination of alumina and metallic content was concerned. It was hoped at first that cryolite flux contaminations in these materials would also be wholly retained with the residues, but this was not realized in practice.

Observations of tests led to the conclusion that the reaction between the aluminium and hydrogen chloride was accompanied by a secondary reaction which produced a film of low melting point compound on the walls of the reaction tube above and around the boat containing the sample. This film appeared to be sprayed from the sample on to parts of the tube in close proximity and although remaining molten, showed no signs of being volatile at the temperature of the tube (about 220° C.). This secondary reaction was very evident during the treatment of a particular sample of skimmings taken from the surface of molten aluminium.

On completion of this test, the boat was removed and the film, retained on the walls of the reaction portion of the tube, dissolved out with water and tested by analytical methods. Sodium and aluminium compounds were found to be present and both were identified as chlorides. The residue in the boat appeared to be contaminated with the low melting point compound, but this was wholly removed by ignition at 900° C. and the ignited residue (representing approximately 10 per cent. alumina containing a trace of ferric oxide) contained only the slightest trace of sodium.

Considering that skimmings contained flux in the form of cryolite, it was evident that the secondary reaction involved a breakdown of fluorides with the formation, suggested by the observed properties of the film, of a double chloride of sodium and aluminium.

In order to prove that such a breakdown of fluorides occurred under the conditions of the test, a sample of pure aluminium millings was mixed with an equal weight of cryolite and treated in the reaction tube at 220° C. It was found that practically the whole of the cryolite became converted to a low melting point compound, while only a small amount of aluminium chloride (judged by the quantity of condensate) was formed. The melting point of the material in the boat was roughly determined and gave a reading between 180° and 190° C., which sub-

stantially confirmed it to be sodium aluminium chloride. The determination of the actual composition of this double chloride by analytical means was not attempted owing to its deliquescent nature.

The treatment of cryolite alone in the reaction tube, although having but little relation to the main uses of the volatilization process, may be of some interest as no appreciable secondary reaction occurred and the presence of either metallic aluminium or aluminium chloride would appear to be essential to the breakdown of the fluorides.

The figures given in Table III indicate the results obtained on various samples of skimmings and dross using the volatilization process. Some comparative figures by the dilute acid extraction process are also given.

TABLE III.

Sample No.	Description.	Alumina, Per Cent.	
		Volatilization Method.	Dilute Acid Extraction Method.
S. 6832	Dross	66.4	...
S. 6832A	Skimmings	4.7	...
S. 6832B	Metal skimmings	1.3	...
L. 3110	Skimmings from clean metal	0.20	0.23
L. 3110A	Skimmings (coarse oxidized metal)	12.0	13.8
L. 3110B	Skimmings (fines, highly oxidized metal)	19.0	20.7

The results shown in the above Table III are typical of such aluminous materials, and indicate the applicability of the process to the determination of widely varying quantities of alumina. The process can be worked with equal facility when either large or small amounts of alumina are present.

SUMMARY.

The volatilization process for the determination of alumina in the presence of metallic aluminium has been investigated, and details of the apparatus and technique of the process are described.

The application of this process, using pure hydrogen chloride, to the determination of alumina in highly oxidized materials such as metal skimmings, dross, granulated aluminium, &c., has proved very successful and is superior in every respect to any other available method. The complete separation of the metal as chloride and subsequent conversion to oxide allows the metallic content of the skimmings and dross to be accurately determined.

The determination of inclusions such as cryolite and flux in metal is not possible, owing to the breakdown of the fluorides.

It has been shown that the previously used "total oxidation" method gives high results, owing to the alumina being invariably present in the sample in a hydrated form.

The volatilization process has proved equally satisfactory for materials having an alumina content ranging from less than 1.0 to 65 per cent.

ACKNOWLEDGMENTS.

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DISCUSSION.

(Condensed.)

MR. H. H. A. GREER,* J.P. (Member): In view of the large quantities of these materials which are coming into the market from aluminium users, this paper and the subject which the authors are developing is very important. It is becoming a problem for metal refiners to know what to do with these skimmings which they are receiving in such large quantities from the aluminium foundries. Hitherto, these aluminium skimmings have very largely gone into the "coup," because they are of so little value. Anything that can be done to enable us to bring them back into a useful form will be a very important contribution to the industry.

DR. R. GENDERS,† M.B.E. (Member of Council): The determination of oxides in metals in general is a useful feat to be able to perform, and in carrying out this work Mr. Brook and his collaborators have dealt with perhaps the most difficult case of its kind. In that of most other non-ferrous metals the oxide is chemically reactive and capable of measurement by the more simple method of hydrogen reduction.

