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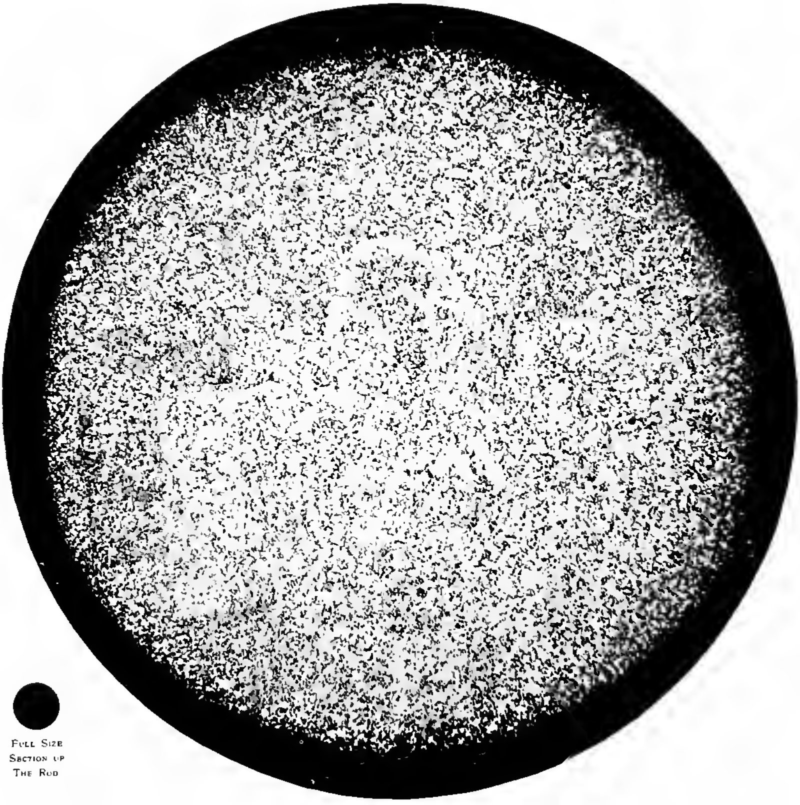
AN INTRODUCTION TO THE STUDY OF PHYSICAL METALLURGY

METALLURGY

A TREATISE UNDER THE
GENERAL EDITORSHIP OF
WALTER ROSENHAIN,
B.A., D.SC., F.R.S.


Full Size
Section of
The Rod

Composite Photo-Micrograph of Complete Cross-Section of a Case-Hardened Steel Rod. magnification 20 diameters.

METALLURGY

AN INTRODUCTION TO THE STUDY OF

PHYSICAL METALLURGY

BY

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E.M.

PREFACE

THE present volume is intended to serve as an introduction to the subject of Physical Metallurgy for those who are interested in the physics and physical chemistry of metals, whether as scientific investigators, manufacturers or users of metals, or students of metallurgy, engineering and allied subjects in which a knowledge of metals plays an important part. The volume also serves as an introduction to the Metallurgical Series which is in course of publication by Messrs. Constable under the editorship of the author. In the various volumes of this series will be found that more detailed treatment of many of the principal subjects touched upon in this book which is required by those particularly interested in any one metal or alloy or in some special aspect of the subject. With these more detailed volumes in view, the treatment of the whole subject in the present work has been intentionally kept somewhat general, the object of the author being to awaken interest and to stimulate thought and ideas rather than to communicate a great mass of detailed data.

In writing such a book the author has necessarily relied very largely upon the work of others, and in the tables of references at the end of each chapter he has endeavoured to make the only real acknowledgement which is possible in such circumstances. These references lay no claim to being an exhaustive bibliography of the subjects touched upon, but they constitute a fair guide to introductory reading. In regard to illustrations also, the author is indebted to many others for the examples he has chosen. As far as possible, the micrographs particularly have been taken from the author's own work or from that of members of the staff of the Metallurgy Department at the National Physical Laboratory. Many of these have already appeared as illustrations of the author's various papers (many of them joint papers), and he is indebted to the Councils of the various Societies and Institutions concerned for permission to reproduce these illustrations here. Specific acknowledgment in regard to these illustrations is made below.

Photo-micrographs and diagrams by other authors have been very kindly placed at the present author's disposal in a number of cases, and he desires to express his indebtedness to the following :—

Sir J. Alfred Ewing, F.R.S., for Figs. 110 to 113 inclusive, and for permission to reproduce a number of illustrations first published in joint papers by Sir Alfred Ewing and the present author.

Dr. J. E. Stead, F.R.S., for the micrograph, Fig. 17.

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The author also desires to record his indebtedness to Dr. R. T. Glazebrook, C.B., F.R.S., for permission to reproduce here a number of photographs of apparatus and appliances installed at the National Physical Laboratory and a large number of photo-micrographs taken there in the course of the regular work of the Laboratory.

Particular thanks are also due to various members of the staff of the Metallurgy Department, who have rendered most valuable assistance in the preparation of the illustrations, particularly to Messrs. W. H. Withey, D. Ewen, S. L. Archbutt and J. L. Haughton. To the two last-named the author is also indebted for much valuable help in the reading of proofs.

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AN INTRODUCTION TO THE STUDY OF PHYSICAL METALLURGY

CHAPTER I

INTRODUCTORY

SINCE the term "Physical Metallurgy," which appears in the title of this book, is not one which is as yet widely used, some definition is perhaps required. Yet the term speaks largely for itself, since it obviously connotes that branch of science which deals with metals in their physical aspect. The term is justified by the need for a distinguishing name for that great branch of the knowledge of metals which has to a large extent grown up during the last fifty years—a branch which concerns itself with the nature, properties and behaviour of metals and of alloys as such, as distinct from the far older branch of metallurgy which deals with the reduction of metals from their ores. Hitherto the term "Metallurgy" has indeed been almost entirely confined to this latter meaning, and those who have grown old in this idea are a little apt to resent an innovation which gives to the old term "Metallurgy" a wider and more general meaning than it formerly bore so as to include the newer knowledge of metals. This inevitable widening of the old term, however, demands a subdivision, so that the department of metallurgy which relates to the reduction of metals and their refining may well be termed "Process" or "Chemical" Metallurgy, leaving to the younger branch of the science the newer term "Physical Metallurgy."

Thus defined and understood, the scope of Physical Metallurgy is an exceedingly wide one, and one which brings it well over the border-land of several sister-sciences—such as chemistry on the one side, physics on another, and that branch of knowledge generally known as "strength of materials" in yet another direction. Besides these, crystallography bears largely on our subject. But while our young science necessarily draws largely upon the resources of these her elder sisters, she is not without gifts in return.

Perhaps this purely scientific aspect of our subject may with advantage be dealt with first. While the greatest practical importance obviously attaches to a deeper knowledge of metals and a better understanding of the phenomena which are met with in connection with them, yet from the point of view of pure science also, the better knowledge of metals is of considerable importance. In the first place—to take the lower ground first—metals and alloys are in constant use for the construction of scientific instruments and appliances. In the uses to which metals are put in this connection some very extraordinary demands are frequently made upon their properties—and a deeper knowledge of those properties and of the factors which govern them must lead to a sounder method of application to the difficult problems of instrument construction. Only too frequently, even at the present time, those who design, make and use scientific instruments are obviously only dimly aware that anything really useful is known about metals; consequently the use of relatively unsuitable materials continues broadcast. New and valuable materials are neglected, others of doubtful utility are at times greedily employed. The contents of the present volume, although they can but touch the fringes of the subject in many directions, should serve to supply a little of this much-needed knowledge to those who often are obliged to employ metals under conditions of special difficulty (1).

But it is not only in connection with instruments that Physical Metallurgy has an important bearing on what may be termed scientific practice. A great many experiments, both of a physical and a chemical nature, are made upon metals. Yet in a great many cases, and until recently in all cases, the exact nature and condition of the metal employed has not been fully stated or—probably—understood by the experimenter. We have endless examples of determinations of physical constants made on metals simply described as " copper " or " soft iron," or at most we find a distinction made between metals "cast" and "wrought." A perusal of the following pages will show very clearly how inadequate and even futile such a description really is. The newer knowledge of metals which forms the basis of this volume, therefore, supplies the means for rendering precise and definite all determinations of physical constants made on metallic materials. In view of the importance which is rightly attached to ever-increasing accuracy in scientific measurements, this consideration is really one of fundamental importance.

There is yet another point of view from which the whole subject-matter of Physical Metallurgy is of considerable scientific importance. The study of the solid state of matter and of molecular physics in general is attracting an increasing amount of attention, both from pure physicists and from those primarily interested in physical chemistry and crystallography. For all those interested in this subject, however, metals possess a very special importance because they are—in all probability—the simplest form of solid matter. This follows from the fact that they are in the pure state simple elementary substances. Accordingly it is in the study of metals that advances in our knowledge of the constitution of solid matter are likely to be made. For that reason the results and theories of Physical Metallurgy may well be commended to the careful attention of pure physicists—an attention which they have hitherto received in only a few instances.

Turning to the more immediately practical aspects of our subject, the importance of Physical Metallurgy scarcely requires either explanation or emphasis. To all the industries which are concerned with metals, and at the present time there are very few indeed which are not to a large extent thus concerned, every real advance in our knowledge of metals must be a real and important advantage. This makes itself felt most directly in the great industries which deal directly with the production and treatment of metals ready for technical or industrial use—such as the iron and steel industries and the non-ferrous metal industries. Every process which the metals undergo, from the moment when they first leave the refining furnaces as metals, until they reach their ultimate user, forms the direct subject-matter of our science—for in each and all of such processes, are involved those properties of metals and those phenomena associated with them which it is the object of this science to study and to elucidate. And already there are many great achievements which stand to the credit of this comparatively young science, for although the source of many of these improvements in our metal products cannot be directly traced to any one scientific publication or to the results of any one research laboratory in which the methods of Physical Metallurgy have been pursued, yet these things stand as the outward and visible tokens of the new knowledge of metals which has grown up in recent years. We may call to mind a few of the more striking examples, such as the alloy steels and the high-speed cutting steels, modern guns and armour-plate and armour-piercing projectiles, non-corrodible alloys for the construction of vessels for chemical manufactures, new light alloys of remarkable strength and durability utilised in our air-craft, and many others which, if enumerated, might well fill several pages of this book with a catalogue of modern achievement in the immediate province of our science.

Nor is it only in the evolution of new and strikingly important materials or products that the new knowledge has made itself felt; in the improvement of manufacturing processes its influence has already been great, and is destined to become still greater, since it opens up entire new ranges for methods of control and new understanding of what is really vital and what is accidental or unimportant in the processes now in use or in others whose use is suggested. This is a benefit which the leaders of our technical industries have been somewhat slow to avail themselves of, particularly in the industries connected with metals. These are necessarily old industries, in which modern ideas have had a somewhat severe struggle for supremacy. Even now that supremacy has not yet been won as fully as it should so far as Great Britain is concerned. Manufacturers are still too slow to make use of the methods which scientific research along the lines of Physical Metallurgy has rendered available. On the other hand, too, it must be remembered that our science is still in its infancy and that, much as it has already achieved, great regions of darkness still lie over the majority of our industrial and technical processes. The new science can lay no claim even to proximate completeness, and for that reason we have said that the manufacturer should utilise the *methods of research* developed in this subject—for in many cases the results he requires for his practical guidance are not yet available and must be found in his own laboratory or, at all events, at his own expense. But the science has progressed far enough to furnish the capable investigator with methods powerful enough to give a prospect of success in an attack upon the most difficult practical problem, provided that the requisite means and the requisite time are allowed for obtaining the solution. But it must be borne in mind that many of these "practical" problems involve the very deepest questions of our science, and they cannot be solved with anything but the best aids to research, nor by any but the best-trained of investigators. For that reason, perhaps, the rather halting efforts at the practical application of our science which have been made in a good many Works have led to somewhat disappointing results. Once the conditions of the case are fully understood and properly met, however, far-reaching success is certain to follow, and, as a matter of actual fact, has already been obtained in many cases.

There is another special aspect of the practical importance of Physical Metallurgy which perhaps deserves emphasis at this point. The importance of the subject to those who are concerned with the production and manipulation of metal has just been discussed, but the subject is of at least as high a degree of importance to those who have to deal with the uses of our metals. In the widest sense this embraces the whole of civilised mankind; in the narrower sense the "users of metals" are engineers and constructors generally. To these a better understanding of their most important materials of construction is obviously of paramount importance. At the present time, engineers in all branches of design are forced to adopt what are known as large "factors of safety"—*i.e.*, to employ quantities of material from three to eight or even ten times in excess of what would really be required to afford the necessary strength if all the factors of the case were completely known and the behaviour of the metal fully understood and its consistent performance entirely to be relied upon. In spite of this expensive precaution, however, failures and breakages still occur at intervals in engineering practice, thus proving that even these " factors of safety " do not really entirely ensure the degree of safety which their numerical value would suggest. Of course to some extent uncertainties exist in all engineering work, and these are by no means confined to questions of the quality and exact mode of behaviour of metals. Yet this latter factor is a very important one—in part because the precise behaviour of metals is really subject to considerable apparent vagaries and uncertainties, and partly because in the absence of complete knowledge or of searching investigation it is easy to throw the responsibility for any given failure upon the material of construction, and thus to overlook or to evade the real lessons of the failure from the point of view of design. From this point of view the development of the methods of Physical Metallurgy has already placed at the service of engineers and metallurgists powerful weapons for the exhaustive investigation of cases of failure or breakage. These methods are not at present utilised as fully as in the interests of the advancement of technical knowledge they should be. The reason lies partly in want of acquaintance, on the part of those under whose jurisdiction practical failures occur, with the nature and extent of the investigation which is now possible, and partly also from a desire to avoid or shirk searching investigation for business reasons. The maker of a metal article which has failed frequently shows an easily understood anxiety to melt up the broken parts, and dislikes having the whole case thoroughly studied, perhaps by an independent expert. Yet such a course—of covering up traces of failures as rapidly as possible instead of studying them carefully and drawing valuable conclusions from them—is not in the long run wise even in the immediate interests of the manufacturer himself, and is certainly inimical to technical progress generally. For unless the manufacturer has knowingly supplied a defective article, he himself is generally ignorant of the cause of these failures, and it is only by the careful study of such cases that his knowledge of his own processes, and of the risks of failure attaching to them, can be materially increased. It may, however, be hoped that, as the value of the methods of Physical Metallurgy becomes more widely known and appreciated, those concerned with cases of failure or breakage will avail themselves of these means of investigation to a steadily increasing extent, either by themselves establishing properly manned and equipped research laboratories or availing themselves of the services of public laboratories or of private consultants competent to deal with such matters.

It may perhaps be pointed out here that the systematic utilisation of the methods of Physical Metallurgy need not, and, indeed, should not by any means be confined, even from the practical point of view, either to the direct control of Works practice in the manipulation of metals, or to the investigation of failures. Apart from definite research of an exploratory nature, another very important function remains to be mentioned. While the study of failures occurring either under test or in practice indicates very clearly the sources of trouble, and thus shows what must be avoided by rational practice, its indications are still of a somewhat negative character, and something more is required to point out in a definite and systematic manner the path towards the best possible results. The real test of " best results " lies, of course, in the continued test of actual use, and experience quickly shows that few, if any, industrial metallic products are so uniform in quality that this searching test of practical service does not distinguish widely between different batches or even between different individual pieces which are all nominally exactly alike. We have in this circumstance a further most valuable point of attack to which the methods of Physical Metallurgy could be most profitably applied, although at the present time a vast amount of valuable material of this nature is allowed to go to waste. The problem which is suggested by these variations of behaviour so often met with in practice is simply that of ascertaining what are the real, although possibly minute, differences between the articles which have given the best results and those which have behaved either in a merely average or even in a barely satisfactory manner. There are two ways in which the methods of Physical Metallurgy could be readily applied to the solution of this problem. The first consists in making a very thorough examination, by the most searching methods available, of a considerable number of articles as delivered by the maker or as sent out for use. This is not a question of tests to be made merely for the purpose of determining whether the goods in question come up to the standard required by the specification under which they have been purchased, but something much more far-reaching. It is a question of determining as many of the properties and constants of the material as can reasonably be examined. These data should then be recorded and the behaviour of the individual articles followed through their career of actual service ; these service results will then be correlated, by systematic tabulation and comparison, with the investigatory test data obtained before the articles were put into use. It will not be long, if such a system is followed in a thorough manner, before relations between certain test results and service value become evident, thus furnishing guidance of the highest value in framing future specifications. To the user of metals the value of such a course is obvious, even though the labour and cost involved is not inconsiderable. We may take an example from railway work, such as rails and tyres. The service conditions and useful life of such objects could be followed up, in a selected number of cases, with moderate ease, even though a considerable number of cases would require to be studied in order to eliminate, as far as possible, the disturbing effects of local variations in service conditions. But what railway engineer would not be glad to have before him to-day, when called upon to draw up a specification for a fresh supply of rails or tyres, the data of chemical analyses, full mechanical tests, the micro-structure, macro-structure and thermal data covering several hundreds of rails or tyres whose subsequent service behaviour was also recorded ? At present only a few comparatively isolated data of this kind are available, and it may easily happen that the tests which have been made under various specifications did not really test just that property or combination of properties which is of primary importance for these very articles.

Nor need the manufacturers of metal objects fear the results of such a systematic correlation between preliminary exhaustive tests and service behaviour. What a manufacturer whose aim it is to supply sound and reliable goods and thus to build up a reputation in the engineering world, has to dread are chiefly two things—the first and most serious is a faulty specification which may, perhaps, impose very severe tests of the wrong kind, tests which the maker finds it difficult to comply with, but which depend upon properties not really vital to the particular object for which the goods are intended. The second is the risk that, either through lack of adequate systematic data or through prejudice, goods which are in reality inferior may attain a spurious reputation. Both these dangers would be steadily eliminated by the systematic application of the methods of Physical Metallurgy which is here suggested, so that ultimately the manufacturer, as well as the user, must benefit materially by the advancement of technical knowledge which would result.

The method of preliminary investigatory testing which has just been discussed has one material drawback—that its results can only be arrived at gradually in the course of time, as experience of practical behaviour is obtained in correlation with preliminary data. For that reason the second way of applying the methods of Physical Metallurgy in correlation with the results of practice is worthy of some consideration, although its results are obtained on a far less satisfactory and conclusive basis. This second method consists in the systematic study and examination of what may be described as "favourable examples." In the case of railway work already cited, rails and tyres which have behaved particularly well in service might be utilised in this way, and investigations undertaken in order to ascertain not only the causes of failure or unsatisfactory behaviour, but to determine the principal characteristics of metal which has been found particularly successful in the searching test of actual practice. To some extent this method also requires time to mature its results, since many "favourable examples" would need to be studied before definite conclusions could safely be drawn. But at least the long period of waiting for the tested objects to wear out or fail would be eliminated. This latter method also has another obvious advantage, which lies in the fact that in a great many cases the exhaustive physico-metallurgical study of an object implies its destruction so far as future practical use is concerned. This does not apply to such a thing as a rail, from which relatively small pieces can be cut at either end, but it applies very markedly to the case of a tyre. In many cases, if not in all, this difficulty can be overcome by the use of special methods of testing and examination, but in the case of "favourable examples" withdrawn from service for purposes of study no such difficulty arises, and in many cases much more thorough examination can then be undertaken.