In Table III the authors give some results obtained by the dilute acid extraction method, which are so good that that method could probably be used for a large amount of routine work on aluminium. It is also the method which is used for the determination of alumina in steel (as distinct from the metallic aluminium present), and it is reassuring to find that it is reasonably accurate.

MR. WADDINGTON (*in reply*): With reference to Mr. Greer's remarks, our process is mainly concerned with the evaluation of the amount of oxide in skimmings, and offers no solution as to their industrial disposal. The work

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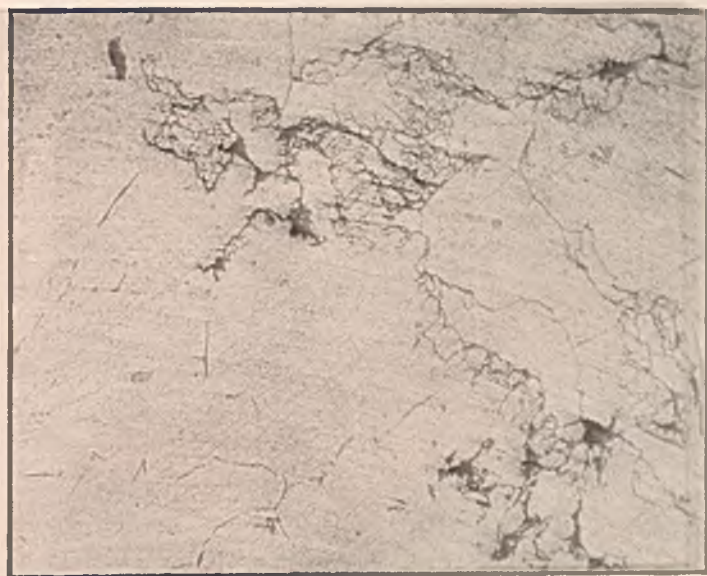


FIG. A.—Films of Oxide in Cast Aluminium. $\times 150$.

is to proceed further, and we hope that the results may be of greater interest than those now given.

It should be pointed out, in connection with Dr. Genders' remarks, that according to the manner in which oxide is produced in dross or skimmings so will its properties and resistance to acid attack vary. The dilute acid extraction method may not always give the correct result, so we feel that the volatilization process alone is dependable where oxidized aluminium has to be tested for its alumina content.

CORRESPONDENCE.

DR. L. H. CALLENDAR * (Member): This paper interests me, as about eight years ago, while at the Warrington Laboratory of The British Aluminium Company, I worked out a gasometric method for the determination of the metallic content of aluminium skimmings and dross. Mr. Brook does not recommend the use of gasometric methods, and I agree that his method would be more accurate where very small amounts of alumina are present. However, he does not give any results on metal of this type, such as commercial metal and alloys, where his method would seem to be particularly applicable.

The question is often raised whether repeated re-melting increases the oxide content of aluminium, some observers stating that pouring into fine moulds becomes more and more difficult after each melting. If this is so, it is most important for the foundryman, and Mr. Brook's method could settle whether it is due to alumina, nitride, or anything else.

For routine analysis of dross and skimmings for metallic content the method is not nearly so suitable as the gasometric method, for the samples that can be used appear to be very small, and this material, owing to its uneven nature, requires large samples to be taken. Further, the time of each analysis is too long (up to 10 hrs. is stated) and the apparatus is too complicated and expensive. Since the method estimates alumina, to get at the metallic content, corrections would have to be made for the cryolite, nitride, &c., usually present in dross and skimmings.

In the gasometric method it is possible with a very simple apparatus, easily duplicated, to make six simultaneous determinations in less than 1 hr., and the determination of the metallic content, which is commercially a more important figure than the oxide content, is, I believe, just about as accurate by the gasometric as by other methods.

The authors do not refer to the presence of nitride or carbide in the materials tested (I have found as much as 12 per cent. nitride in a sample of dross from an ordinary re-melting furnace) which might interfere with the accuracy of their results. Are nitride and carbide both decomposed at the low temperature of the experiment by *dry* hydrochloric acid gas?

Herr. H. RÖHRIG †: There is, I think, no doubt that the aim of the authors' work is to distinguish original aluminium from badly remelted metal. This should be assured if the process which has been laid down could be refined; so that one may look ultimately to the determination of aluminium oxide of the order of say 0.005 per cent. There is a great need for a precise determination; a good deal of the chemical and mechanical properties of the metal depend on the oxide content. The interesting results obtained by the authors on aluminium dross and powder lead the way to this desirable end.

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† Vereinigte Aluminium-Werke A.-G., Lautawerk (Lausitz), Germany.

Having heard, through the International Bureau for the Application of Aluminium, that the authors were carrying out work in this field, I asked Mr. Brook if he would mind investigating a sample which I knew to be badly oxidized. It had been prepared by melting down a lot of thin foil heated to 450° C. for half an hour before melting. This, of course, is as bad an instance of scrap melting (especially from the oxide point of view) as could be chosen, but it seemed to lead to a specimen containing an appreciable amount of thin films of oxides. It is satisfactory, therefore, to note that by their method the authors have succeeded for the first time, I believe, in getting determinations of oxide. Even more remarkable is the agreement of the results (0.024–0.027 per cent.). As may be seen from Fig. A (Plate XXIX) some parts of the metal are more or less totally enclosed by oxide. The volume occupied by the oxide is of course much greater than is apparent by the value 0.026. This may be due (the photograph has been taken from the unetched microsection) to the gas absorbed by the oxide films. The oxide in such a specimen is naturally not equally distributed, which makes it advisable to use large samples and select many fields.

Supported by such a valuable and reliable analytical method as the one developed by the authors, the metallographic estimation of the oxide content could also be used as a valuable aid in this field of investigation.

THE AUTHORS (*in reply*): We agree with Dr. Callendar that the gasometric method that he has used may give very satisfactory results for the metal content of highly-oxidized aluminium skimmings and dross, but the volatilization process not only is applicable to the determination of oxide in such materials, but may be successfully employed for the evaluation of skimmings of very low alumina content. We have shown values as low as 0.2 per cent. alumina in skimmings, and we do not think that the gasometric method could be accurately applied in such instances. We fully realize that the volatilization method is particularly suited to the determination of oxide content of commercial metal, and it is hoped that, with suitable refinement of the process, the investigation may continue in this direction.

Regarding the amount of sample which may be tested by the volatilization method, this is governed by the amount of condensed aluminium chloride, and, although the time required is long, up to 10 grms. of lightly-oxidized material could be tested; that is approximately 10 gm. of metal may be volatilized. From this feature it may be realized that, in highly-oxidized material, the amount of sample tested could be very much greater provided that the metal content did not exceed 10 gm. We therefore consider that the volatilization method possesses advantages over the gasometric method in respect to the amount of sample which may be taken as the gas evolution from about 10 gm. of metal would appear excessive for accurate measurement.

Regarding the possible presence of aluminium nitride and carbide in dross, we found, by experiment, that both these compounds were decomposed under the conditions of the test. The nitride produced a double chloride of aluminium and ammonia which was volatilized. Methane and aluminium chloride were presumably produced from carbide, but this was not fully investigated, beyond proving that carbide added to samples could not be detected in the residues after treatment.

OBITUARY.

SIR JOHN DEWRANCE, G.B.E. (*Past-President*).

It is with deep regret that we record the death of Sir John Dewrance, G.B.E., Past-President of the Institute, which took place at his home, Wretham Hall, Thetford, Norfolk, on October 7, 1937, after a short illness. By his death the engineering profession has lost one of its most distinguished engineers, and the country a great English gentleman.

To know Sir John intimately was to be impressed by his remarkably fine character—upright, just and human, of great personal charm, of true culture, learned in the sense known to the academic world, but distinguished moreover by the practical application which he made of that learning in an every-day life of far reaching usefulness to his fellow men. He was possessed of an unswerving devotion to the cause of right, with a rare ability to infect others with the appeal of such a cause. His conversation was a privilege to listen to, for he had the ability of leavening his remarks with a fund of entertaining stories and a host of personal experiences.

The success of his father placed him in a position that, had he so desired, he could have lived a life free from the cares of an active engineer, but such was not his nature. Educated at Charterhouse and King's College, London, and later becoming the engineering pupil of the late Colonel Davis, Sir John, as a young man, attained eminence in his profession.

He won the Watt Gold Medal and a Telford premium of the Institution of Civil Engineers. That he took out over 100 patents is more than sufficient testimony to the alertness of his mind. At an early age, he assumed direction of the family business, Dewrance and Company, in partnership with his step-father, Colonel Davis. In 1880, as a separate venture, he took over the Research Laboratory and Staff of Professor Barff, eventually developing it into the Albion Chemical Company. In this Laboratory he carried out extensive investigations of the problems of lubrication, the corrosion of boilers, the composition of bearing metals, and also the production of aluminium, an ingot of which he succeeded in producing by electrolysis as early as 1882.