The growing extent to which the importance of physico-metallurgical methods in connection with engineering is being recognised may be seen from the rapid growth and vigorous work of various societies and associations which are largely concerned with Physical Metallurgy. Thus the International Association for the Testing of Materials, which was founded by Bauschinger in 1884, has shown a steadily increasing membership and rapidly increasing vigour. While perhaps at the outset this Association was primarily interested in the purely mechanical testing of metals, work of a more or less distinctly metallurgical type soon made its appearance in its Proceedings, and this side of its activity has grown very much in more recent years. At the present time the scope of the work of the Association (Metals, Section A) is practically co-extensive with the subject of Physical Metallurgy as here defined, and the questions of mechanical testing, both commercial and scientific, are rightly considered as closely related to the study of metals by microscopic, thermal and other physical methods. The foundation and rapid growth of the Institute of Metals, whose scope is exactly co-extensive with that of Physical Metallurgy so far as the non-ferrous metals are concerned, is another indication of the increasing recognition of the value and importance of our subject.

In dealing with so wide a subject in an introductory volume it is obvious that it will not be possible to attempt an exhaustive treatment, either in regard to the subjects to be touched upon or even in the treatment of those subjects which are dealt with. All that can be aimed at is to present a general survey, not so much for the purpose of giving detailed information or instruction as with the object of arousing an interest in the whole field of inquiry and of conveying some idea of what has already been achieved and in what directions further advance is to be sought. For those who are only indirectly interested in metals, such a general survey will perhaps prove sufficient; for others who wish to take up the subject in detail, much fuller study is required, and the present volume can only serve literally as an introduction to the literature of the subject. Indeed, although Physical Metallurgy as a whole may be looked upon as the branch of a specialist, yet for the worker in that field still further specialisation is required, so that each subdivision of the subject requires separate treatment in an individual volume.

The general survey of Physical Metallurgy which is contemplated in this book may perhaps be best undertaken if the whole subject is approached from some distinct single point of view. The one which it is proposed to adopt here is based upon the view that the fuller understanding of metals is dependent upon a knowledge of their internal structure and constitution. The methods of studying that structure and constitution, and the resulting knowledge, will therefore be dealt with first, the useful and interesting properties of metals and alloys being subsequently dealt with—so far as space permits—from the point of view of their structure. In the first instance we shall confine our attention to substantially pure or "simple" metals, since their nature and behaviour is better understood than that of alloys in many respects. Subsequently the nature of alloys will be considered, and our knowledge of pure metals will be applied to them so far as that is possible. As far as possible it will be well to deal with general ideas and principles rather than with detailed facts, but in order to offer to the reader a survey of the subject possessing any degree of completeness, it will be necessary to include a section dealing directly with the more important groups of metals and alloys.

In dealing with the subject in the manner just indicated it will not be possible to retain any direct connection with the chronological order in which the various branches of the subject have been developed. Historical references, however, are of little direct importance to those making their first acquaintance with the subject, and little space can be devoted to them in the present volume. The history of the subject is, however, largely contained in the references to original papers which are given at the end of each chapter. A very brief general outline of the history of the subject is all that can be given here.

Observations on metals in some form or other go back as far as the uses of metals themselves, and metal objects of very great age have been found in the East. In that very vague sense, therefore, Physical Metallurgy may well lay claim to great antiquity. On the other hand, as a more or less self-contained science, it is of quite recent date. The great modern growth of interest in the detailed study of metals has, in fact, arisen from the remarkable results which have flowed in the first instance from the application of the microscope and the pyrometer to the examination of metals. The first systematic application of the microscope to the study of metals was made by Henry Clifton Sorby, of Sheffield, in the year 1864. Sheffield is rightly proud of her distinguished son, who thus laid one of the foundation stones of our science. There is, however, less ground for local pride in the fact that, although Sorby lived among workers in steel who should have been the first to value the work which he did in their midst, yet that work was allowed to fall into forgetfulness. The whole matter was, indeed, completely neglected, both in Sheffield and elsewhere in England, until it had been independently taken up by Martens in Germany and Osmond in France, neither of whom were aware of Sorby's earlier work. Among other early workers in this subject may be mentioned Werth, Grenet, Charpy and Le Chatelier in France; Heyn, Wüst and Tammann in Germany; Andrews, Arnold, Roberts-Austen and Stead in England; and Howe and Sauveur in America. The fact that the present author was privileged to count Roberts-Austen and Osmond among his personal friends, and that Arnold and Stead are still actively at work in this field, serves to show how very recent this whole development has been. Another sign of the same kind is that ten years ago there was not only no text-book of Physical Metallurgy, but not even a book or manual on metallography in existence, so that students of the subject were restricted to the reading of original papers, many of which—as is often the case with a new and rapidly developing subject—were of a decidedly controversial character.

The mechanical properties of metals have, of course, been studied both by engineers and physicists for a very long time, and in that direction also our science is of no recent origin. Galileo was probably one of the first to make a strength test on a metal, since he determined the length of a copper bar which, if suspended vertically, would just break under its own weight (2). Curiously enough, this method of stating the strength properties of a metal has recently been revived under the term "specific tenacity" (3), for the purpose of allowing comparisons on a sound basis between light alloys of considerable strength and other materials, such as steel, whose greater strength is more or less outweighed by their higher density. As a matter of fact, however, the men of the earlier middle ages had little interest in the strength of metals, except possibly in regard to arms or armour. The great architectural achievements of the "Gothic" period, although dependent upon some fair knowledge of the laws of equilibrium and stability, called for little knowledge of the strength of materials, since in these great structures of stone the material is entirely in compression, and stone possesses great strength against this type of stress. Consequently, even in the absence of accurate knowledge, the Gothic builders rarely overloaded their material so far as compressive strength goes, although they did frequently overload the foundations of their buildings.

It was really the requirements of bridge-building that began to lead engineers to undertake mechanical tests of their materials, and early efforts in that direction are associated in France with the names of Perrouet, Rondelet and Labardie, and in this country with Brunton and Brown, Bramah, Fairbairn and Hodgkinson. Probably the first tensile testing machine provided with an hydraulic ram for the application of the load and a lever for its measurement was installed at Woolwich Arsenal before 1837, the early applications of the hydraulic press being, of course, associated with the name of Bramah. Somewhat later came the work of Eaton Hodgkinson, who described his experimental researches on the strength of pillars of cast iron and other materials in 1840, while the work of Fairbairn followed in 1850. Since that time there has been a steady development in mechanical testing appliances, some of those most prominently associated with this movement being Kennedy, Unwin, Ewing, Baker and Kirkaldy in this country, and Bauschinger and Martens in Germany.

With regard to the magnetic, electrical and other properties of metals, the diversity of subjects is so great that it is difficult to indicate even outstanding events in the history of the subject. The whole trend of events, however, can be briefly summarised to this effect, that all the properties of metals—including their mechanical properties—have been studied and investigated in the first place essentially for their own sake or for the light which they might throw upon that particular branch of knowledge with which they were concerned. It is only quite recently that the grouping together and the correlation of all these properties has been undertaken and that these things have begun to be studied not so much for their own sake as for the light which they could throw upon the nature, structure and constitution of metals. It is this manner of regarding the properties of metals and the methods of studying them that has brought into being the new science of Physical Metallurgy. But on the other hand this very development owes its inception very largely to the fact that the exploration of the internal structure and constitution of metals and alloys which constitutes modern metallography has itself thrown so much light upon the nature and behaviour of metals that it has awakened interest in all the properties of metals and has stimulated efforts in their study by holding out promises—which in many cases have already reached fulfilment—of still further valuable light, where light is so much needed, in that region of comparative mystery and imperfect knowledge which still lies much too near the whole field of our most important materials of construction and technical use.

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PART I.

THE STRUCTURE AND CONSTITUTION OF METALS AND ALLOYS

CHAPTER II

THE MICROSCOPIC EXAMINATION OF METALS

SINCE the whole subject of Physical Metallurgy is to be treated in the present book largely from the point of view of the internal structure of metals, it becomes essential to understand at the outset the manner in which that structure can be studied. This study is undertaken principally by the aid of the microscope, and the present chapter will therefore deal with the preparation of specimens of metal for microscopic examination. In this branch of the subject, as indeed throughout the book, more attention will be devoted to the principles underlying the various operations and the laws which govern them than to the detailed description of apparatus or of experimental methods.

Looked at in the ordinary way, metallic objects possess an appearance of complete homogeneity, but the existence of a structure at once becomes obvious when a piece of metal is broken. It is not surprising, therefore, that Martens began his work on the application of the microscope to the examination of metals by the microscopic study of fractures (1). This, however, proved a very limited field at the outset, as the irregularities of fractured surfaces make it impossible to use more than very moderate magnifications, while the path of the fracture itself is not necessarily a fair cross-section of the material—*i.e.*, the fracture may, and in some cases does, pick out a path through a weak constituent. The necessity of using cut sections having a plane surface had been recognised by Sorby, who worked on the strong analogy which undoubtedly exists between metals and igneous rocks so far as micro-structure is concerned. Sorby, having developed the methods of microscopical petrology by the study of thin sections or slices of rocks, attacked the corresponding problem for metals. The use of thin sections through which light could be transmitted in the ordinary manner employed for the microscopic study of organic tissues or of most rocks was, however, soon found to be impracticable. The earliest objection arose no doubt from the practical difficulty of grinding and polishing such sections, since, owing to the opacity of metals to light, they would have to be extremely thin—a slice of iron, for example, in order to transmit even 10 per cent. of the light falling upon it would require to be less than 1×10^{-4} millimetres thick. Even with more modern resources it would be difficult and expensive to prepare such sections; the attempt to do so systematically for microscopic study, however, has never been made, since it is now recognised that the very operations of cutting, grinding and polishing alter the structure of the metal to a certain depth below the surface, which varies with the amount of force employed in the processes; even with very gentle rubbing, however, alterations of structure to a depth of one thousandth of a millimetre are produced in all but the hardest metals ([2]), and for that reason we should anticipate that the structure of the very thin slices of metal which would be required for use with transmitted light would be entirely altered throughout their thickness by the process of preparing them. The use of Röntgen rays for the purpose of penetrating greater thicknesses of metals has been tried by Heycock and Neville ([3]) in the case of alloys of gold and aluminium, which contain constituents of widely different densities, and thus afford reasonable contrasts in their power of transmitting X-rays. When those experiments were made, however, the technique of radiology was yet in its infancy, and it seems probable that with modern appliances it might be well worth while to study this method more thoroughly, particularly with a view to the use of moderate magnifications.

For practical purposes, at the present time at all events, the microscopic study of metals is only possible by the process of looking at suitably prepared surfaces by reflected light; but this method has proved sufficiently powerful to yield an entirely new insight into the structure of metals and alloys. If any ordinary metallic object is looked at under a microscope, the surface will generally be found to be covered with markings —grooves, scratches, smears, etc.—which have obviously no connection whatever with its internal structure, but which simply owe their origin to the treatment which that particular surface happens to have received. Even if an ordinarily "polished" article be examined in this way it will be found to be covered with such accidental markings. The photograph (Fig. 1, Plate I.) shows the appearance of the "polished" brass case in which a microscope objective is kept—its surface shows some resemblance to a ploughed field. It is obvious that if the true structure of the metal is to be observed, the surface must be treated in such a way as to leave it as free as possible from any accidental surface markings. This is accomplished by the process of polishing by methods which have been evolved and perfected for this special purpose; these methods, however, differ widely from the relatively crude and rapid processes employed in commercial polishing—a difference which arises not only from the more perfect character of the polish required when the surface is intended for examination under the microscope, but also from the fact that, while for microscopic study the metal should be treated as gently as possible in order to avoid disturbance of its structure to any considerable depth below the actual surface, in the commercial processes rapidity is the principal object, and actions of a "burnishing" nature are freely utilised without regard to the internal disturbances which they produce.

The preparation of a specimen of metal for microscopic examination necessarily begins by the choice of the surface to be examined. This is a matter in which the knowledge and powers of observation of the worker come into play to a very large extent, for the choice of the section must depend in every case upon the particular object to be attained and upon the conditions of the case. Thus where an investigator is studying the structure of a series of alloys in order to assist him in understanding their constitution, he will, in general, be dealing with small experimental ingots, and will, as a rule, find it desirable to examine an entire vertical cross-section of such an ingot in order to detect variations arising from any possible lack of uniformity of composition from top to bottom, or effects of variations in the rate of cooling from the centre to the outside of the ingot. The whole of such a cross-section may, of course, be inconveniently large for the purpose, since, as a rule, it is not wise to undertake the preparation of areas much larger than four or five square centimetres (about one square inch) in a single piece. Where larger areas are required, the specimen is best cut up into two or more pieces and each polished separately.

More complex conditions affecting the choice of specimens arise where the material to be examined forms part of a larger mass of metal, whether cast or wrought. In castings there are the effects of variations in cross-section and rate of cooling, as well as possible variations in chemical composition, to be considered, while in rolled or forged metals the influences of mechanical treatment always produce differences of structure according to the direction in which the section is cut relatively to that in which work has been applied. As a rule, therefore, it will be necessary to cut several sections, in different planes, from each larger piece of metal to be examined. Where breakages are under investigation it will further be necessary to compare the structure close to the fracture, and in the neighbourhood of any fine cracks, with that of the material at a distance from the fracture. No general rule can be laid down for the selection of the surfaces to be examined, but it is probably the mistake which is most frequently made in this connection to examine too small a number of specimens, or too small a total sectional area of the material. Quite apart from the possibility of finding, by the aid of numerous specimens and extensive examination, some local feature or defect in the metal, this extended examination has the further advantage that it serves to impress on the mind of the observer certain features of the structure which, while really most significant, are not very prominent in any single area. Often enough some such feature is disregarded, even by careful observers, as being accidental or unimportant, but when the same peculiarity is repeatedly observed on a number of sections it begins to make its proper impression on the mind, and thus saves the investigator from overlooking an important line of evidence. It has several times been the experience of the present author that, on examining the first few sections of a piece of metal which had shown entirely abnormal mechanical behaviour, no abnormal structural feature could be detected, but that by the prolonged examination of numerous sections the somewhat less obvious, but none the less real, abnormality was noticed and ultimately traced to its origin.

The rule thus indicated, of examining the largest possible number of specimens, need not, of course, be followed in a considerable number of cases—where either the examination of the very first section shows an obvious and unmistakable feature of a kind which must repeat itself throughout the mass of metal, or in cases where the microscopic examination is undertaken for the specific purpose of determining whether the material exhibits some special feature, such as segregation, or the typical coarse angular structure due to overheating. The whole question of the choice and number of sections to be examined is thus a matter essentially for the judgment of each worker, and what has just been said can only serve as a rough guide.

The manner in which a specimen of convenient size for purposes of polishing should be cut off from the rest of the material will, of course, depend upon the size and shape and nature of the object in question. This is, however, a simple question of a kind which constantly arises in all engineering workshops, and requires no further consideration here beyond the remark that in every case care must be taken to avoid anything which may affect the structure or constitution of the metal to be examined. Thus the modern methods of cutting metal by the aid of the oxy-acetylene blow-pipe must be avoided, or at least carefully controlled, if employed for the present purpose, since the temperature attained by the metal, even at a considerable distance from the line on which the blow-pipe has been used, is quite high enough to alter the structure appreciably, and thus—possibly—to efface the very features which the microscopic examination is intended to detect. The use of such a method of cutting must, therefore, always be looked upon with suspicion, particularly as it is not impossible that the process may be intentionally resorted to by some interested party with the direct object of interfering with the microscopic diagnosis of the case. Violent mechanical methods, such as shearing or punching, or breaking off by blows after preliminary nicking, are also to be avoided, since these processes are also liable to introduce disturbing features into the microscopic appearances presented by the metal.

When a piece of convenient size has been obtained in some satisfactory way—and in a great many cases it is simply a question of the skilful use of a simple hack-saw for a few minutes—that surface of the piece which corresponds to the section selected for study must first be cut down to the nearest possible approach to flatness. This may be done either by means of the file or the grinding wheel. There is no doubt whatever that the latter is far preferable. The necessity of gripping the specimen in the vice—with its attendant risk of mechanical injury and distortion—is entirely avoided ; but a much greater advantage lies in the fact that the process of grinding, particularly in the case of the softer metals, causes much less disturbance of the metal below the surface. It is found that the marks, particularly of a rough file, are difficult to remove entirely by the subsequent rubbing on comparatively fine emery papers, and, even when apparently completely effaced, there appear to be residual regions of disturbed structure for a slight depth below the deepest file-cuts. The individual cuts produced by the grains of emery or carborundum in a wheel are much smaller and more numerous than the cuts of a file, and the disturbance which they cause does not penetrate so far into the substance of the metal.

A disadvantage which attaches to the use of the grinding wheel in the ordinary way is that the specimen rapidly becomes heated by the energy dissipated in friction at the grinding surface. This heating is not intense enough to affect a great many materials, but in others—such as hardened steel—serious changes may easily be caused by this rise of temperature. In any case, however, it is far safer to guard against this heating by constantly dipping the specimen into cold water and never holding it in contact with the grinding wheel long enough at a time to allow it to become seriously heated. This process of repeatedly removing the surface from contact with the wheel, however, makes it difficult to grind anything like a flat surface, since the angle of contact is apt to change slightly every time. This results in the formation of a fresh facet on the surface every time it is brought against the wheel, and, finally, a somewhat convex surface is produced. This is extremely undesirable, since it not only renders the subsequent polishing operations more difficult, but also interferes with the definition of the images furnished by the microscope from the finished specimen.

In order to avoid some of these difficulties and at the same time to render the whole grinding operation less violent, the author has adopted the use of large, slow-running grinding wheels. Those actually employed have a diameter of ten inches and run at speeds of approximately seventy revolutions per minute. Grinding with these is, of course, much slower than with the ordinary wheel running at several thousand revolutions per minute, but the slight loss of time is more than compensated by the fact that, first, the specimens do not get seriously heated even after several minutes of continuous grinding, and, second, it is easy to replace the specimen in contact with the grinding wheel—if it has been taken away for purposes of examination—by the simple method of feeling for the position of best contact. With a fast-running wheel a fresh facet is formed at the very first instant of contact, and any endeavour to adjust the position of the specimen merely results in grinding a curved surface. With the slow-running wheel one has time to get the specimen adjusted in its former position before material grinding has taken place. A further advantage of the slow-running wheels is that the " cut " of the abrasive is not so deep and does not cause so much internal disturbance as that of a wheel of the same grade running at a high speed. In actual practice the use of these slow-running wheels has been found to effect a material saving of time over the whole process of grinding and polishing.

Although the grinding process by the use of rotating discs armed with abrasives can be carried right down to the finest available grade of emery, etc., this is not found desirable. The objection to mechanical violence becomes greater as the grade of abrasive becomes finer, for the simple reason that less of the material remains to be removed in the subsequent operations, so that any disturbances produced are likely to remain behind, only to be detected when the polished surface is chemically attacked in that stage of the process known as "etching." For that reason many workers, including the author, employ the finer grades of abrasive entirely by hand, using the well-known device of turning the specimen through a right-angle on passing from one grade of emery to the next finer one. In this way it is possible to see that the visible scratches left by each grade are completely effaced by those due to the finer grade. Ultimately the surface of the specimen is left covered with a system of more or less parallel scratches or marks from the finest available grade of emery, and these are then removed by the process of polishing proper, which is usually carried out by means of a rapidly revolving disc, covered with soft cloth or leather, and fed with water and some form of "polishing powder." If the emery grinding has been correctly carried out at every stage, the final removal of the emery marks by the aid of the wet disc should not occupy more than four or five minutes with specimens of steel of the size indicated above. If a longer polishing process is needed some of the earlier stages have not been properly carried out, and a really satisfactory metallographic polish will not be obtained. With softer metals the conditions may be somewhat different, and success in polishing these is a matter requiring the most scrupulous care in regard to cleanliness throughout the entire operation, and also a certain degree of skill, which is only acquired by prolonged experience and requires something of a natural gift of touch.