On April 5, 1899, he was elected a Director and Chairman of the Board of Directors of Babcock and Wilcox, Ltd., in the place of Mr. Andrew Stewart, a position which he continued to hold until the present year, and the success



of that Company is due in no small measure to his guiding hand. As a prominent resident of Kent, in which county he lived until 1926, he took an active interest in the exploitation of the Kentish coal fields, and in 1914 succeeded the late Mr. Arthur Burr in the Chairmanship of the Deal and Walmer Coalfield, Ltd., Kent Coal Concessions, Ltd., and a number of Associated Companies in which he was intimately concerned with the financial reorganization then instituted.

He gave freely of his time to the organizations of his profession. During the war he served on various committees of the Ministries of Munitions and of Labour, on a Treasury Committee, and as a referee in matters arising from the maintenance of copper supplies. He was President of the Institute of Metals in 1926-1928, and was made a Fellow in 1929, a past-President and Honorary Member of the Institution of Mechanical Engineers, and a Member of the Institution of Civil Engineers, the Iron and Steel Institute, and the Institution of Naval Architects. He was President of the Engineering and Allied Employers' Federation 1920-1926. In 1923 he was Master of the Worshipful Company of Armourers and Braziers, an Honorary Member of the Institute of Royal Engineers and an Associate Member of the Royal Engineers' Board. As a Member of the General Board of the National Physical Laboratory, and of the Engineering Research Board, he gave valuable assistance to the development of organized research, of which he was an active advocate, and which he was wont to declare must supersede the private small-scale efforts of individual firms. He was also a Director of the Iron and Steel Trades' Employers' Insurance Association, Ltd., and his standing in academic circles was testified by the fellowship of King's College and membership of the Commercial Degrees Committee of the University of London. For ten years (1920 to 1930) he was a Governor of the London School of Economics, and in 1925 served the office of High Sheriff of Kent.

He was made a K.B.E. in 1920, and promoted to G.B.E. in 1928.

Sir John was the third of five children and the only son of John Dewrance, erector of George Stephenson's "Rocket," and subsequently Locomotive Superintendent of the Liverpool and Manchester Railway. Edward Woods, Engineer of the Line, had a brother Joseph, who established a small engineering business in London in 1835. With him John Dewrance, Senior, became associated in partnership and thus began Dewrance and Co., as it was named after Woods' death in 1842. In a sense it may be said that with his death the Institution of Mechanical Engineers suffers the severance of one of its closest links with the earliest days of its existence, for his father, as already stated, was associated with George Stephenson, the first President of that Institution.

At the age of 24 Sir John married Isabella Trevithick, the grand-daughter of the famous Richard Trevithick, and they had two children, a son and a daughter.

In 1926 Sir John went to reside at Wretham Hall, Thetford, Norfolk, one of the best shooting estates in the Eastern counties, and country pursuits and the management of his Estate provided him, during his later years, with his principal activity and enjoyment. He was a fine shot, with both gun and rifle, a deer stalker of repute, and a first-class fisherman. He was also intensely interested in all forms of wild life in the country, and he was a keen supporter of local sports in his district. He was President of the Thetford Ex-Service Men's Club, Vice-President of the local branch of the British Legion, Vice-President of the Thetford Chamber of Trade, and of the Thetford Y.M.C.A. His daughter, Mrs. Rich, who lived with her father, is well known as a breeder of both agricultural and race horses, and a keen supporter of the turf, and both these activities of hers were of constant interest to Sir John.

Thus we record the passing of a truly great English gentleman, trans-

parently honest and open, kindly and unassuming, whose life in every sense forms a pattern and encouragement for those who follow. Essentially one such as Pasteur had in mind when he recalled to the students of Edinburgh University: "To remember the past and look to the future, associate the cult of great men and great things with every thought."

J. H. M. G.

LORD RUTHERFORD (*Honorary Member*).

By the death of Lord Rutherford, an Honorary Member of this Institute, science has lost one of its greatest and most inspiring leaders, who also did much to bring science and industry into close contact and co-operation with one another. A New Zealander, born on August 30, 1871, he came to Cambridge in 1894 as the holder of an 1851 Exhibition scholarship, having already shown his originality and practical skill by experiments on the detection of electric waves. Working under J. J. Thomson, he soon became interested in radioactivity, and pursued the subject actively at McGill University, Montreal, where he was appointed professor of physics in 1898. There, he, with his chemical colleague Soddy, proposed and elaborated the theory of atomic disintegration to account for the strange phenomena which had been studied by many workers, but not explained. The researches which followed this brilliant discovery, conducted at McGill and at Manchester, after his transfer there in 1907, not only added much to the knowledge of radioactivity, but led to the theory of the structure of the atom which, perfected by Niels Bohr, forms the foundation of modern atomic physics. In 1919 he was appointed to the Cavendish Professorship of Physics at Cambridge, as the successor of Clerk Maxwell, Rayleigh, and Thomson, and here, as the Director of the greatest school of physical research in the world, he conducted a long series of experiments on the transmutation of elements, while guiding and inspiring a host of students and assistants. His powers were at their height at the time of his death.



Although his own work was in the high realms of experimental physics, Rutherford realized most clearly the importance of scientific progress to industry, and with his great gifts of exposition he would explain to gatherings of industrialists, or, after receiving a peerage in 1931, in the House of Lords, how the advance of industry must depend on the use it makes of the resources of science. For the last seven years he was chairman of the Advisory Council of the Department of Scientific and Industrial Research, and his energy and wisdom counted for much in the success of that Department. Many honours came to him, chief among them the Nobel prize in 1908, and the Order of Merit in 1925, and he was President of the Royal Society from

1925 to 1930. He was elected an Honorary Member of the Institute of Metals in 1927 and delivered the 1922 May Lecture on "The Relation of the Elements."

He was essentially an experimenter, and his theoretical conclusions, abstruse as they might seem, were always close to the experimentally observed facts. For wild speculations he had no use, and his expositions were always admirably clear to the non-mathematical reader or hearer.

Rutherford's personal qualities were as outstanding as his scientific accomplishments. Full of enthusiasm, and always interested in life, he could communicate his enthusiasm to his pupils, so many of whom have reached distinction as original workers. Few leaders have been so popular with their colleagues, and the scientific world will seem a different place without him.

C. H. DESCH.

PERCY CLAUDE M. ASH

Mr. Percy Claude M. Ash, died on July 20, 1937. He was the eldest son of the late Mr. Claudius James Ash and the great-grandson of Claudius Ash, the founder, in 1820, of the business which in later years was known as Claudius Ash, Sons & Company, Ltd. He was connected with the business for about forty-three years, becoming a Joint-Managing Director in 1905, when it was converted into a public Company.

He was actively engaged in the development of the business until the outbreak of war in 1914, when, as Captain and later as Major in the Post Office Rifles, he served in France. He was severely wounded, being shot through one lung, and was invalided for nearly two years. A recent X-ray disclosed that shrapnel had remained in the lung ever since, and this may account for the fact that he never really recovered robust health.

When convalescent he returned to the business, and in 1925, on the amalgamation of the Company with de Trey & Company, Ltd., he was appointed a Joint-Managing Director of the new Company. The office of Managing Director was subsequently abolished, but he continued to be actively associated with the Company until the end of 1934, since when he held an advisory position on the Board.

Mr. Ash was elected a Member of the Institute in 1912.

GEORGE WILLIAM MULLINS, M.B.E.

By his death on September 28, 1937, the non-ferrous metal industries have lost a leader who has exerted a most important influence on the establishment of their trade organizations. All who are concerned with metals, whether in industry or research, will mourn the loss of a loyal friend and wise counsellor.

From as early as 1885 Mr. Mullins was connected with the commercial side of the Birmingham brass and copper industry, ultimately becoming Director of the Cold-Rolled Brass and Copper Association in 1920. In this position his influence upon the other Trade Associations and thus upon the whole industry was very great. The respect and confidence which he commanded was most exceptional, but was based on his tact, wisdom, and thorough honesty, which were exhibited sometimes under most difficult circumstances.

Despite the handicap of very poor sight, Mr. Mullins was a man of wide reading and culture, which was not only of value as a member of the Council of the British Non-Ferrous Metals Research Association, for which he did yeoman service, but in private life was demonstrated by his work as President of the Midland Institute Scientific Society of Birmingham, and in many other ways.

Under his almost patriarchal appearance, Mr. Mullins possessed a youthful and energetic spirit. No task was too great for him, and the masterly way

in which he assembled and utilized statistics and other data frequently won him his case, without any need for him to use the logical and shrewd arguments with which he was always ready to support it.