Extreme difficulties of this kind are only met with in dealing with such metals as lead or thallium, but to a lesser extent they are also encountered with aluminium and, in a decreasing degree, with copper, brass and bronze.

Although in the first place the operations of grinding and polishing are of interest from the point of view of experimental practice, careful study of the phenomena connected with them has led to most interesting results—in the first instance at the hands of Beilby (4)—and although these can only be considered in detail at a later stage, when the whole theory of the amorphous condition in metals will be discussed, some reference to them is required at this point in order to afford some insight into the real meaning and nature of the operation of polishing.

The nature of the processes involved in ordinary cutting operations are now fairly well understood. Essentially the action of an edged cutting tool consists in bringing to bear upon a very small area of metal a stress sufficiently intense to produce rupture. Obviously, however, although actual rupture is confined to a single line or surface, severe strain will be produced in the immediate vicinity, so that in an ordinary machined or filed surface the visible grooves are accompanied by corresponding sub-surface regions of strained metal. This region will be deeper, the deeper the " cut " which has been taken and the greater the force which has been employed, and also the blunter the tool—*i.e.*, the larger the area to which the intense pressure of the tool has been applied. When a grinding-wheel or emery paper is substituted for a file, then the same process continues, at all events so far as the coarser grades are concerned, only that the actual cutting edges of the individual grains are exceedingly minute and sharp, while the depth of cut taken by each of them is very small. Consequently the depth of disturbed metal beneath the surface is correspondingly slight, particularly if the emery grinding is done gently.

There are, however, other actions which accompany the cutting and grinding process, and these—although unimportant when a coarse cut is being taken—become predominant when the finest grades of abrasive are employed. A fuller understanding of these actions will be obtained when the chapter on the effects of strain on the structure of metals is studied, but for the present it will be sufficient to state that severe mechanical strain may in certain conditions break up the essentially crystalline structure and convert the metal locally to an intensely hard and brittle amorphous condition. In the process of such transformation from the crystalline into the amorphous, however, it appears that the metal passes through a temporary or transition stage in which it is capable of undergoing a certain small amount of flow, much like a viscous liquid such as pitch or ordinary oil paint. Now when oil paint is somewhat thickly applied with a brush, the bristles of the brush as they pass along the surface leave behind them a system of ridges and furrows similar to those after filing or rubbing on emery paper. In the case of the paint, however, the viscous liquid, acting under the influence of surface tension, gradually rounds out and smoothes over these ridges and grooves, finally assuming the smooth surface typical of a liquid at rest before it sets hard enough to prevent further flow. Now, as Beilby has shown, this analogy is so far complete that in metals, too, the sharp angular grooves left by the abrasive grains show a considerable tendency to become smoothed out. When the grooves are still fairly coarse the distances involved are too large and the metal does not retain its mobility long enough, nor is a sufficient quantity of disturbed metal available to smooth out the furrows to a notable extent. When, however, the grooves become very fine—as they do with the use of the specially fine grades of emery paper employed for metallographic work—then the effects of this flowing action become important and quite easily visible under high magnifications. The grooves left by these very fine abrasives " run together " and show the peculiar broken-up, drop-like forms which are typical of the effects of surface tension. Fig. 2, Plate I., shows a photograph, under a magnification of 150 diameters, of such a system of grooves or scratches. This photograph was taken from a surface as obtained direct from a No. 000 emery paper, without subsequent treatment of any kind.

Now when such a surface is subjected to the action of a

with rouge it occasionally happens that particles of rouge are subsequently exuded from the polished surface.

It is a further significant fact in this connection that not every finely-divided substance can be successfully employed as a polishing agent. This might perhaps be ascribed to variations in hardness or in the shape of the ultimate particles, but such suppositions do not account for the fact that all the good polishing materials—such as alumina, magnesia, rouge, putty powder, oxide of chromium, etc., belong to one particular chemical class, viz., that of oxides. Now many metals are known to possess the power of dissolving their own oxides, and this property may have some considerable bearing on the polishing action of these bodies. At all events, if the polishing agent is forced to interpenetrate the surface layers of the metal, the "forced solution" thus formed may well exhibit a greater degree of mobility than the pure metal—just as the mobility of a metal is increased by the addition of a second alloying metal which lowers its melting point.

By the combined mechanical and chemical actions of the polishing disc and powder the surface layers of molecules are given a certain degree of temporary freedom, and are thus able to form a smooth "polished" surface, such as that of a liquid at rest. Indeed, if we look at the really smooth surfaces found in nature, we see at once that, apart from the faces of single crystals, they are all surfaces of liquids—even ordinary sheet glass has a natural smooth surface, known as "fire polished," because it is simply the congealed smooth surface formed on the glass when it was fluid. It is thus interesting to see that polished surfaces are in reality also formed by the smoothing out of an extremely thin fluid layer under the action of surface tension.

From the point of view of practical metallography this view is of particular importance, because it serves to explain a number of features which are met with in polished surfaces. One of the most striking and, at first sight, perplexing of these is the manner in which an apparently perfectly polished surface shows, even after very slight etching, a number of scratches and holes which were certainly not visible before. The beginner is apt to assume that he has somehow managed to scratch the delicate polished surface during the handling of the specimen while he was etching it, but, although this may occur to some extent, yet such scratches and grooves still make their appearance even if the utmost precautions are taken to avoid all risk of injury to the surface. The real cause of this phenomenon is that these grooves and scratches were really present all the time, but that they were filled up and covered over by the amorphous layer which was formed during polishing. This layer is at once removed, more or less completely, when the surface is attacked by some etching reagent, and the original markings are thus laid bare. This fact can be readily verified by photographing a marked place on a specimen which shows some well-defined features of this sort after a first etching. Then let the surface be re-polished on the disc (without the intervention of any emery grinding) until all signs of the markings have disappeared; then, if the surface be again etched, it will be seen that the deepest and most prominent of the original markings have reappeared. The extent to which this recrudescence of scratches, etc., will take place will depend entirely upon the depth of the markings left on the surface before polishing was begun, and it is in order to minimise annoyance and delay, or even error, from this cause that the use of gentle methods of grinding and polishing is advocated here.

The appliances to be employed for polishing, being of a simple mechanical kind, need not be described here, but a few words are required in regard to the material of which the polishing disc, or rather its working surface, should be made, as well as to the polishing powders to be used.

For the great majority of ordinary work the polishing disc is best covered with some soft material, such as fine wash-leather, "Selvyt," or best quality woollen cloth of the kind used for liveries. The latter material gives much the longest wear, and, if the right quality is obtained, gives very satisfactory results. "Selvyt" polishes very well, but wears out rather rapidly, while wash-leather is not particularly well suited to the modern polishing powders, such as alumina or magnesia, although it worked excellently when rouge was universally employed. For extremely fine work, where the erosion of soft materials and the rounding off at the edges of minute holes which results from the use of thick, soft fabrics for polishing is objectionable, the best material is old, well-worn and washed calico, used in several thicknesses. It may be possible to " age " this material artificially, but, if purchased new, it is never successful—the fibre appears to be hard enough to scratch the metal, even in the case of steel. A still less yielding bed for polishing purposes is formed by pitch, which is widely employed for the polishing of glass. Glass, however, is much easier to polish than metals, and in the author's hands pitch has never proved very satisfactory.

In the early days of the microscopic study of metals rouge was practically the only polishing material employed. It is the merit of Le Chatelier to have drawn attention to the fact that certain other substances yield a polish at least as good as that given by rouge and attain that object with much greater speed. Le Chatelier ([5]) at the same time described an elaborate method for the preparation of these new and superior polishing media, such as alumina, oxide of chromium, etc. While the materials prepared by his method are very excellent, the methods themselves are lengthy and expensive, as the yield of useful polishing powder is decidedly small compared with the cost of such materials as ammonia alum, ammonium chromate, etc. Many of these materials may at the present time be purchased commercially, while the best quality of " heavy oxide of magnesia," if carefully sifted and kept from the air and moisture, serves as a very good substitute. Alumina may, however, be prepared by the direct oxidation of metallic aluminium. This can be brought about by inoculating the metal with a little mercury, when oxidation proceeds rapidly for a time. The product, kept free from dust or other contamination, is an excellent polishing powder.

When a properly polished surface has been duly obtained by the processes which have just been discussed, it will be found that under the microscope such a surface appears a nearly featureless blank—the more nearly perfect the polish, the fewer are the features to be seen on the surface. If the surface is examined under a low magnification—say fifty or one hundred diameters—and with oblique illumination, a very severe test of the perfection of the polish is obtained, since under these conditions, especially if the specimen is rotated, even the minutest scratch or hole becomes apparent. For most purposes, however, no such searching test is required, and a surface can generally be regarded as fairly satisfactory if under a magnification of one hundred diameters and "normal" illumination the field of view does not show more than one or at most two fine scratches and few or no holes. The few remaining scratches and defects do not as a rule interfere to any material extent with the subsequent examination of the structure, and it is a useless expenditure of time and energy to strive after greater perfection of polish except for very special purposes. When the metal under examination is an alloy containing constituents which differ very considerably in hardness, the polished surface is not generally a featureless blank, since the process of polishing usually erodes the softer constituent and leaves the harder one slightly in relief—this "relief polishing" is seen as a faint pattern under the microscope, but its indications are not always to be relied upon, and it is to be regarded as rather an undesirable feature.

In order to afford any insight into the structure of the metal, the polished surface of a specimen must be treated in some way calculated to produce a surface pattern corresponding to the section of the internal structure presented by the polished surface. As we have seen, over the polished surface itself is spread a very thin film of amorphous metal, filling up and smoothing over not only the surface irregularities originating from the mechanical treatment, but also the irregularities of structure of the metal itself. This surface film must, therefore, first be removed more or less completely by the action of some suitable reagent. Accordingly we find that the universal practice is to "etch" the surface by means of some reagent which slowly attacks and dissolves the metal. The amorphous surface film is more readily attacked than the rest of the metal, and is thus rapidly and easily removed. The subsequent action of the etching agent then depends upon the nature of the agent and upon that of the metal to which it is applied. The reagents most frequently employed are weak organic acids or dilute solutions, in alcohol or water, of mineral acids. In the early days of the science dilute nitric acid, varying from a strength of 1 per cent. in alcohol to 0·1 per cent. in water, was very widely employed. The tendency of nitric acid to cause uneven oxidation and consequent tarnishing of the surface, particularly of iron or steel, has, however, led to its almost complete abandonment in favour of more reliable and satisfactory reagents. For iron and all its alloys a solution of picric acid in alcohol (either 4 per cent. or saturated) is now almost universally employed, although nitric acid much diluted with amyl alcohol, and hydrochloric acid in ethyl alcohol, are also useful. For other metals and alloys special reagents are employed in nearly every case. Copper and its alloys are frequently etched with a solution of ferric chloride acidified with hydrochloric acid, while for aluminium and its alloys either caustic soda, hydrochloric acid containing a small addition of nitric acid, or hydrofluoric acid are frequently employed. The exact choice of an etching reagent, although a matter of considerable importance, is a question of the chemical relationships of the metal or alloy under investigation, and it is not possible to consider these matters in detail here.

The reagents just mentioned all act in the same way, viz., by the gradual solution of the metal—a process which is of the nature of a gradual unbuilding of the structure of the metal from the surface downward. It is obvious at the outset that such a process must not be carried very far, otherwise considerable surface irregularities will be produced and the plane character of the surface, so necessary for microscopic examination, will be destroyed. The extent to which etching may be carried depends, in fact, upon the magnification with which it is desired to examine the metal. In the case of mild steel to be examined under a magnification of 1,000 diameters, an etching with picric acid for a period of five seconds is satisfactory; if the same steel is to be examined under a magnification of one hundred diameters, it is preferable to carry the etching on for thirty seconds in order to obtain a clear, bright image, but the surface thus treated would be too deeply attacked to be readily focussed under the higher power. When the surface is to be examined under very low powers indeed, or with the unaided eye, then the etching process must be carried very much further, and it is usually preferable to employ an agent which acts more rapidly, such as—in the case of steel—dilute sulphuric acid or a 10 per cent. solution of copper-potassium chloride.

The chemical attack, or structural unbuilding of a metal by means of an etching reagent, however, does not take place uniformly over the entire surface ; the exact manner in which the attack takes place depends upon the character of the metal, *i.e.*, whether we are dealing with a simple or a duplex material. The " simple " material here understood is one in which only a single constituent is present and in which all parts of the metal are of exactly the same chemical composition ; in the case of a duplex structure, on the other hand, the surface is made up of two different constituents which differ in chemical composition. In the latter case we usually find that one of the two is electro-positive to the other to such an extent that chemical action is almost entirely confined to the one, while the other remains unaffected until the etching process has been carried to a very considerable depth. In these circumstances we find that the more easily attacked constituent is roughened by the etching reagent, with the result that, as will be more fully explained below, it appears dark under the microscope, while the more resistant constituent remains smooth, and consequently appears bright under the microscope. The result is the formation of a sort of mosaic pattern, which is really a sectional plan or map of the structure of the metal.

In the case of a pure metal, or of an alloy having only a single constituent, there can be no such preferential attack on one constituent with corresponding protection for the other, and one would at first sight expect such a pure metal to be uniformly attacked all over without the formation of any pattern at all. Actually this is the case to this extent, that an etching reagent which produces a well-marked pattern on a duplex alloy in a few seconds produces no visible pattern at all on a pure metal in the same period of time. If the attack is continued, or if a more rapidly acting reagent is used, however, a very definite pattern is produced—the uniform surface of the specimen is found to become divided up into more or less polygonal, but somewhat irregular, areas bounded, apparently, by black lines when seen under normal illumination. We shall see in a later chapter that these polygonal areas are in reality sections of the crystals of which the metal is built up, and that each of them has been dissolved to a different depth according to the direction in which the plane of the section has cut through the crystal system in each individual case. For the moment it is sufficient to note that the slower rate of etching observed with pure or "simple" metals as compared with duplex alloys arises from the fact that, while in the latter case there are chemical differences between the two constituents, the various crystals of the pure metal are chemically all alike, but differ merely in crystalline position or "orientation." In etching a pure metal, therefore, we are dependent upon very minute differences of chemical activity, and there is a corresponding difficulty in preventing the interference of accidental circumstances which tend to produce stains or even spurious patterns on the surface. Much greater care must, therefore, be taken in both the polishing and etching operations when pure metals or "simple" alloys are dealt with than in the case of duplex alloys.

The method of gradual chemical attack or solution is not the only one open for the purpose of developing a structural pattern, as it will be readily understood from what has been said above that any process which acts differently upon the various constituents or upon the individual crystals of a single constituent will develop the structural pattern. The process of "relief polishing" has already been mentioned, but by itself it does not yield satisfactory results. It has however, been employed successfully, in the first place by Osmond (6), in combination with a very mild form of chemical attack, thus constituting what is known as "polish attack." Here the polishing process is carried on in the presence of a slightly corrosive liquid which would not, by itself, produce satisfactory etching in any reasonable time. Combined with the polishing action, however, an exceedingly uniform and very gradual etching is obtained. The resulting patterns generally consist entirely of fine lines indicating differences of level or depth, and there is little roughening or darkening of the attacked surface.

Another method of developing the structural pattern of a polished surface is by the formation of surface films, whose thickness varies according to the constituent of which each particular element of the surface consists. These surface films may be formed in various ways. One of the best known is the process of "heat tinting," first developed by J. E. Stead ([7]), where the specimen is heated in contact with air, and surface films are formed by the gradual oxidation of the metal. The depth of film formed at any point varies according to the chemical composition of the metal at that point, and the surface becomes more or less deeply coloured accordingly. Stead has employed this method for a variety of purposes, but primarily for detecting the distribution of phosphorus in iron and steel. The presence of very small proportions of this metalloid produces a marked effect on the rate of oxidation of iron, with the result that very clear and beautiful patterns are obtained. A word of caution is, however, needed. The use of the heat-tinting method requires, in the first place, a perfectly clean surface—solid or liquid matter of any kind remaining on the surface affects the rate of oxidation and spoils the resulting pattern. Beyond this, however, the heat-tinting method is peculiar in that there is no material removed from the "etched" surface. As a consequence of this peculiarity it follows that the amorphous surface film which, as we have seen, is formed during the polishing operation, is not removed by the process, and if there has been any material amount of "smearing" of the amorphous forms of the various constituents over one another, the boundaries of these constituents, as revealed by the oxide films, may not strictly correspond to the internal structure. It is, therefore, always safer to etch a polished surface very lightly with a weak or dilute acid before undertaking heat-tinting, since such a proceeding certainly removes the amorphous surface film. The thickness of such a film being very small in the case of hard materials like iron or steel, this precaution is not so essential with these metals as it is with softer ones like copper or its alloys.

Surface films somewhat similar to those produced by the oxidation process which is employed in heat-tinting may be obtained in other ways. With metals containing silver or copper, exposure to an atmosphere containing hydrogen sulphide gas is sufficient to bring about a development of surface colours, but this is not very easily graduated to the right extent. Another and much more promising method was first employed in dealing with the alloys of copper and tin by F. Giollitti ([8]), and has recently been worked out more particularly for the case of steel; it consists in bringing about upon the surface a very gradual deposition of metallic copper by a process of electro-chemical replacement. When a piece of iron or steel is exposed to contact with a solution containing a copper salt, the iron is attacked, a portion of it passes into solution, and an equivalent quantity of copper is deposited as a film on the surface of the iron. As a mere method of etching, employing copper salt solutions as solvents for attacking iron or steel, this process has long been used, Heyn ([9]) having employed solutions of copper-ammonium chloride for revealing more especially the details of crystalline structure, and also for that deep form of etching used when the surface is to be examined for its broad features without the use of magnification. The present author, together with J. L. Haughton ([10]), has quite recently found that, when a suitable solution containing ferric chloride, hydrochloric acid, cupric chloride and stannous chloride is employed, the copper is deposited in a very interesting manner. In a very pure, mild steel, for instance, it is found that the appearance of the constituents as seen after "etching" with this new reagent is exactly the reverse of that seen after etching with picric acid; when, however, the steel contains impurities—as all commercial steel does—which are not present as separate micro-constituents, but are diffused in solution throughout the metal, the effect of the new reagent varies according to the amount of such impurity present at each point of the metal. The purest part of the iron appears to receive the deepest deposit of copper. Accordingly, in a steel containing phosphorus, the deposition of copper affords a picture of the phosphorus distribution exactly similar to that obtained by heat-tinting. The copper deposition method is, however, very much quicker than heat-tinting.

The process of etching is not quite the last which the specimen must undergo before it is ready for microscopic examination. When removed from the etching bath, the specimen must be very thoroughly washed in order to remove all traces of the etching reagent. This is essential, not only in order to arrest the etching action at the desired point, but also in order to prevent the surface of the specimen from being subsequently disfigured by the formation of crystals of the etching reagent or its salts. This is very apt to occur in the case of specimens containing holes or cracks into which the etching solution finds its way; there it evades the washing, unless that is carried out very vigorously, and then it creeps out and spreads a fringe of crystals around the edge of the crack or cavity. This can be prevented only by washing the specimen under a strong jet of water for several minutes.

For many purposes it is then quite sufficient to dry the surface of the washed specimen by gently wiping it with a clean, old handkerchief, although this is liable to produce a few scratches on the surface. Where greater care is required, the specimen should be washed in absolute alcohol to remove the water, and it may then be dried by simple evaporation, aided perhaps by a fan or, better still, by a current of heated air. The alcohol sometimes leaves a slight film where it has last dried, and this can be avoided by washing the specimen, after it has been rinsed in alcohol, in clean, pure ether. This is, however, a somewhat difficult matter, as the ether is such a good solvent for all manner of substances that it is very liable to take up some impurities in the course of a few weeks' use, and then the ether leaves a worse deposit than the alcohol used alone.

As a rule specimens for microscopic examination are of somewhat transient interest and need not be kept very long; the properly washed and dried surfaces remain useful for examination for several days or even weeks if kept in a well-made desiccator provided with a suitable drying agent—calcium chloride is one of the best for this purpose. The specimens can, however, be given a considerable degree of protection from corrosion or tarnish by coating them with not too thin a layer of collodion or celluloid, dissolved in the form of a varnish in amyl acetate or acetone respectively. The majority of varnishes of this kind are too thin for this purpose, the tendency being to yield a coating of such tenuity that it shows the interference colours of Newton's rings. By using a rather stronger solution this can be avoided, and the coat of varnish is still thin enough and transparent enough to allow the specimens to be examined and photographed—even under the highest powers of the microscope—without loss of definition and without removal of the varnish. Specimens thus protected will keep for several months without tarnishing materially. In the case of iron and steel specimens permanent preservation is possible in another way, viz., by storing the specimens immersed in a solution of chromic acid or of one of the other reagents which render iron "passive." Not only do the specimens remain free from rust while immersed in such a liquid, but, if carefully handled, they retain their passivity for some time after they have been removed from the liquid.

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CHAPTER III

THE METALLURGICAL MICROSCOPE

While it would lie beyond the scope of this volume to offer any attempt at a complete account of the theory of the microscope or a detailed guide to practical microscopy, it is perhaps desirable to deal with this aspect of our subject to a certain extent. A rudimentary knowledge of the principles which underlie the working of the modern microscope is essential if that instrument is to be used to full advantage, and while there are many admirable treatises dealing with the microscope as such, they generally approach the subject from the standpoint of the more usual uses of the microscope where the application of the higher powers is confined to the study of thin transparent sections. The application of the instrument to the study of metals, where we have to examine approximately flat surfaces by reflected light, introduces a series of different conditions. A further justification—if such were needed—for the introduction of a chapter on the microscope into the present volume is provided by the numerous evidences of the abuse or inadequate use of the microscope which is furnished by the photo-micrographs published with some otherwise valuable papers on metals.

We may begin by considering the manner of illuminating the metal surfaces which have been polished and etched for microscopic examination. We are confined to reflected light, but the incident light may be made to fall upon the surface either obliquely or normally, and these two alternative methods are both employed. Oblique illumination, produced when a suitably arranged beam of light falls upon the metal surface from some direction outside the lenses of the microscope, is in many ways the simplest, since no special appliances or fittings are required. Its use is of considerable importance and value, particularly where it is a question of recognising the differences of level and other features of the surface configuration. On the other hand, the use of oblique light is bounded by certain limitations. In the first place, the character of the optical effects produced by this mode of lighting is peculiar and in some respects exaggerated or distorted; minute surface defects are apt to become unpleasantly prominent, and slight differences of surface texture appear as vivid contrasts of brightness. This exaggerated character becomes increasingly apparent as the light becomes more oblique. Accordingly, the use of oblique lighting is confined to the lower powers of the microscope (the 16 mm. is the highest power of the Zeiss apochromatic objectives which can be usefully employed in this way). With higher powers the free distance between the mount of the lens and the surface under examination is too small to allow an oblique beam to reach the surface at a reasonable angle. A further difficulty in the use of oblique light lies in the fact that the proportion of the incident light which is reflected into the microscope is very small, so that the images are not as a rule bright enough to lend themselves to photography. The extreme contrasts of light and shade also render photography difficult and the result unsatisfactory, except in special cases.

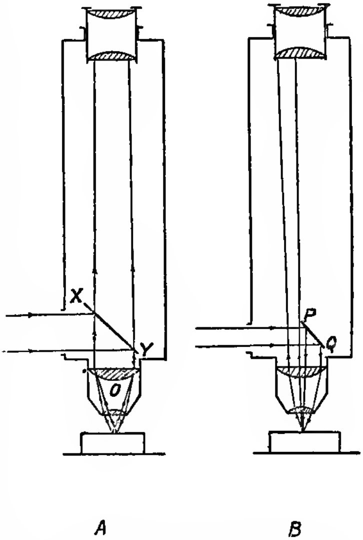

FIG. 3.—Diagram of "Vertical" or Normal Illuminators.

The second, and most widely used, mode of lighting metal specimens under the microscope is generally known as "vertical" illumination, although it is more correct to call it normal illumination. By this method the light is caused to fall upon the surface of the specimen in a direction at right angles to that surface, *i.e.*, if the microscope is used in the vertical position (which is—by the way—a very undesirable practice), then the light falls upon the specimen vertically from above—hence the term "vertical illumination." The manner in which this mode of illumination is obtained is shown diagrammatically in Fig. 3, A and B. Both figures represent sectional views of a microscope and metal specimen, with indications of the paths of light-rays. In A we see at *xy* the section of a small disc of very thin, plain glass placed at an angle of 45° across the axis of the microscope, directly opposite an aperture in the side of the tube. The light enters the instrument at this aperture and falls upon the disc of glass, which allows the greater part of the light to pass through; a certain small proportion, however, is reflected by the surfaces of the slip of glass, and is thus directed downward upon the back of the objective lens of the microscope, shown at *o* in the figure. This lens condenses the light and produces a relatively bright spot of light upon the surface of the specimen. The light reflected by the surface of the specimen is collected by the objective and passes upward on its way to form the image in the instrument; in its upward path, however, it again encounters the thin slip of glass and, although this time the greater part passes through unchanged to the image above, a part is reflected and returned to the source of light outside the microscope. It will be seen that this method of illumination is very wasteful of light, but for ordinary eye observation no great intensity of illumination is really wanted and for photographic purposes a very powerful source of light—such as an arc lamp—can be used. Apart from the question of intensity of light, the use of such a plain glass reflector has the advantage that it is possible to obtain perfectly axial (central) illumination, with no tendency to throw shadows towards one side more than another. On the other hand, all the rays that go to form the image have to pass through the slip of thin glass, and this undoubtedly affects the perfect sharpness of the image, so that for the highest magnifications and the greatest clearness the use of the glass reflector is inadmissible. Another and perhaps more widely used form of reflector is shown in Fig. 3, *b*. In this case the line *pq* indicates the section of an opaque reflector, such as a slip of silvered glass, or what is known to opticians as a "totally reflecting prism," placed not centrally in the tube of the microscope, but in such a position as to cover one half the area of the tube. Of the light that enters the aperture at the side of the instrument, nearly all that portion which falls upon the reflector is sent down through the lens and thus on to the specimen. If the beam of light is properly directed, the resulting spot of light on the specimen can still be circular—although originating from a semi-circular reflector—and of very nearly equal brightness all over. In practice, however, it is very difficult to secure perfectly even illumination by this means unless the reflector itself can be moved about in all directions; usually there is a decided falling off in brightness towards one side of the field of view. From the specimen, the rays of light in this system pass upwards through the objective; all those rays, however, which come from one half of the objective are stopped and sent outwards by the reflector and are thus lost to the image, but the remaining half of the rays are amply sufficient to form a very perfect image which is free from the disturbing effect of the thin glass slip which is present in the other system. While this system has thus the advantage of giving more perfectly-defined images, it has the disadvantage of less uniform illumination and of somewhat one-sided lighting, as the beam can never be sent down upon the specimen in a strictly axial direction. It will thus be seen that both systems have their special advantages, and the true solution of the question as to which should be used is to employ an arrangement whereby both kinds of reflectors can be used and readily interchanged with one another.

The methods of lighting metal specimens which have just been described carry in their train certain mechanical requirements in the construction of the microscope which have been met more or less completely in those instruments which have been specially designed for this work; these are generally known as "metallurgical microscopes." One of the simpler of these instruments is shown in Fig. 4 (Plate II.). This instrument is, in many respects, very similar to the simpler forms of ordinary microscope employed for biological and other studies;

The type of microscope just described suffers from a number of serious disadvantages which become evident in use—particularly when the instrument is to be used for the study of metals from the mechanical rather than the chemical point of view. For the purpose of overcoming these disadvantages, the present author has designed a special form of metallurgical microscope, which is shown in Fig. 5 (Plate II.). Both in appearance and in mechanism this instrument differs from the older forms, but the optical system is the same and the same lenses are employed. To begin with, the stand is of a rigid form, which avoids the tendency to vibration and displacement found in other microscopes—the instrument can be carried about without risk of disturbing the focus of the lenses ; for work with the highest magnifications this is very important, and where measurements are to be made it becomes vital. This rigidity is further assisted by the fact that the body tube, *bb*, is rigidly attached to the stand or " limb," *ss*, all focussing movements—coarse and fine adjustment—being attached to the stage. This arrangement has the additional advantage that the delicate fine adjustment is placed actually in the axis of the microscope, so that there is no overhang to magnify minute defects in the slides or screw ; the stage itself can be completely rotated and presents a clear surface with no projections to obstruct beams of oblique light in any position. The milled heads which actuate the mechanical movement of the stage and the fine and coarse focussing screw are, by this arrangement, placed within comfortable reach of one hand, and the operator soon learns to work these screws together with different fingers in such a way as to keep the image in sharp focus while the specimen is being moved about beneath the lenses. This arrangement greatly facilitates the systematic examination of large areas, which is often required. Another important feature of this microscope is the arrangement of the illuminator; this is not a separate fitting to be screwed to the end of the tube—that arrangement involves an extra risk of unsteadiness and also makes it impossible to interchange different forms of illuminator without removing the lens entirely. In the author's microscope the objective is screwed direct to the end of the body-tube, and the illuminator—or rather the reflector—is carried on a small fitting which slides into an aperture in the lower end of the body-tube; this is so arranged that the reflector can be moved at will both across the tube and along it, thus enabling the operator to find the position which best suits the particular lens he is using—and in practice this position is found to differ considerably with different types of objective. While this adjustability is of very considerable use to the expert worker, it is apt to be a little awkward for the beginner, as the latter will probably place the reflector in the worst possible positions to begin with. For that purpose, however, the instrument can be supplied with an illuminator, fitting into the same aperture but in a fixed position, which is reasonably good for some of the most usual lenses.

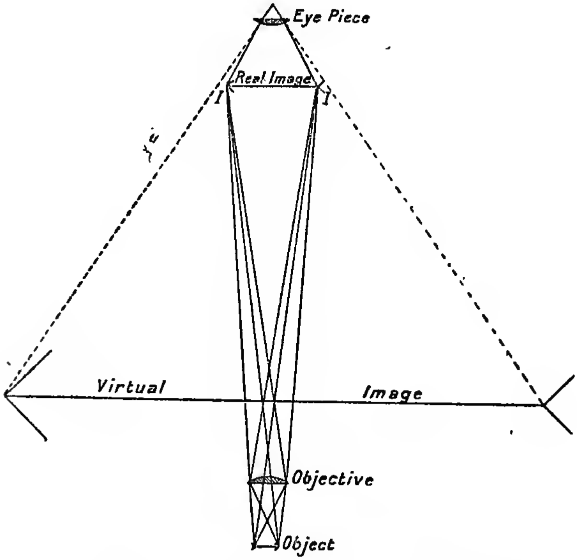

Fig. 6.—Diagram of Image Formation in the Microscope.

Turning now to the optical system, we find that in the modern compound microscope—which is the instrument always understood when we speak of "the microscope"—the images are formed by two lenses, or systems of lenses, known as objectives (or object glasses) and eye-pieces respectively. We need not enter into the details of their design or construction, but it will be well to consider some questions which affect their performance and their limits of usefulness. The diagram of Fig. 6 shows in a general way how images are produced in such a microscope. The objective, which is always a lens of very short focus, is placed close to the object and produces an image, I, I, at a certain plane in the tube of the instrument; this image is already magnified in a definite proportion which depends upon the relative distances between lens and object and lens and image, the power or focal length of the lens itself determining what each of these two distances must be in order to yield a sharp image. Theoretically the actual choice of these distances should be immaterial, so long as the object to be examined is always kept outside the front focal distance of the objective. With the highly-corrected modern microscope objectives, however, the best results are only obtained if the lens is used so as to form its real primary image at one particular distance from the lens. This distance is determined by the actual length of the microscope tube and is generally spoken of as "the tube-length"—this determines the distance between the objective and the eye-piece. It is accordingly important that each objective used should be employed at the proper tube-length for which it has been designed. This length is usually marked on the mount of the objective.

The primary real image produced by the objective is then examined by means of the eye-piece, which acts as a magnifying glass or—in the case of photo-micrography—as a projection lens. The point which is of importance here is that the performance of the object glass is of much greater importance than that of the eye-piece. The latter merely enlarges to a convenient size or projects to a convenient distance the image produced by the former; the detail and its sharp definition must all be present in the initial image produced by the objective—the best of eye-pieces cannot improve the image, while the enlargement produced by the eye-piece serves as a severe test for the perfection of the image to which it is applied. The quality of the image produced by the objective depends upon the general excellence of the construction of the system of lenses—the completeness with which the optical defects, such as chromatic aberration, spherical aberration, and others are removed or "corrected," and also upon what is known as the "aperture" of the lens.

As regards the optical corrections of his lenses, the microscopist is largely in the hands of the opticians, but there can be no doubt that the best of modern lenses, such as the "apochromatic" objectives of Zeiss, leave little or nothing to be desired in the completeness with which the defects inherent in simple lenses have been overcome. There are, however, circumstances in the use of the microscope which sometimes place the objectives under very severe conditions, and then the small residual defects become apparent. This can largely be avoided if the operator possesses the necessary knowledge of optics; here we can only indicate two devices which are frequently useful, particularly where photo-micrographs of difficult subjects have to be prepared. One of these is the use of monochromatic light. Such light can readily be obtained either by isolating the light of one particular colour from a beam of white light by means of a prism or other apparatus which is used so as to split the white light into a reasonably wide spectrum, or a similar, although less perfect, isolation may be obtained by means of coloured solutions placed in glass cells in the path of the beam of light. A very effective solution of this kind, giving a nearly monochromatic blue light very suitable for photographic work is obtained by preparing a saturated solution of copper-ammonium acetate. A still better approximation to monochromatic light may be obtained by the use of thin sheets of gelatine, mounted between sheets of clear glass. Such gelatine light filters, stained with suitable dyes, are now obtainable from Messrs. Wratten and Wainwright, specially for use in photo-micrographic work. By the use of such monochromatic light it is possible to eliminate from the image the effect of a small amount of residual chromatic aberration which is sometimes found in microscope objectives, particularly in regard to the parts of the image lying away from the centre of the field of view. This chromatic aberration arises from the fact that the lenses affect the light of different colour (*i.e.*, of different wave-length) in a different degree, so that the images produced by the red rays, for instance, do not quite coincide with the images produced by the blue rays. In a simple lens this would be the case to such an extent that the resulting image would be badly blurred by blue and red edges, but the skill of the optician has so balanced the action of different kinds of glass as almost entirely to overcome the formation of these coloured edges ; by the use of light of a single colour, however, the formation of coloured edges can be entirely avoided. The use of such light has the further advantage, especially for photography, that there is no longer any possibility of a difference between the visual and the photographic focus of the image. The rays of light which most affect the eye are of much longer wave-length than those which principally affect the photographic plate, and consequently it sometimes happens, if white light is used, that an image which appears perfectly sharp to the eye is slightly out of focus when photographed ; if monochromatic light (preferably blue) is used, and the final focussing is done by that light, there is no risk of this occurring—since only the rays which have been used for focussing are then allowed to act upon the photographic plate.

The other device to be mentioned here as an aid to obtaining the best results from a given lens is that known as " stopping down." Without entering into the somewhat intricate theory of the question, it may simply be stated that some of the defects which exist in optical images produced by lenses arise from the fact that the rays which have passed through the outer edges or zones of a lens are not readily brought into coincidence—at the image—with the rays coming from the same point of the object which have passed through the lens nearer to its centre. As a result, when the outer zones of a lens are covered, so as to cut off the light passing through them, the sharpness of the image tends to increase, although the amount of light which is transmitted by the lens is reduced and the image thus loses in brightness. This process of reducing the effective diameter of the lens is known as " stopping down," and produces two other important effects besides that of eliminating the aberrations due to the outer regions of the lens. The first of these is a decided advantage, while the other entails such serious disadvantages as to put a practical limit to the application of the process. The advantageous effect of stopping down is to increase the " depth of focus " and also the " flatness of field " —in other words, to cause the image to appear sharp over a larger area.

The manner in which a reduction of the effective diameter of the lens affects depth of focus can best be seen from the diagram of Fig. 7, in which the objective is represented by OO; *p* is a point in the object from which a bundle of rays, *rrr*, diverges, passing through the lens, OO, and being again converged to the point P in the image. If we think of a second point, *s*, in the object situated at the same distance from the lens as the first point, *p*, then S, the image of *s*, will be situated at the same distance behind the lens as P, the image of *p*. If the lens is so placed that the points P and S fall upon the focussing screen or into the focal plane of the eye-piece, then the images represented by these two points will appear perfectly sharp. But now consider a point, *q*, situated a little further from the lens than either *p* or *s*—such a point might represent one of the lower or deeper places in a somewhat deeply-etched specimen. The image of such a point will lie at Q, nearer the lens than P and S. The result will be that if the screen or focal plane is set to suit P and S, that part of the image representing points like Q will not be sharp—the bundle

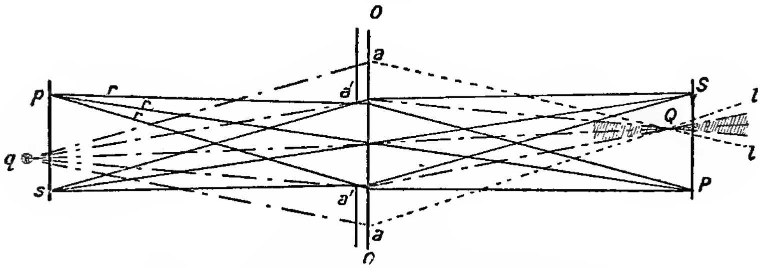

FIG. 7.—Relation of aperture to depth of focus.

of rays coming from *q* does not meet at a point where it crosses the focal plane but constitutes a cone of small angle, *l*Q*l*, and the section of this cone on the focal plane is a small circle or disc and not a point. So soon as these discs are of appreciable size, the image becomes blurred. Now the size of such a disc depends on two factors—the distance of the true image point, Q, in front of or behind the focal plane, and the angle of the cone of rays, *a*Q*a*. In practice all those parts of the image appear to be sharp in which these little discs do not exceed a certain minute size (about ·005 inch), and consequently an objective possesses a small " depth of focus "—that is, a range of distances for points on the object for which sharp images are still possible. This range of distances or depth of focus decreases rapidly as the width, *aa*, increases, but it can be very considerably increased by " stopping down." In the diagram, if the lens be covered by a stop in such a way that *aa* is reduced to *a′a′*, then the angle of the cone of rays meeting at an image point is reduced to *a′*Q*a′*, and the distance at which Q may be situated from the focal plane without causing a blurred image is very considerably increased.