He will also be remembered for the fine work that he did on Committees of the British Standards Institution, of some of which he was Chairman; as also on the Council of the Federation of British Industries, as a member of which he attended the Ottawa Conference in 1932.

As a member of the Institute since 1920, Mr. Mullins always took a keen interest in trying to secure the exposition of its work in a manner attractive to wider circles in the metal industry. He originated the idea of the Autumn Lectures and was local Honorary Secretary at the memorable Birmingham meeting in 1921 and Chairman of the Local Reception Committee at the even greater meeting in 1933. Our deep sympathy is felt for Mrs. Mullins, who so constantly supported him, both in his attendances at the Institute Meetings and throughout his active life.

R. S. HUTTON.

FREDERICK VALENTINE RAMSDEN.

Mr. F. V. Ramsden, Chief Assayer of the Rand Refinery at Germiston, South Africa, died in London on April 22, 1937.

He was born in Australia in 1884, and was educated at the Melbourne Grammar School. He took up chemistry as a career, and, as a young man, joined the staff of the Victoria Geological Survey. In 1907 he received an appointment in the Assay Office of the Royal Mint, Melbourne, and remained there until 1921. In that year the Rand Refinery, Ltd., commenced operations in Germiston, South Africa, and Mr. Ramsden was appointed Chief Assayer, which position he held until the time of his death.

He was a member of the Australian Chemical Institute, a Fellow of the Chemical Society, London, and a member of several other scientific bodies.

He was elected a member of the Institute in 1921.

FREDERICK TOMLINSON.

By the death of Mr. Frederick Tomlinson, Manchester and Salford have lost an outstanding figure in metallurgical and engineering circles, and the non-ferrous industry has lost a personality who always took a great interest in organizations connected with the Industry. He participated in the inception of the Institute of Metals, the foundation of which was laid in Manchester, and he followed its progress with very great interest from its foundation (he was an Original Member) until ill health precluded further active service. He served on the Council from 1921 until 1937.

Mr. Tomlinson was born in 1872, and at the age of 16 years joined the Broughton Copper Company, starting work in the Laboratory. Having a leaning towards the electrical side, he specialized on the electrical installations and plant of the Company, laying down, in due course, a new electrodeposition plant which was at that time the most up to date in the country.

In his technical training he had the great advantage of collaboration with Dr. David Watson, Works Manager of the Broughton Works, in the development of many of the processes with which the Broughton Copper Company's name has been associated for so many years. On the death of Dr. Watson, in 1905, he became Technical Manager of the company, and later Works Manager. He joined the Board of the Company in 1921, and remained in that capacity until the merger with Imperial Chemical Industries, Ltd., four years ago. Some years previous to this, Mr. Tomlinson's health had been affected, and he retired after very honourable and long active service, at the age of 62, though he remained a consultant to Imperial Chemical Industries, Ltd., until the time of his death.

With Mr. Tom Bolton, Mr. Tomlinson was instrumental in forming the British Non-Ferrous Metals Research Association, and for many years he acted as Chairman of one of its most important committees. He also served on various committees of the British Standards Institution, and on the Executive Committee of the Brass and Copper Tube Association.

During the War Mr. Tomlinson spent himself in the interests of the Country at the request of the Ministry of Munitions, when he was responsible for the output of large projectile shell bands.

His was a vivid personality, imbued with the Lancashire characteristics of grit and determination. A charming colleague and a loyal friend.

E. A. MERCER.

WILLIAM HENRY WILLIAMS.

Mr. W. H. Williams, Chairman and Managing Director of the Aston Chain and Hook Company, Ltd., Bromford, died, after a long illness, on November 2, 1937.

He was born and educated at West Bromwich, and was apprenticed to Kynoch, Ltd., at Witton. By the time he came of age he was in charge of a section of the sporting department of the company, and afterwards held managerial positions in the case rolling, fuse, cycle chain and cycle fittings departments. He left Kynochs in 1903 to become manager of the Aston Chain and Hook Company, and after about a year was appointed managing director. Ultimately he took over full control of the business from its former owners. When he joined the company its employees numbered about forty-five; they now number about five hundred.

Mr. Williams was a director of the Midland Laboratory Guild, Birmingham. In 1919 he was made a member of the Order of the British Empire for his wartime services. He was for many years keenly interested in the work of the Royal Cripples Hospital, and was a generous contributor to its funds.

Mr. Williams was elected a member of the Institute in 1917.

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