The same effect makes itself felt in yet another way. In the diagram of Fig. 7 we have supposed the points *p*, *q* and *s* to lie near that part of the object opposite the middle of the lens, *aa*, but in the case of microscope lenses the objects to be examined are often large compared with their perpendicular distance from the lens itself and we then find a systematic variation in the distance from a point on the object to the centre of the lens, arising from the fact that the rays of light travel in an increasingly oblique direction when they come from points at increasing distances from the axis of the instrument. The result is that the image of a perfectly flat object assumes a concave form, the image-points representing the outer edges of the object lying nearer the lens as compared with those which represent the central points of the object.[1] This is known as the

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[1] This account of the causes of " curvature of field " is very elementary, and is true only for an ideal simple lens; in actual lenses the combined effects of the components sometimes reverse the direction of curvature.

"curvature of the field" and results in a difficulty which makes itself felt whenever microscopic images are to be photographed or even merely projected upon a flat plate ; when the image of the centre of the field is sharply focussed the outer edges are blurred. The image-points of the outer portions of the field of view lie in front of or behind the plane of the plate or screen and the cones of rays where they intersect the plate produce discs instead of points. These discs can again be reduced in size, and the sharpness of the image extended over a larger area, by stopping down.

With these considerations in view it would be natural to suppose that the best results could be obtained by reducing the effective diameters of our lenses to mere pin-holes. The student will be readily cured of this idea if he will try the experiment of focussing a good microscope on an object showing some rather small features, commencing with the iris of his illuminator wide open and gradually closing it. At first the image will certainly improve in definition and contrast, although rapidly diminishing in brightness, but when the aperture is reduced below a certain amount the appearance of the image begins to change ; narrow lines spread out into bands, minute points into circular or irregular patches, and every dark edge is bordered by alternate dark and light bands. This change in the image is due to what is known as diffraction, which renders the images obtained with unduly small apertures misleading and useless. The reason for these effects is to be found in the undulatory nature of light and the mutual interference of light waves when these are caused to pass through small apertures. Interference always occurs, whether the small aperture is there or not, but the presence of a small aperture cuts off the other light-waves which previously obliterated the effect by "averaging up" the illumination ; when these other waves are stopped by the iris or the edges of the lens, the interference or diffraction effects become very prominent. That they are always present more or less can be readily verified by using eye-pieces of very high magnifying power ; when this is done minute rings and bands can be seen surrounding the dark parts of the image even when large apertures are used. Here, then, we have a very important practical limit to the extent to which the image given by a lens can be improved by stopping down—this process must never be carried so far as to bring about any very marked change in the character of the image.

It has already been pointed out that the effects of diffraction are always present in microscope images and, from what has just been said, it will be seen that the actual diameter of the objective lenses—or their "aperture," as it is technically called—is of vital importance in governing the degree to which the resulting images are affected by these disturbing influences —for the best results, lenses of large aperture must be employed and, indeed, it is the aperture of the objective which governs the amount of magnification which can be usefully employed with it. We have already seen that an objective of given focal length used in the ordinary way gives a real image magnified in a definite ratio ; in the case of very short-focus lenses, such as the so-called oil-immersion objectives, this initial magnification may be as high as eighty or one hundred times. But this initial image may further be viewed with a magnifying eye-piece, or even with a second complete microscope, and thus magnified to almost any desired extent, although with a single eye-piece a further magnification of eighteen or twenty times is the most that can be conveniently applied. The question is, how far is it worth while to carry this magnification ? The existence of the disturbing effects of diffraction makes it evident that there must be a limit of useful magnification for any lens ; the mere enlarging of an image is of no advantage unless additional detail is thereby rendered visible, and such detail can no longer be seen or "resolved" when the distances between the images of adjacent features of these details are so close together that the diffraction bands or rings formed around the image of one feature overlap and blur the image of the other. With the best modern apochromatic objectives this limit of resolving power is attained when the total magnification of the image reaches 1,500. This figure—sometimes expressed as 1,500 diameters—indicates that the length of any line in the object is multiplied 1,500 times as seen in the image. Increasing magnification beyond this point, whether by direct projection or by means of photography, yields no additional information and only shows the diffraction figures more clearly.

This whole question of " resolving power " is too large to be considered fully here, but the knowledge that such a definite limit exists, and of the nature of the causes affecting it, is very necessary to every microscopist if only on account of the caution which it should inspire in the interpretation of the images seen under the highest magnifications. The correct interpretation of these images, especially when the peculiar character of the illumination employed in metallographic work is considered, is a matter requiring some care and caution. A striking example of this kind of difficulty is found in cases where a small area on a specimen is obviously at a different level from the rest ; in such cases some care is required to determine whether we are dealing with a mound or a pit in the surface. This question is further complicated by the fact that we see such images right and left reversed, and it is not easy to interpret shadows. An adjustable reflector in the illuminator is of great assistance in such cases, but the final resource is the micrometer screw of the fine adjustment of the microscope—by observing whether the object and lens have to be moved closer together or further apart to obtain focus at different levels, questions of difference of level can always be settled. A more difficult case arises when features are under observation which lie close to the limit of what the microscope can distinguish. Thus in mild steel, when treated in certain ways, a series of structures can be developed ranging from beautifully laminated " pearlite " on the one side to a dark, almost featureless constituent on the other. The extreme cases are, of course, quite distinctive, but the intermediate gradations are not easily distinguished.

Where fine details, and particularly laminations, have to be resolved the influence of the opaque reflector (Fig. 3 B, p. 39) must be borne in mind, since its presence reduces the working aperture, and therefore the resolving power to one half in one direction. Thus, if laminations are placed parallel to the edge of the reflector, they may be completely blurred, while they appear sharp and clear when turned through a right-angle. This case is particularly instructive, as showing the care required in interpreting such images and the need for a rotating stage on metallurgical microscopes in order that the specimens may be examined in every azimuth—no specimen showing fine detail should be examined without passing through a complete rotation of the stage and subjecting it to varying illumination by moving the reflector of the illuminator—slightly oblique illumination often reveals details which are invisible in the full glare of central illumination.

The general considerations of the conditions which govern the resolving power of the microscope lead to certain definite rules in the use of the instrument which may be summed up thus: For a given magnification it is desirable to obtain as much of the magnification as possible by means of the objective—for most purposes an eye-piece magnification of eight or ten times is the best. The objectives used should possess a large aperture, and for extremely high magnifications a lens of larger aperture is preferable, even if its focal length is somewhat greater and its initial magnification consequently somewhat less. Finally, to obtain the best resolution in examining minute objects, the aperture of the lens should not be unduly diminished by the use of the stop or iris, and when the stop is closed down very much the observer must expect serious interference from diffraction effects. For most purposes of visual microscopy on opaque objects it is found desirable so to regulate the beam of light entering the microscope that about two-thirds of the full diameter of the objective is utilised. This can be readily judged by removing the eye-piece and seeing how much of the back lens of the objective appears to be " filled " by the beam of light.

In order to obtain the best results from good microscope lenses it is essential, beyond the observance of the guiding rules just given, to secure a proper illumination of the object. The manner in which opaque objects are illuminated by reflected light has already been indicated in general terms, but the actual illuminants and their best arrangement deserve some attention. The best methods of lighting differ somewhat according to the circumstances, *i.e.*, whether the object is to be examined visually or whether a photograph is to be taken.

For purposes of visual examination the source of light should not be very minute, but should preferably possess an equally illuminated area about one half-inch square at least. Perhaps the most satisfactory source of light for this purpose is produced by means of an incandescent gas-mantle placed inside a white opal chimney. A somewhat similar effect can be obtained with a metallic-filament electric lamp having a large number of loops of filament and provided with an opal bulb or an opal shade placed close to it. The illuminated surface of the opal glass is then to be regarded as the real source of light, and the best manner of utilising this light is to place the front surface of the opal glass in the position indicated on the diagram, Fig. 8, by the letter O. In this diagram the point F represents the focal plane of the eye-piece and l and m are the distances of F and O respectively from the reflector, R, of the vertical illuminator. If now O is so placed that $m = l$, then a sharp image of O will be formed on the surface SS of the specimen when the objective is brought to focus. The reason for this result lies in the fact that when the objective is in focus the image of SS is formed at F, and, as all optical processes are reversible, it follows that the lens would form an image at SS of any object situated at F; but O is situated not at F, but at its image in the mirror of the reflector, and consequently the objective forms a sharp image of O on the surface of the specimen. This condition gives what is known as "critical illumination," and is far the best mode of illumination possible, particularly as it does not require the intervention of any condensing lenses or other elaborate appliances. Two points only have to be remembered: since a sharp image of the

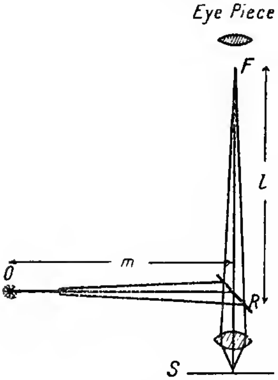

Fig. 8.—Diagram of "Critical Illumination."

source of light is formed on the specimen, the source of light itself must be uniform and free from detail, which would otherwise be superposed on the structure of the specimen in a confusing and irritating manner. For this reason a bare incandescent mantle or incandescent electric lamp, Nernst lamp or similar illuminant cannot be employed, nor can ordinary ground glass be used in place of the opal glass, since the details of the surface of the ground glass are seen very clearly under the microscope in these circumstances. A second consideration arises from the fact that the lamp with its opal shade must be placed quite close to the microscope in order to fulfil the requirement $m = l$, and if an unprotected or uncovered lamp is used the general lighting of the microscope and its surroundings becomes unpleasantly intense, while direct light from the lamp may reach the eye of the observer at the eye-piece. In order to avoid such serious inconvenience it becomes desirable to enclose the whole lamp in a metal or other opaque chimney, provided with an aperture on the side opposite the microscope and at a suitable level to allow light to reach the opening of the illuminator of the instrument. If arranged in this way this mode of lighting not only gives the best possible illumination of the specimen, but also affords great comfort to the eye of the observer. The author has used several simple forms of lamp for this purpose. In one of these an ordinary upright gas burner with incandescent mantle is placed inside a vertical brass tube. At a suitable level an aperture is provided, and this is fitted with a side tube about one inch in diameter, running out at right angles. The light from the opal shade of the gas burner passes along this side tube and, if the lamp is so placed that the open end of this tube is close to the aperture of the illuminator of the microscope, the desired result is at once attained, as the length of the side tube is so adjusted that it acts as a distance-piece for focussing

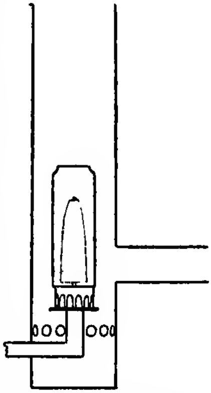

FIG. 9.—Diagram of gas lamp for microscope.

the light. The arrangement is shown in the diagram, Fig. 9. For electric light the author uses the arrangement shown in the diagram of Fig. 10, where N is the glower of a Nernst lamp, while R is a rod of optical glass having one end finely ground. The light entering this rod at one end is repeatedly reflected at the periphery of the rod and, finally, leaves the rod at the other end. This end of the rod then acts as a uniformly illuminated source of light, and may be so placed as to yield "critical illumination," while the arrangement of tubes shown in the diagram is sufficient to screen the light from the eye of the observer. The light from this lamp is rather bright and somewhat yellow in colour; it is easily softened and rendered whiter by the interposition of a screen of glass having a slight blue tint.

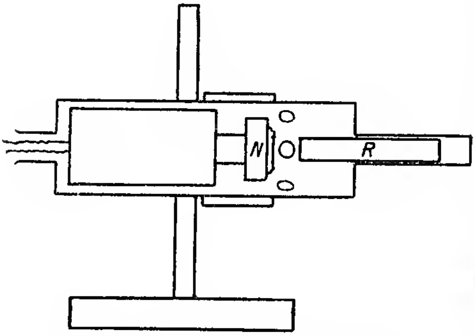

Fig. 10.—Electric Microscope Lamp.

For photographic purposes this mode of illumination is not, unfortunately, available at present; even when a piece of opal glass is illuminated by the concentrated beam from a powerful electric arc lamp, the light which it emits is not sufficiently powerful for photographic purposes; the images formed upon the ground glass of the camera are too feeble to be readily or accurately focussed, and thus much of the advantage of this form of lighting would disappear. It is, in fact, in order to facilitate the arrangement and focussing of the image upon the ground glass or other screen of the camera that extremely powerful illuminants are to be recommended for purposes of photo-micrography; the photographic plate itself is amply sensitive to take good photographs with very feeble illumination. The illuminants actually used are, as a rule, either the electric arc or the limelight. Both these sources of light consist of small areas of highly heated incandescent matter giving out a powerful beam of light. These minute bright areas cannot well be employed by placing them in the position of O in Fig. 10, since the images which they would yield upon the surface of the specimen would not be large enough to cover the field of view, while even the area covered by the image would not be uniformly lighted. The plan is, therefore, adopted of concentrating as much as possible of the light emanating from the limelight or the arc by means of a condensing lens into a parallel, or nearly parallel, beam of light. This beam is then passed through a water jacket in order to arrest the heat-rays which accompany the light coming from such a source, and then the beam is further concentrated by means of a lens until a small but intensely brilliant image of the craters of the arc, or of the limelight, is formed. The most favourable arrangement is such that this image of the source of light falls upon the iris of the vertical illuminator. Theoretically the best point would be the "back principal focus" of the objective, since in that case the light would leave the lower face of the object-glass in an approximately parallel beam, and would then be reflected as such from the face of the specimen back into the lens. In practice, however, it is not worth while to locate this point with any great care, since the manner in which microscope objectives are constructed does not render them capable of emitting a satisfactorily parallel beam of light even in the best circumstances, and the point for focussing the light which has been suggested above is sufficiently near the theoretically correct point to give practically equally good results. At all events a patch of very brilliant illumination will be seen upon the specimen immediately beneath the objective, and by this means images of such brightness can be produced that they can not only be photographed and focussed with the greatest ease, but they can even be projected upon a screen and exhibited to audiences of moderate size. This method of showing microscope images by projection is of great use whenever it is desired to explain the detailed features of a given microstructure to two or more persons, but it must be remembered that in clearness of definition and width of view the projected image cannot approach the image as seen visually under the

that enters the microscope and the rays that leave the objective to form the magnified image are reflected through a right-angle. The appearance of such an instrument is shown in Fig. 12, Plate III. There can be no doubt that these microscopes offer certain advantages which make them particularly convenient for quick working at moderate magnifications. The specimen requires no mounting or levelling, but on the other hand, as the polished surface lies on the stage, injury by scratching is very apt to result. The multiplication of reflecting surfaces is also a disadvantage, which makes itself felt at the highest magnifications, and for this class of work the author has not found this type of instrument very successful.

Another type of instrument which is often useful, especially for the examination of fractures, and of small objects generally, by oblique illumination only, is the "Greenhough" stereoscopic binocular microscope, in which the specimen is looked at through two convergent microscopes. The stereoscopic effect obtained is very beautiful, and for magnifications up to about seventy diameters the instrument is very useful.

For the ordinary type of metallurgical microscope (as distinct from the Le Chatelier inverted type) it is usually necessary to mount the specimen on a slip of glass, wood or metal in such a way that when this slip is laid on the stage of the microscope, the etched surface of the specimen shall lie exactly at right angles to the optic axis. Most of the older appliances used for thus "levelling" the specimens involve laying the specimen face downward on some level surface, and then adjusting the carrying slip parallel to that surface and attaching the specimen to it either by wax, plasticine, sealing wax, plaster, etc. Among these is the device formerly used by the author, in which the mounting slip is brought down upon the back of the specimen by a parallel motion guided by four accurately-made links. A much more perfect device, not requiring the polished surface to be touched in any way, has, however, been devised and adopted more recently. In this device a telescope is used with an internal reflector, somewhat like the clear-glass illuminator. Light from a suitably placed lamp is sent down the telescope tube and leaves the objective as a parallel bundle of rays.

These strike the polished surface of the specimen lying upon the stage of the instrument, and are reflected back into the telescope. Matters are so adjusted that if the surface of the specimen is accurately at right angles to the axis of the telescope the observer at the eye-piece would see the image of the source of light reflected by the specimen falling accurately upon the centre of a pair of cross-wires placed in the eye-piece of the instrument. As a rule this will not be the case when the specimen is first looked at, but if it is mounted on soft wax or plasticine, its position is easily adjusted with the fingers until the image of the source of light falls exactly on the right place. In this way it is possible very quickly to level the specimen to a very high degree of accuracy. The arrangement has the advantage that it can be adjusted to work with a particular microscope in such a way as to allow for any want of complete accuracy in the adjustment of the stage of that microscope. A further advantage lies in the circumstance that if a specimen has a rounded surface, so that the whole of it cannot be set at the proper angle, the setting can be made for any particular small portion from which a photograph is to be taken. For that purpose it is only necessary to cover the surface of the specimen, while it is being adjusted, with a piece of paper or other mask in which a small hole has been cut in such a position as to expose the small area in question.

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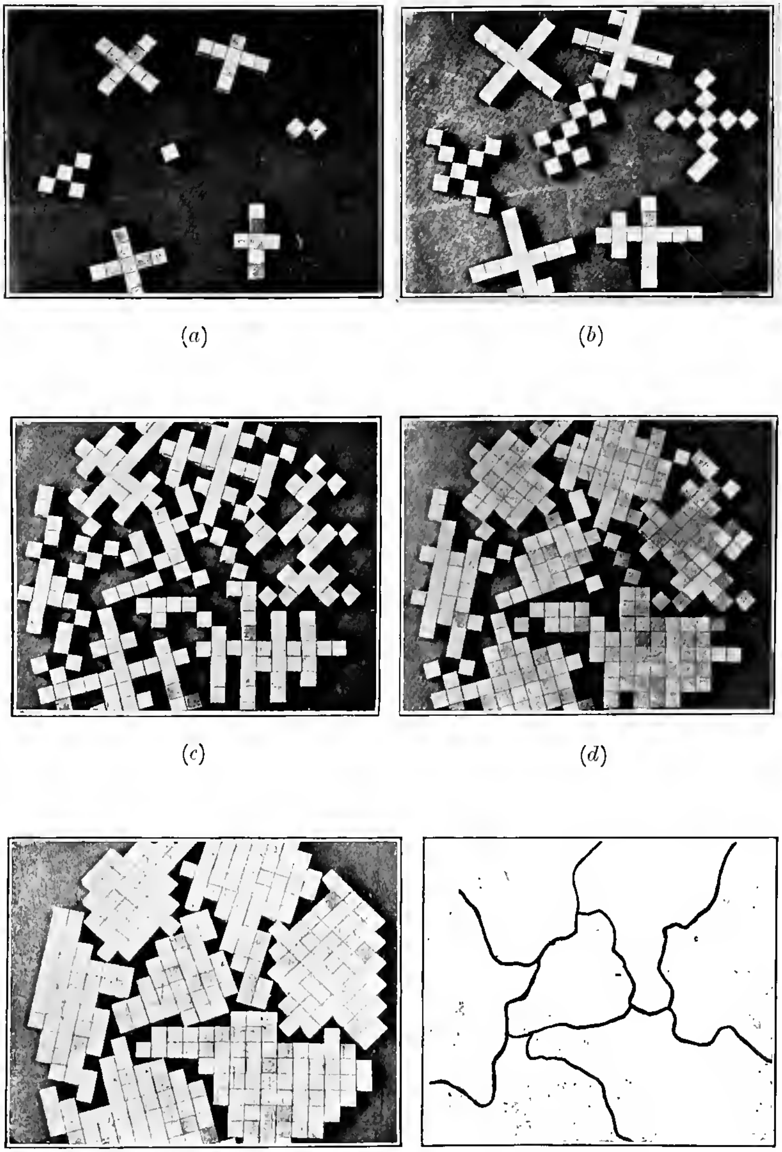
CHAPTER IV

THE MICRO-STRUCTURE OF PURE METALS AND OF ALLOYS

When a specimen of any pure metal, in either the cast or the "annealed" state, is prepared and examined under the microscope in the manner indicated in the previous chapters, a typical appearance is always seen—an appearance typical of the structure of pure metals as a class rather than of any individual metal. The appearance thus presented by the purest iron (good Swedish charcoal iron) is shown in Fig. 13, Plate I., and also in Fig. 97, Plate XX., where the structure is photographed under a magnification of 150 diameters. The appearance of other pure metals is very similar; and, indeed, the similarity of all pure metals as seen under the microscope serves to show that microscopic examination cannot generally be employed in place of chemical analysis for the purpose of distinguishing different metallic elements from one another, for although the practised observer might be able to distinguish some of the more typical metals by the aid of minor peculiarities, the similarities between many of them are so great that much uncertainty would remain. On the other hand, in many cases, as will be evident later, microscopic examination will at once decide whether a given specimen consists entirely of one metal or is an alloy of two or more. For the present, however, the important fact is that all pure metals, when free from the disturbing effects of mechanical treatment, show a strikingly similar appearance under the microscope. As the figures show, this "structure" consists of a number of mutually adjacent roughly polygonal areas, separated from one another by narrow dark lines, but otherwise practically free from any marked features. These polygonal areas are readily recognised as representing a sectional view of roughly polyhedral grains, which evidently constitute the entire mass of such a metal.

Microscopic research has, however, elucidated the nature of these grains, and they are now recognised to be true crystals, the metal being thus an agglomerate of crystals, much as a mass of rock-salt or of granite is an agglomerate of minute crystals. It is true that these crystals lack one of the most striking features of many crystals, and that is the regular geometrical outline which we see in specimens of Iceland Spar or Rock Crystal; but this absence of geometrical form is due to the fact that none of these crystals have had the opportunity for free growth which is requisite for the development of geometrical forms; when a crystal of a salt is formed in a solution its surfaces remain free to grow in the liquid surrounding them, but in the crystallisation of a metal the growth of each crystal has been stopped by the interference of a neighbouring crystal, so that each of these grains is bounded, not by any regular geometrical outline, but by the more or less irregular surface upon which two adjacent crystals have met in the process of their initial formation. The manner in which this occurs may be made clearer by an analogy with the way in which children's building blocks might be piled up to cover a given area. If the blocks were all exactly alike in size and shape it would, of course, be possible to lay them all exactly parallel to one another in a single continuous pattern all over the surface to be covered. But for this purpose it would be necessary to begin the process at a single point and to work outward from that alone. If the work were begun by several operators at the same time, each starting from their own chosen centres and working each to his own scheme, without reference to that adopted by any of the others, a very different result would follow: each man would build up a regular pattern, and all the patterns would be essentially alike, but they would not be parallel or "similarly oriented," so that where they met they would form irregular joints. The diagram of Fig. 14, Plate IV., shows five stages of such a process, and the final result, with the blocks themselves left out and only the outlines of the joints traced where the various differently-oriented areas have met. This outline is exactly like the boundary between adjacent crystals in the micro-section of a pure metal—it is the "acci-

PLATE IV.



(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

FIG. 14.

[*To face p.* 62.

dental " meeting-line of adjacent growing crystals of different orientation.

The essence of crystalline character does not reside in geometrical outlines or shapes, but in the regular arrangement of the molecules or groups of molecules within the mass. The geometrical outline is merely one result of that internal structure—a result which is only apparent in favourable circumstances. This regular arrangement or orientation is fully present in the crystals which constitute the mass of any specimen of pure metal. Some of the evidence upon which this statement is based is so striking and interesting that a brief account of it is desirable.

The photo-micrographs typical of pure metals given in Figs. 13 and 97 are, as already indicated, taken under normal illumination, but these same specimens yield a different appearance when viewed under oblique light. The characteristic beauty and lustre of this appearance must be seen direct through the microscope to be appreciated; Fig. 15, Plate I., gives a photographic representation of the same field of view as that shown under normal light in Fig. 13. The polygonal outlines of the crystals are still visible, but now they appear as bright lines on a dark background; the areas of the polygons, which in the former view appeared almost uniformly white, are now greatly differentiated; some appear perfectly dark, while others shine out brilliantly. If a specimen thus lighted be slowly rotated on the stage of the microscope, a very striking phenomenon is witnessed—the crystals which at first appeared bright rapidly wane and become dark, while others flash out brightly. This phenomenon may be briefly called "the rotation effect," although it is more correct to refer to the "oriented lustre" of metals. To understand its nature and meaning we must consider for a moment the manner in which the surface of the specimen has been prepared. The important point in the preparation for the present purpose lies in the etching process, since before that was applied the surface of the metal was practically a uniform plane. Now the etching reagent—such, for example, as dilute nitric acid—is, as we have seen, merely a weak or slow solvent of the metal, and it effects this solution by gradually unbuilding or taking down the structure of the metal exposed to its action ; if now the different crystals which have been cut through by the plane of the polished surface are each built up on separate systems or arrangements of their own, each will also be unbuilt according to this system. If this unbuilding process be stopped at any given moment, the part of the surface belonging to each crystal will be covered with some more or less distinct traces of the plan upon which the unbuilding was proceeding. These traces actually consist of a number of very minute facets, differing in size and position, but all of the same shape and similarly oriented, *i.e.*, all facing the one way over the entire part of the surface belonging to the same crystal, but—as a rule—differing in shape and orientation from one crystal to another. Further, it is found that the unbuilding of the crystals by the process of gradual solution does not go on at the same rate upon all the crystals exposed in a section—in fact the rate of attack differs slightly, but distinctly, from each crystal to its neighbour, according to the different orientation of the molecules or groups of molecules of which the crystal is built up. The etched surface, therefore, consists of a series of polygonal areas, corresponding to the various crystals intersected by the surface, each at a slightly different level, and thus necessarily connected by short, steeply-sloping surfaces, and each covered with a system of very minute facets which are similar and similarly oriented over each of these polygonal areas, but differ in shape and orientation when we pass from one area to another. What, then, are the microscopic appearances to be derived from a surface of such configuration ?

Under normal illumination, if the etching has not been very deep, the facets just referred to are too minute in depth to be readily seen except under the highest magnification, but the differences of level between the adjacent polygonal areas become very markedly evident on account of the short, steep connecting surfaces. These are so steeply inclined to the horizontal that light falling downward upon them, instead of being reflected back into the lens of the microscope, is thrown out to one side, and the short surface thus appears, as seen from above, as a fine black line ; these are the black lines which bound the polygonal areas of the crystals. When examined under oblique illumination, however, these steep surfaces, or at all events those of them which face the direction from which the light happens to be coming, catch the obliquely incident light and reflect it into the objective, so that these bounding surfaces now appear as narrow bright lines. The diagram of Fig. 16 will make this clear, if it is remembered that only those surfaces will appear bright to an observer looking into the eye-piece of the microscope which reflect rays of light into the objective of the instrument. From these diagrams it will readily be seen that the comparatively horizontal surfaces of the polygonal areas themselves will, as a rule, appear dark when viewed under oblique illumination. There is, however, an important exception to this rule, and this occurs when the minute facets with which each of these areas is covered are so turned that they catch the incident light and reflect it into the objective. Among the multitude of crystals of differing orientations found in a single field of view, this will happen here and there in almost any position of light and specimen, with the result that several crystals will generally shine out brightly in these circumstances. This brightness will naturally differ somewhat from one of these crystals to another, according as the facets direct the whole of the light full into the objective or so direct it that only a portion is caught by the lens. As the specimen is rotated under the oblique illumination, the facets which at first reflected light into the microscope are gradually turned in such a way as

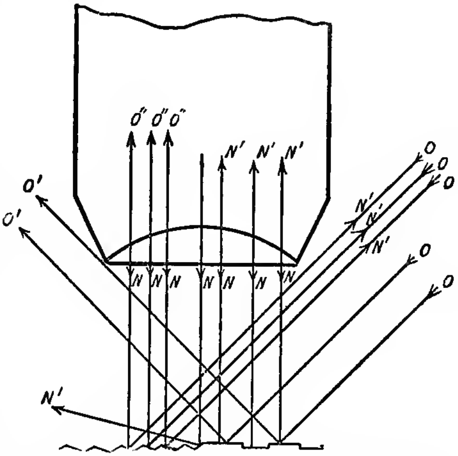


Fig. 16.—Diagram of normal and oblique rays falling on an etched surface.

next. A striking example of this kind is given in Fig. 19, Plate V.

With this brief outline of the evidence, the reader must be asked to accept the view—now generally recognised—that the polygonal grains seen in pure metals are true crystals so far as their internal structure is concerned. We should perhaps hint at once that the somewhat natural tendency to regard crystals as necessarily brittle in their nature is a misconception based upon ordinary experience of such crystalline bodies as sugar or spar; recent discoveries have, in fact, revealed the existence of crystals so plastic as to be practically fluid, so that they are usually called "liquid crystals," while among metals the crystalline character is perhaps most readily observed in one of the softest and most plastic, viz., lead.

We now turn to the question of the manner in which the crystalline structure of a pure metal is originally formed. At all events in the case of artificially prepared metals, excepting only those prepared by electro-deposition, the genesis of the micro-structure is to be sought in the process of solidification from the molten or fluid state.

Judging from the analogy of the process of freezing as we see it in the case of water or other pure liquids, which can be more readily observed than molten metals, the course of the process is somewhat as follows: as the temperature falls no very definite change occurs until the freezing-point is reached; then at a number of points in the liquid, solidification commences—minute crystals are formed, and each of these rapidly grows in size. As a rule, this growth does not take place simply by the accretion of concentric layers; the crystal is seen to throw out a number of arms into the surrounding liquid, from these arms numerous secondary branches are thrown out, and these in turn throw out other spines. The familiar figures made by the frozen moisture on window panes in winter are examples of this process of "dendritic" crystallisation, only that on the window pane the process has been arrested at an early stage for want of further material. In the interior of a mass of water—or of molten and freezing metal—there is no lack of material, but there are a number of crystals growing out from adjacent centres which vie with one another in appropriating both the material and the space in which it exists. In this way the crystalline arms which are thrown out by adjacent centres soon meet and thus put an end to further growth, the further development of the process then taking the shape of a gradual filling in of the space occupied by the dendritic arms which formed a species of advance guard for the final progress of the fully-formed crystal. The actual rate of progress of the arms of each of these growing crystals is in reality determined by the rate at which heat is abstracted from the different parts of the mass. Thus a crystal arm which grows outwards in a direction away from the coolest and towards the hottest part of the liquid will not readily meet with any other crystal arm, since in the hotter portions of the mass crystallisation has not yet begun—an arm growing in that direction will, therefore, grow on without interruption for a much longer time, and therefore for a much longer distance, than an arm which endeavours to grow in a direction at right angles to the direction of the flow of heat.

It has already been indicated that the dendritic arms which grow rapidly outward from the centres or nuclei of crystallisation, which are formed when a molten pure substance cools below its freezing-point, continue their growth until they are checked by encountering similar dendritic arms emanating from adjacent centres. Similarly, when the interstices of the dendrites come to be filled up by the growing crystals during the completion of the solidification or freezing process, this growth also continues until stopped by meeting with the advancing edge of an adjacent crystal. This process has been illustrated diagramatically in Fig. 14, Plate IV., but that figure also illustrates a further point. Where the two systems of cubical blocks meet, a series of interstices are necessarily left, each vacant space being too small to allow of the introduction of an additional block. One may well ask if there is anything of the same sort where two crystals meet, and if so, how the adjacent crystals adhere to one another ? The view that there really are such interstices has been held by a number of investigators, but the author cannot accept it, for several reasons.

Among these may be mentioned the fact, to be considered more closely in a later chapter, that the cohesion across the bounding surfaces of two crystals is actually stronger, in normal pure metals, than the cohesion across any of the surfaces within the mass of a crystal, so that when such a crystalline aggregate is broken, the crystals are not pulled apart from one another, but are actually broken across. Normally the intercrystalline boundaries, in fact, behave like strengthening ribs, and not as surfaces of weakness. It would be hard to account for this fact if the existence of actual interstices were assumed, but one may none the less assume that there are interstices between the adjacent crystals, but that these are filled with matter which has not become crystalline.

This hypothesis leads to a series of most interesting conclusions, and some of these the author and his collaborators have been enabled to verify experimentally. At the present time, however, it cannot yet be claimed that the theory of the existence of an amorphous or non-crystalline cement between the adjacent crystals in a metal has received general acceptance. Its bearing on the behaviour of metal when undergoing deformation or fracture will, however, be discussed when that portion of the subject comes to be dealt with. Here it is only necessary to draw attention to the special conditions which exist at the crystal junctions.

The process of solidification as an aggregate of crystals all having the same chemical composition and all formed at one particular temperature (*i.e.*, the freezing or solidifying point) is typical of pure substances, *i.e.*, of substances which are chemically homogeneous and are neither mechanical mixtures nor solutions. It is particularly typical of pure metals, and it follows that the micro-structure of all pure metals will show a strong similarity. This is true of the general type of structure —as we have already seen—but there are some minor differences due to the peculiar properties of each metal. For instance, the size or scale of the entire structure habitually varies enormously between different metals, although it may be accepted as a rule that the size of crystals depends upon the rate of cooling during the process of solidification. For this reason alone metals having a very high freezing-point, such as copper, silver, platinum and iron, will usually present a very minute structure, while metals which solidify at more moderate temperatures—such as tin and lead—usually possess a much coarser structure. By suitably modifying the conditions of cooling, the size of the crystals in any metal can, however, be enormously altered, a reduction of the rate of solidification always resulting in the formation of larger crystals. In many cases, as we shall see later, other processes, such as prolonged heating at temperatures considerably below the melting-point, will cause the crystals to grow, and may thus ultimately produce a structure on a larger scale than that which existed in the metal as first formed on freezing. It is important to note that a large and coarse structure invariably accompanies undesirable mechanical properties. For this reason the temperature at which metal is cast very materially affects its strength, for the rate of solidification is necessarily reduced if the metal is cast at an unduly high temperature; in those circumstances the surplus heat of the metal has raised the temperature of the mould to an undesirable extent before the metal itself has cooled to the freezing temperature, with the result that the rate at which the mould is able to abstract heat is unduly diminished and the rate of cooling of the metal during the freezing process is thereby reduced.

Apart from the mere size of the crystals which result from gradual solidification, the rate of crystallisation and the precise manner in which it occurs has a very important effect on the mechanical properties of the metal. This is due to an effect which occurs at the boundaries of the crystals forming the mass of the metal, and arises from the greater or less degree of mutual interpenetration of the dendritic arms or branches which shoot out from the centres of crystallisation in the early stages of the process. Fig. 20, Plate VI., is a photograph of such interpenetrating dendritic arms sent out from centres of crystallisation—in this case not of a metal, but, for convenience of observation, of a salt (ammonium chloride). Metals, however, as Figs. 21, Plate VI., and 51, Plate X., show, crystallise in a precisely similar manner. The extent to which this interpenetration occurs depends upon both the rate and the mode of crystallisation, and the strength of the metal and its power to resist external forces which tend to tear the crystals apart from one another will in turn depend upon the extent to which adjacent crystals are locked together by the mechanism of such interpenetration. Where there is much "interlocking" the bounding surfaces of the adjacent crystals will not be straight and smooth, but serrated and indented, thus providing the metal with a much greater length of junction surface and with the additional strength which appears to reside in these junctions.

It is interesting to consider in this connection what factors other than rate of cooling, which has already been mentioned, are likely to affect the formation and interpenetration of dendrites. In the case of crystals forming in salt solutions it has been observed that the presence of quite small traces of an impurity is often enough to alter the crystalline "habit," and the shape and arrangement of the dendrites very considerably, even though the impurity does not enter into the composition of the crystals themselves. It seems probable that some such effect as this may also occur in metals, and that in this way we can account for the very large effects produced by certain minute additions to some metals. Thus the presence of less than 0·1 per cent. of vanadium in steel produces a disproportionately large effect on the mechanical properties, and yet there is no special micro-constituent which is formed as the result of the addition of this minute quantity of vanadium. In other metals similar, although rather less marked, effects can be observed. In some of these cases the effect of the added material on the micro-structure can be seen in a slight alteration in the appearance of the crystal boundaries; the presence of vanadium in steel, for instance, renders the whole structure decidedly less distinct—an observation which lends some support to the explanation here suggested.

Before leaving the subject of the crystallisation of pure metals it should be remarked that the crystalline system according to which the molecules or groups of molecules within each crystal are arranged has been definitely determined in some cases. In the case of iron, for example, an examination of the etching figures leads to the view that the metal has crystallised in the cubical system, since all the etching figures present shapes which are readily recognisable as sections of either cubes or octahedra, and these are the typical forms of the cubic system. This view has been fully established by the work of Osmond ([3]) and his collaborators, who obtained actual crystals of iron by chemical processes which allowed these crystals to attain their natural external geometrical shapes. Other metals have received less attention, but in the majority of cases the evidence available is at all events consistent with the view that they also belong to the cubic system. Marked exceptions are, however, presented by cadmium and zinc, which have been shown to belong to the hexagonal system ([4]), and by bismuth and antimony.

Leaving for the moment the subject of the micro-structure of pure metals, we turn to the much larger group of metallic bodies known as alloys. For the sake of simplicity, and in order to remain on ground which has now been fairly well explored, we will confine our attention for the present to alloys containing only two elementary metals—such alloys being known as " binary alloys "—the whole range of alloys between two metals being known as a " binary system."

In order to understand the nature and constitution of alloys, it is preferable to commence our consideration with reference to the simplest state in which such bodies exist, viz., that of homogeneous fusion. Although certain pairs of metals cannot be made to mix in all proportions while in the molten condition, this is an exception, for in the great majority of cases two molten metals can be mixed with one another in the fluid state in any relative proportion. In this respect these fluids resemble such liquids as water and alcohol, or water and sulphuric acid. We may, in fact, safely carry this analogy much further, and regard mixtures of molten metals, *i.e.*, all molten binary alloys, as simple solutions of the two ingredient metals in one another. Sometimes, it is true, the two ingredients of such a solution enter into chemical combination with one another, and in that case it might be more correct to regard the resulting liquid as a solution of the excess metal and of the compound metal in one another, but this is a distinction of minor importance in the present connection. Since our interest naturally centres in the solid metal which results from the solidification of molten alloys, the question which lies before us is: "What happens to the mutual solution of two molten metals when the temperature is so far lowered that the metal undergoes solidification?" The answer is that, apart from the formation of definite inter-metallic compounds, there are two opposite modes of solidification adopted by binary alloys and a range of intermediate modes connecting these extremes. These extremes are simply (*a*) the case in which the state of mutual solution remains undisturbed by the process of solidification and the alloy crystallises while still remaining a solution, *i.e.*, each of the crystals which are formed ultimately attains the same average composition as the molten liquid from which it was deposited—such crystallised solutions are usually termed "solid solutions." (The German term for these substances, "Mischkrystalle," is sometimes translated—most undesirably—as "mixed crystals"; since this term suggests a mixture of crystals of different kinds, it is liable to convey an entirely erroneous impression, and should be avoided in the interests of clearness.) The other extreme (*b*) is that the state of solution existing in the liquid condition is entirely destroyed by the passage into the solid state, and the two constituents separate during the process of crystallisation; in this case the solid alloy can finally attain the condition of a mixture of crystals of the two pure metals. Intermediate between these two extremes are those alloys—and these are by far the most numerous—in which the state of mutual solution is partially maintained in the solid state, *i.e.*, alloys containing up to a certain limiting proportion of the second constituent crystallise according to group (*a*) as solid solutions without any separation of the two constituent metals, but alloys containing a higher proportion of the second constituent than the limiting proportion just referred to undergo a partial separation during freezing, the excess of the second metal above the limit of "solid solubility" being separated as crystals of a different constituent.

These alloys resemble those of group (*b*), except that the two kinds of crystals present in them are not those of the pure constituent metals, but consist of the saturated solid solutions of each of the metals in the other.

The micro-structure of any given alloy depends both upon the type to which the system of the particular metals in question may belong, and also on the place of the alloy in its binary system. Alloys of group (*a*), of which those of gold-silver, iron-manganese, and copper-nickel are examples, when allowed to crystallise sufficiently slowly to attain their condition of final equilibrium, present a micro-structure exactly similar to that of a pure metal—the homogeneous character of the molten solution is in that case so completely maintained that the microscope cannot detect the presence of any second constituent. As a rule, however, this state of complete homogeneity is not attained by solid solutions; for reasons which will presently be explained, a certain degree of temporary separation occurs during the freezing process, and usually persists to an extent readily recognised under the microscope. An example of this kind is shown by Fig. 21, Plate VI., which represents the micro-structure of an alloy of copper and zinc containing about 25 per cent. of zinc (a kind of brass, therefore), which when very slowly cooled appears entirely homogeneous, but when rapidly solidified exhibits the dendritic structure shown in the figure. The characteristic feature of such structures, however, is that the arms or branches of the dendrites are usually ill-defined, and that they lie wholly within polygonal boundaries which readily recall the crystal boundaries of pure metals.

The micro-structure of alloys of class (*b*) is rather more complex. Theoretically the addition to the pure metal, forming one end of a binary system of this type, of a minute trace of a second element should result in the appearance in the micro-structure of traces of crystals of a second constituent. In some cases this is true to a surprising degree of accuracy. Thus the addition of five parts of carbon to 10,000 parts of pure iron at once becomes visible under the microscope, while the presence of one part in 1,000 is readily seen, as shown in the photograph

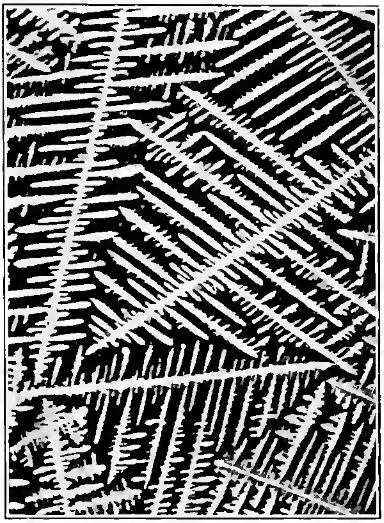


FIG. 20.

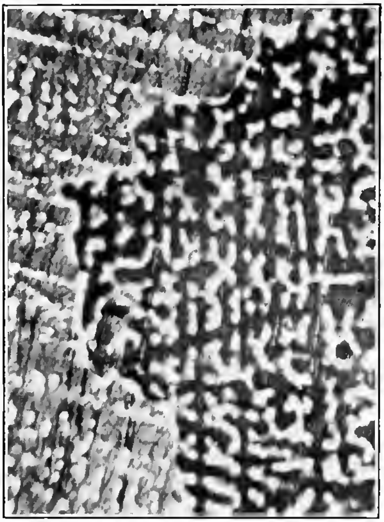


FIG. 21.

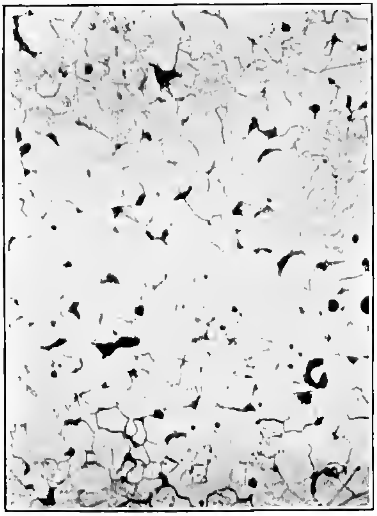


FIG. 22.

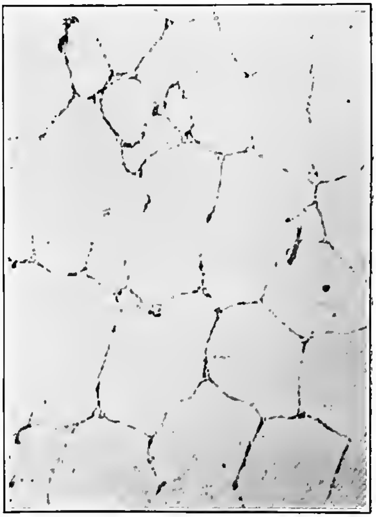


FIG. 23.

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Fig. 22, Plate VI. The polygonal grains of the pure iron crystals are readily recognised, but here and there between them are seen small dark patches which are entirely absent in the pure metal. These are patches of the carboniferous constituent, and in steels of increasing carbon-content the relative area occupied by these dark patches rapidly increases. The reason why the second constituent appears dark in this case, as in the majority of others, is simply due to the fact that, when the polished surface is attacked with an etching reagent, the more soluble, *i.e.*, more readily attacked, constituent is affected almost exclusively, while the other remains practically unaffected until the attack is carried to a considerable length. In this way the areas occupied by the more readily soluble constituent are eroded and roughened by the action of the etching reagent, and consequently scatter the light which falls upon them; under normal illumination they therefore appear darker than the other constituent, while under oblique light they shine out brightly on a dark background.

The effect produced upon the micro-structure of an alloy of this type by successive additions of the second metal are illustrated by a series of micrographs of the alloys of tin and lead, commencing from the tin end of the series. Figs. 23 to 26, Plates VI. and VII., represent the micro-structures of alloys containing respectively 95, 85, 74 and 45 per cent. of tin by weight.

In these alloys the white areas represent the crystals of tin, which are much less readily attacked by reagents than the accompanying crystals of lead. In Figs. 23 to 26 it will be seen that increasing lead content leads to an increase of the dark constituent, which at first appears merely in the form of thin veins in the inter-crystalline boundaries of the tin, thickening up into wider patches and bands until the crystals of tin appear as islands in a ground-mass composed of a mixture of small crystals of tin and of the dark constituent. Ultimately, when the lead content has risen to 37 per cent., the crystals of free tin disappear entirely and the whole alloy consists of a mixture of minute patches of dark and light constituents (see Fig. 46, Plate IX.). A further increase of lead content causes the appearance of isolated larger patches of the dark constituent. But while at that end of the series from which we started we were dealing with alloys rightly described as belonging to class (*b*), at the lead end of the series we find that the white constituent disappears—in alloys which have been allowed to approach the condition of final equilibrium—while some 16 per cent. of tin are still present; at this end the lead-tin system is therefore of the intermediate type possessing a considerable, but still limited, power of forming solid solutions.

The series of photo-micrographs of the lead-tin system (Figs. 23 to 26) show an additional feature deserving of special attention, because it is a very striking characteristic of the micro-structure of all alloys of the type (*b*) and of most of the alloys of the type intermediate between (*a*) and (*b*). In these figures we see a second constituent appearing, but when we examine this constituent in the alloys in which it is present to a larger extent, we find that it is not a simple body, but itself possesses a duplex structure, although in the present case, and, indeed, in the majority of cases, this structure is very minute. The cause of this duplex structure of the second constituent lies in the fact that during the crystallisation of the alloys of this type the separation of solvent and dissolved metal from one another only occurs finally at the moment of complete solidification; that portion of the alloy which crystallises last contains both metals, and these, on freezing, separate from one another in the form of minute crystal plates or granules, thus forming together the fine-grained duplex constituent shown in the photographs. It will be seen that the alloy containing 37 per cent. of lead and 63 per cent. of tin consists entirely of this duplex constituent. For reasons which will appear when the thermal phenomena connected with the freezing of metals and alloys are discussed, this duplex constituent, and particularly the alloy which is composed entirely of this constituent, is known as the "eutectic" alloy of the two metals in question. In many respects the micro-structures of all binary eutectic alloys are very similar to one another.

Having now passed in rapid review the most important types of micro-structure met with in metals and alloys in their normal

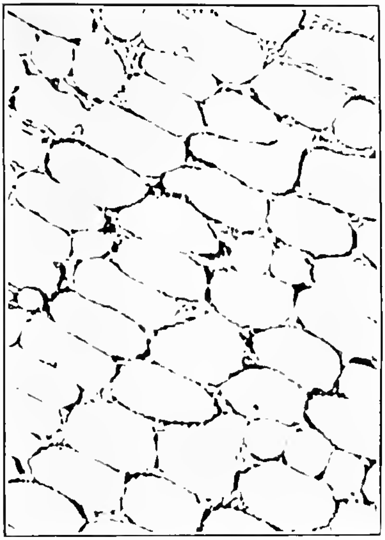

FIG. 24.

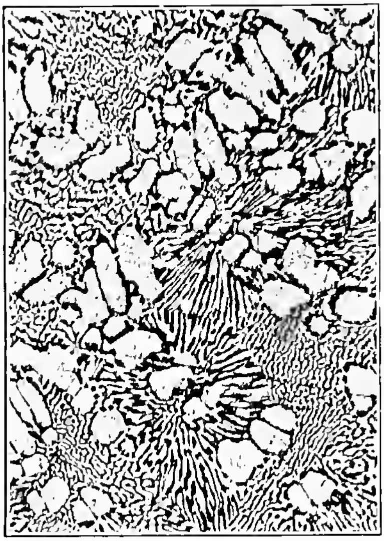

FIG. 25.

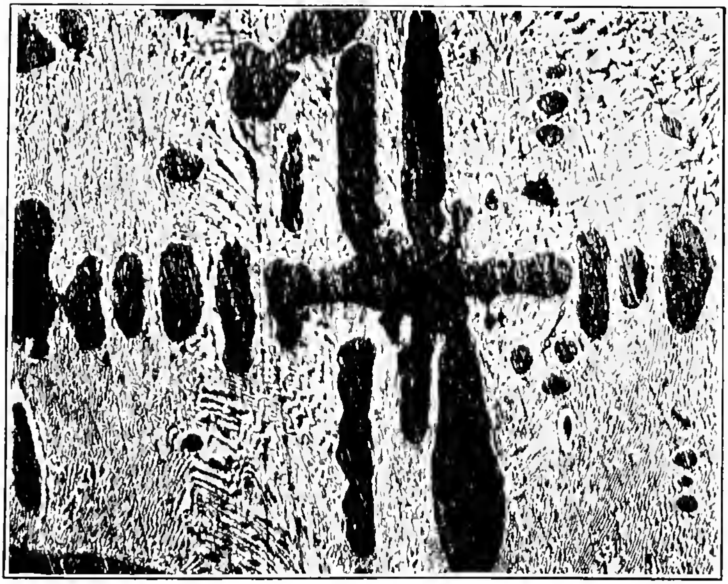

FIG 26.

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state (*i.e.*, when not disturbed by mechanical deformation), we shall pass in the next chapter to a consideration of the modes of solidification of metals and alloys as revealed by a study of the thermal phenomena which accompany the process of crystallisation.

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CHAPTER V

THE THERMAL STUDY OF METALS AND ALLOYS

THE study of the phenomena which occur when metallic bodies are heated and cooled has thrown a flood of light on the nature and constitution of metals and alloys, so that the phenomena in question, which relate to fusion and solidification and to the many internal changes which occur in metals or alloys while they are wholly or partly solid, constitute an important branch of Physical Metallurgy. The importance of this subject lies primarily in the fact that our most comprehensive and satisfactory method of describing the nature and constitution of alloys of a given system consist of a diagram—known as the "Equilibrium Diagram," or, perhaps, better as the "Constitutional Diagram"—which is based primarily on thermal data. We shall see in a later chapter how it is possible to deduce from the constitutional diagram or to correlate with it a number of important properties of alloys, so that an understanding of the manner in which these diagrams are established, and the validity of the evidence upon which they are based, is essential. We will begin by considering the manner in which suitable specimens of metal can be heated and cooled for the purposes of these observations; we shall then briefly consider the instruments used for measuring the temperatures involved, and, finally, the methods of representing the data in the form of "heating and cooling curves."

The means of heating a comparatively small specimen of metal steadily to any desired temperature and allowing it to cool down again appear at first sight to be very simple—any laboratory furnace capable of reaching the desired temperature would seem to be adequate. This is only correct where observations of a very rough character are to be taken. The difficulty lies in securing a sufficient degree of steadiness in both the heating and cooling process, while uniformity of rate of heating and cooling is still more difficult to attain. With most laboratory furnaces it is necessary to begin by heating with considerably reduced power—the gas or the electric current being increased step by step as the temperature rises. But every step of this kind produces a sudden change in the rate of heating and brings with it a disturbance in the heating curve which is being determined. During cooling, on the other hand, there need be no such steps if the furnace is simply allowed to cool down "naturally"; here, however, the difficulty arises that at a high temperature the furnace cools with excessive rapidity, while at the lower end of the temperature range there is a wearisome delay, due to the extremely slow rate of cooling which obtains there. Both these difficulties can be overcome to some extent by the use of suitable devices, such as controlling the temperature of the furnace by an electric current passing through a suitable heating coil or winding, regulated by some form of automatic rheostat whose resistance is steadily changed in order to keep the heating or cooling of the furnace as steady and uniform as possible. These devices are, however, always elaborate and expensive and never completely satisfactory. The author has, therefore, recently adopted a different plan, which gives excellent results with very little elaboration.

In all the older methods of heating and cooling specimens of metal for purposes of thermal study, the specimen has been placed in a furnace and allowed to heat up and to cool down with the furnace. In the author's new arrangement the temperature of the furnace is kept steady throughout the entire experiment. The furnace consists of a long vertical tube, which is kept at the highest temperature required at one end, while the other end is cold or nearly so. The specimen is then lowered into this tube or raised out of it in such a way as to pass in a perfectly steady and uniform manner from the cold to the hot part of the furnace, or *vice versâ*, at any desired rate within the range of the raising or lowering mechanism employed. With a little care the tube furnace can be arranged to have a perfectly uniform temperature distribution from one end to the other. By means of this arrangement it becomes possible to obtain heating and cooling curves at any desired rate, over any range of temperature within the range of an electric resistance furnace, with great ease and regularity, as the temperature of the hot end of the furnace can be controlled very accurately and kept quite constant by means of a thermocouple permanently fixed in the hot part of the tube. A photograph of the apparatus employed for this purpose is shown in Fig. 27, Plate VIII.

An additional advantage of this apparatus is the facility which it provides for submitting a specimen of metal to heating and cooling in any desired atmosphere. By placing the specimen in the closed end of a tube of porcelain or silica of suitable length and diameter, the upper end being closed by a stopper and tap, the atmosphere in which the specimen is placed can be varied at will, from a high vacuum to air, hydrogen, nitrogen, or other gas. The influence of gases on the thermal phenomena, particularly of steel, has lately received some consideration and cannot be left out of account in present day research work.

The instruments employed for the measurement of the temperature of metal specimens next require consideration. For the purpose of taking heating and cooling curves the thermo-electric couple is in almost universal use, as it possesses indisputable advantages over any other device. Most frequently the couple employed consists of a fine wire of pure platinum and one of platinum alloyed with 10 per cent. of either rhodium or iridium. The latter has the advantage of being rather more sensitive, and in the author's hands it has proved extremely constant in its indications, even under difficult conditions. The opinion is, however, widely held that the rhodium couple is more reliable in its indications.

For temperatures above 500° or 600° C. the platinum type of thermo-couple is the only one sufficiently permanent to be suitable for laboratory use. For lower temperatures, however, "base metal" couples can be employed with considerable advantage—such a couple as that of copper with the alloy known as "Constantan" being very satisfactory as regards permanence and constancy of indications, while it yields more

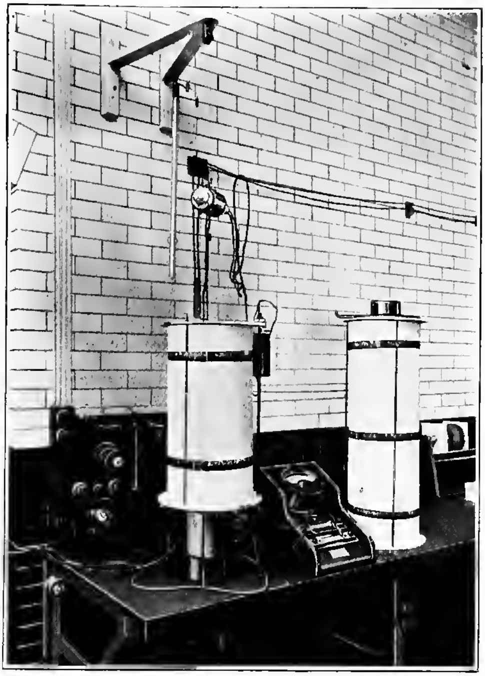

Fig. 27.

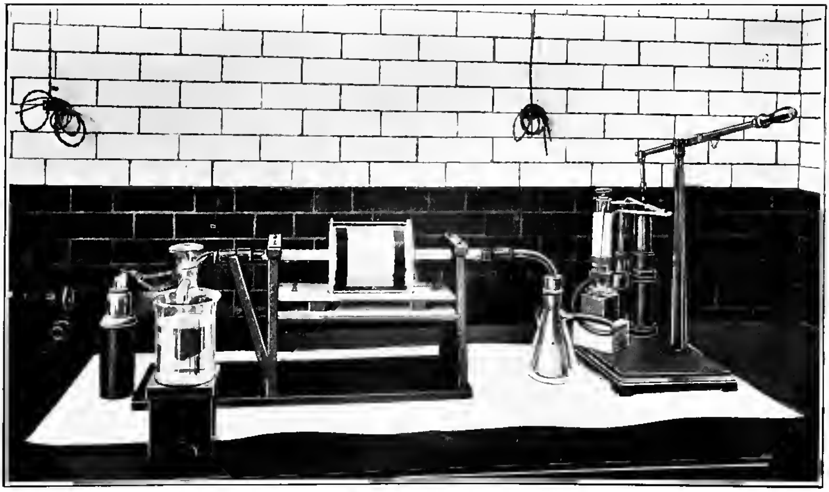

Fig. 36.

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than three times the electro-motive force per degree of temperature which is obtainable from a platinum-iridium couple.

The action of the thermo-couple consists in setting up an electro-motive force which is proportional to the difference between the temperatures of the hot and cold junctions. In the case of cooling or heating-curve work in the laboratory, the hot junction is placed in the specimen of metal under examination, care being taken to insure that the junction is properly placed as nearly as possible at the centre of the mass of metal. The " cold junction " is always kept at a temperature of 0° C. by being placed in a glass tube, which is itself plunged into a mass of melting ice. The ice-box usually employed in the author's laboratory consists of an ordinary (cheap) glass vacuum vessel in which the ice only melts very slowly. Such an " ice-box " in a horizontal position is seen in the photograph (Fig. 27, Plate VIII.), where the cold junction is allowed to travel up and down with the moving specimen. The whole of the thermo-couple and the wires leading to it must be carefully insulated electrically so as to remain entirely unaffected by the electric currents employed for heating the furnaces ; the hot junction must further be protected from actual contact with the metal specimens in order to avoid contamination of the couple wires. This protecting sheath—generally of fire-clay or of "alundum," or silica, undoubtedly introduces a slight " lag " of temperature between the couple and the metal, but, provided that the thermo-couple has been calibrated with the intervention of precisely the same kind of sheath, no error is introduced by this lag.

The actual calibration of the thermo-couples employed for this work is usually carried out by the aid of determinations of the freezing-points of certain metals, whose true temperatures are well known. These generally include the following :—

Copper (under charcoal)	1,083° C.
Silver (under charcoal)	960·5° C.
Aluminium (99·7 per cent., pure)	658·7° C.
Zinc (99·98 per cent., pure)	419·4° C.
Lead	327·4° C.
Tin	231·9° C.

The thermo-couple furnishes an electro-motive force which is proportional to the temperature difference between the hot and the cold junctions. To utilise this indication the thermo-couple must be attached to some form of electrical measuring instrument by means of which the electro-motive force can be read or registered. The simplest form of such an instrument is a galvanometer of high resistance whose deflections are read as measuring the indications of the couple. The resistance of the galvanometer must be high in order to avoid serious interference from changes of temperature in the couple wires themselves and in the connecting wires, for the galvanometer used in this way merely measures the small electric current which the thermo-couple is able to send through the circuit; this current depends both upon the electro-motive force of the couple and on the resistance of the circuit. In the latter factor the resistances of the couple wires and of the connecting leads play a part which becomes important if the resistance of the galvanometer is low. Beyond this, the simple deflection method has two very serious disadvantages. The first is that, with most sensitive galvanometers, the position of the zero is not constant; it follows that the actual value — in temperature or in "micro-volts"—of a given scale reading is not constant, and the observer has no means of telling, during the course of a series of observations for a heating or cooling curve, whether the zero has shifted from its original position. The second disadvantage is that the sensitiveness of the simple deflection method is somewhat limited. A scale one metre long is probably as much as can be conveniently employed, and if the curves are to be traced over a range of 1,000° C. then the scale value is 10° C. per millimetre. By one of the devices mentioned below, the effective length of scale for a range of 1,000° C. can easily be extended to as much as eight metres.

This increase of sensitiveness—and consequently, under proper conditions, of accuracy—is obtained first by the use of a more sensitive galvanometer, and in the second place, by balancing the greater part of the electro-motive force of the couple by a known electro-motive force taken from an instrument known as a "potentiometer." In this arrangement if, for example, the thermo-couple indicates an E.M.F. of 12,456 micro-volts (= ·012456 volts) then the stops of the potentiometer are set to give a counter E.M.F. of 12,400 micro-volts and only fifty-six micro-volts are read off by deflection. The process can be carried further so that the entire E.M.F. of the couple is balanced at each temperature and the galvanometer always kept at zero, but where the temperatures are changing somewhat rapidly, as in the taking of thermal curves, this is not convenient. The details of the electrical measuring instruments (potentiometers, etc.) employed for this purpose cannot be given here, but the reader will find full details in the literature of the subject (^{1}) and in the catalogues of the instrument makers. Only the outlines of the methods have been given here in order to enable the reader to appreciate the principles adopted.

With one of the better class of thermo-electric apparatus just referred to, the observer can readily determine accurately the temperature of the specimen of metal which is under thermal observation at any time during the heating and cooling process. The observations thus made can be recorded in various ways. The simplest of these consists in taking temperature readings at fixed intervals of time and then plotting the results with temperatures as ordinates and times as abscissæ. A "time-temperature" curve is obtained which indicates the behaviour of the metal in the most direct way. So long as the metal is simply being raised or lowered in temperature at a steady rate, this curve follows a smooth course; a departure from this smoothness indicates that there has been either an evolution or an absorption of heat within the specimen. The only objection to this type of curve is that the irregularities produced in it by comparatively small evolutions or absorptions of heat are themselves extremely small unless the curve is plotted to an impracticably large scale. Consequently a method of plotting the observations is adopted which is more economical of space and, therefore, allows of the use of a very much more open scale, with the result that even minute thermal phenomena appear quite clearly. This result is obtained by the use of what is known as the "inverse rate" curve first adopted by Osmond (²) in 1887. For this purpose the observer notes the intervals of time which are occupied by the metal in rising or falling through successive equal differences of temperature. Thus one might take the times occupied by successive rises of 3° C. and plot these as abscissæ against the actual temperature of the metal at each observation. In this way is obtained a curve whose ordinates are T (temperature) and whose abscissæ are $\frac{dt}{dT}$ where t is time. With a uniform rate of heating or cooling, this curve becomes a vertical straight line; an evolution of heat during cooling or an absorption of heat during heating causes the curve to deflect outwards and to form a hump or "peak." It can be shown that, if the rate of heating is uniform, the area of this peak is proportional to the quantity of heat evolved or absorbed. Some examples of curves of this kind are shown in connection with special metals later in this book (Figs. 50, 66).

Mention must also be made of another type of heating and cooling curve, known as the "differential" and the "derived differential." These are obtained by a method devised by Roberts-Austen (³), which consists in comparing the rate of heating or of cooling of the metal under experiment with a standard piece of metal placed in the same furnace and heated and cooled along with the experimental specimen. This method has the advantage that no clock or chronograph is required and that the results are capable of a high degree of accuracy, even when no extremely sensitive galvanometer is available. This is attained by the use of a "differential" thermo-couple which possesses two thermo-junctions arranged to oppose one another and placed one in the experimental piece and the other in the standard piece of metal—usually a platinum cylinder. The readings of this couple simply indicate the difference of temperature between the platinum cylinder and the specimen, and if these are plotted against the actual temperature of the specimen as obtained from the readings of an independent thermo-couple placed in the specimen, the "differential" curve of Roberts-Austen is obtained. Since the uniform cooling or heating of the platinum cylinder, which serves as a basis for this type of curve, is in reality proportional to the time which elapses between successive readings, this "differential" curve is practically identical with a time-temperature curve, the clock having been replaced by the platinum cylinder. Consequently, in order to make the differential curves comparable with the inverse-rate curves, we must plot, not the actual readings of the differential thermocouple at each temperature, but the change in its reading since the previous observation. If these are plotted against the temperature of the specimen, we obtain the curve first employed by the author (^{4}) and termed the "derived differential" curve. This is very similar to the inverse-rate curve and is practically identical with it in physical meaning.

We may now consider the forms which the thermal curves of metals and alloys will assume in various circumstances, in order to arrive at an understanding of the use which may be made of data furnished by these curves.[1] Beginning with the simplest case, the cooling of a pure metal from the molten, liquid state may be considered. If thermal observations—which we may assume to be made and plotted on the "inverse rate" principle—are taken, the resulting curve will run down regularly and smoothly until a certain temperature—known as the freezing-point—is reached. Down to this point the rate of cooling has remained constant or nearly constant and the time occupied by each successive fall of, say, 1° C. has remained the same or has merely undergone a gradual increase as the metal has cooled. The resulting inverse-rate curve therefore is a smooth, nearly straight and nearly vertical line (as in Fig. 28). As soon, however, as the metal reaches the "freezing-point" the fall of temperature is arrested. The process of solidification which then commences is accompanied by a very considerable evolution of heat, *i.e.*, the energy which had been stored in the liquid metal in the form of movement and mutual separation of the molecules, is liberated in the form of heat when the molecules assume the relatively close juxtaposition and comparative immobility of the solid state. Since the metal is losing heat by radiation and conduction to surrounding bodies, this evolution of heat does not lead to a rise of temperature, in fact, if a rise of temperature were to occur the process would be arrested, since the metal would then be raised above the temperature at which freezing can begin. Consequently the freezing process goes on at just such a rate that the heat set free by the process exactly balances the heat lost by the metal to external objects, and the temperature of the metal remains constant during the whole process. This constancy of temperature during the entire process of solidification is typical of only three classes of bodies, viz., pure metals, pure compounds of two or more metals, and the special class of alloys known as "eutectic alloys" which we have already mentioned; these three classes of bodies all share this characteristic—that they consist entirely of a substance or substances which freeze at the same temperature. The freezing, then, of a pure metal takes place entirely at the temperature known as the "freezing-point," and in spite of the continuous external loss of heat the temperature of the metal remains constant for the whole duration of the process. During the freezing in this case, therefore, the rate of cooling, *i.e.*, the rate of fall of temperature, becomes either zero or at all events very slow, and the inverse rate therefore very large; in other words, when there is a prolonged arrest in the cooling process the time occupied by a fall of temperature of 1° C. may attain a value of several minutes, and the inverse-rate curve takes a sudden jump outwards from the axis (*c*, Fig. 28). As soon, however, as the solidification of the whole mass of metal is complete, the evolution of heat ceases and the temperature again begins to fall. During the time occupied by the freezing process, however, the heated vessel in which the cooling metal is contained has continued to cool down, while the temperature of the metal itself has been kept constant, with the result that at the end of the freezing process the metal is left considerably hotter than its immediate surroundings. The rate of cooling is, therefore, considerably accelerated and the inverse-rate curve shows a corresponding deflection inwards (*d e*, Fig. 28). These small differences of temperature, however, soon become equalised and the cooling process continues smoothly and regularly until the ordinary temperature is reached. The inverse-rate curve thus produced is shown in Fig. 28 which is reproduced from an actual cooling curve of pure zinc. It will be seen that the peak of the curve is very sharp and narrow, indicating that the retardation of cooling, *i.e.*, the evolution of heat within the metal, was confined to a very short range of temperature.

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[1] Examples of actual thermal curves are given in Fig. 50, p. 140, and Fig. 66, p. 168.

We now turn to consider the more complicated phenomena met with when the cooling of a binary alloy is observed. Up to the point where solidification commences the process is the same as that already described in the case of a pure metal, except for the important fact that the temperature at which solidification commences in an alloy (apart from some special exceptions) is always lower than that at which the principal constituent metal of the alloy would begin to solidify. This is simply a case of the universal phenomenon of the lowering of the freezing-point of a liquid when a foreign element is dissolved

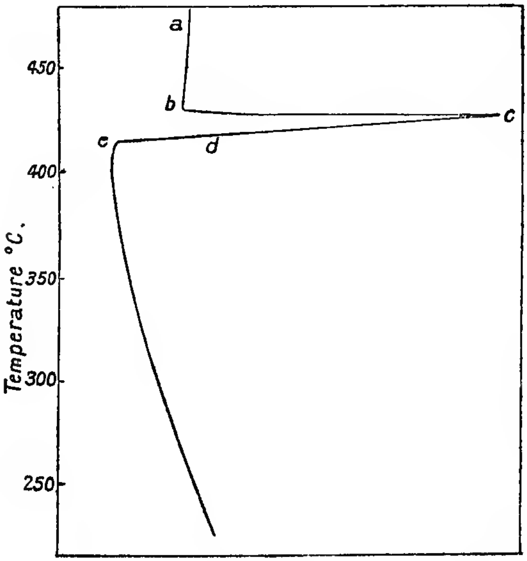

Fig. 28.—Cooling Curve of Pure Metal (Zinc) showing sharp freezing point.

in it, for—as we have already seen—the liquid alloy is simply a solution of two liquids in one another. As soon as the process of solidification commences, however, important divergences between the behaviour of a pure metal and an alloy make themselves felt in the time observations and in the resulting inverse-rate curve. What actually occurs depends on the type of alloy in question. We will first take the case of the type referred to as (*b*) in the previous chapter, *i.e.*, that in which the metals are mutually insoluble in the solid state and, therefore, separate out completely from one another in the process of freezing. Let the constituent metals of the alloy be called A and B and let us suppose that the alloy under observation contains a large proportion of A. In that case the freezing process will begin by the crystallisation, at one particular temperature, of a small quantity of A. The solidification of this small quantity of metal sets free a certain quantity of heat and the curve shows a sudden outward bend, resembling the outward sweep at the beginning of freezing in a pure metal; but in the present case the quantity of metal solidified forms only a portion of the entire mass, and the correspondingly smaller quantity of heat liberated causes a smaller deflection of the curve. The freezing of a relatively small quantity of pure A will, however, leave behind a liquid which contains relatively more of the second metal, B, than the original molten alloy, and this richer liquid will only begin to deposit further quantities of A at a lower temperature. As the temperature gradually falls, therefore, successive quantities of A will crystallise out, leaving the liquid successively richer in B. As solidification is gradually taking place during this entire process, heat is being continuously liberated and the natural rate of cooling of the mass is thereby continuously retarded—the inverse-rate curve therefore remains well out to the right (as at *bb*, Fig. 29) only gradually returning towards its normal position. This process of selective freezing, however, does not go on indefinitely, as might perhaps be supposed, *i.e.*, until the whole of the metal A present in the alloy has crystallised, leaving the liquid as pure molten B which might then crystallise separately. On the contrary, the concentration of B in the liquid cannot pass a certain definite limit, and this limit is arrived at when the temperature of the cooling alloy has also reached a limiting value ; when these conditions are attained, the whole of the remaining liquid solidifies at one temperature, giving rise to a considerable evolution of heat and producing upon the inverse-rate curve a sharp peak resembling that of the initial freezing of a pure metal.

If we compare this description of the solidification process with the account of the micro-structure of alloys of this type as given in the previous chapter, the correlation of the two will at once be apparent. The separation of the constituent A during the earlier process of selective freezing represents the formation of the crystals of pure metal seen in the micro-structure, while the solidification of the remaining liquid at the single lower temperature represents the solidification of the second, duplex constituent which we have already named the "eutectic" alloy. This word "eutectic," derived from the

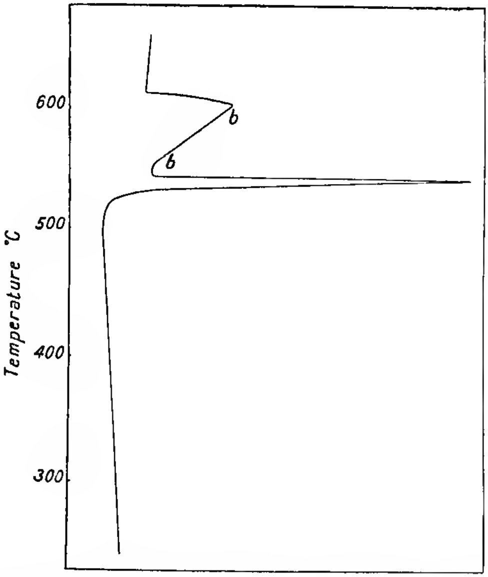

FIG. 29.—Cooling Curve of Eutectiferous Alloy showing Initial Freezing and Eutectic Arrest.

Greek, simply means "most fusible," and indicates that this alloy, or this constituent of an alloy, is the most fusible mixture, *i.e.*, the mixture of lowest freezing-point, which can be prepared out of the binary system in question. We have already indicated that this eutectic constituent has for each system of alloys a definite composition and also a definite freezing-point. It is obvious that an alloy consisting wholly of this eutectic constituent can be prepared, and this, like a pure metal, will solidify entirely at one temperature, viz., at that temperature at which solidification of all other alloys of the same series is *completed.* From the present point of view we may trace the effect of successive additions of a metal B to a metal A much in the same manner as we did in the case of the micro-structure, and this will serve to bring out the correlation more clearly.

The addition of B to A brings about a lowering of the temperature at which solidification begins, and also produces an extended range of temperature over which the freezing process is spread out; when the proportion of B is still small, the freezing process begins by the elimination of pure solid A, and this continues until nearly the whole alloy is solid. The portion which is left liquid, however, attains the eutectic composition and finally freezes as a whole when the temperature of the freezing of the eutectic is reached. With successive further additions of B the temperature of the commencement of solidification is successively lowered, but the temperature of final solidification remains unaltered, while the liquid which freezes last always attains the composition of the eutectic. Finally, by further additions of B the eutectic composition is reached; here the temperature of the initial freezing has been lowered to the temperature of eutectic freezing and the whole mass solidifies at one temperature. Further additions of B gradually reverse the series of changes just described, with this difference that the substance which now separates in the pure state, when freezing commences, is pure B where it was formerly pure A. The composition of the residual liquid and the temperature of final solidification remain unaltered until the whole mass of metal consists of pure B, which, of course, again solidifies in the manner already described for pure metals.

This entire process or group of processes, although somewhat complicated when thus verbally described, is very readily represented by the aid of a diagram. If we plot as abscissæ the percentage compositions of a series of alloys, and then, using temperature as ordinate, insert the points corresponding to the beginning of freezing in each alloy and also the points corresponding to the freezing of the residual metal or eutectic, we obtain a diagram which represents the entire set of processes in a simple manner. Such a diagram is shown for the imaginary case of two metals perfectly insoluble in one another in the solid state, in Fig. 30. Such a diagram is in reality a summary of the indications of the cooling-curves of all the alloys of the system, and from the diagram the nature of the cooling-curve of any of these alloys can be readily foretold. This relationship is indicated in the diagram (Fig. 31) where the cooling-curves of some of the alloys are shown. In looking at this diagram it must be remembered that the "peaks" of the cooling-curves really lie in a plane at right-angles to that of the diagram, since the co-ordinates of the cooling-curve are temperature and time, while those of the diagram proper are temperature and composition of the alloy. The diagram

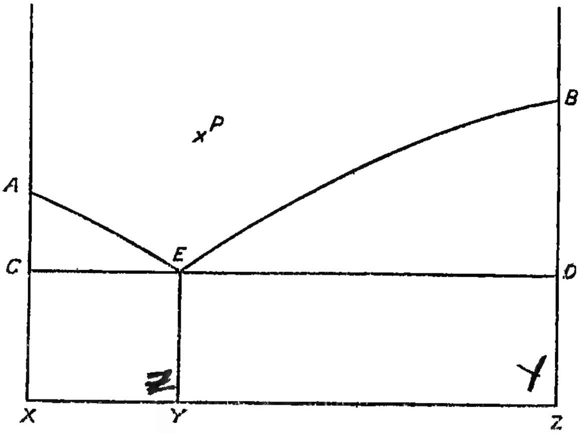

FIG. 30.—Ideal Equilibrium (Constitutional) Diagram of a simple Binary Eutectiferous System.

shown in Fig. 30, while thus representing a summary of a whole series of cooling-curves, has a further meaning, since it also serves as a species of map or chart of the various conditions in which alloys of this particular system can exist at different temperatures. Thus any point in the diagram corresponds to an alloy of definite composition existing at a definite temperature, the composition being that corresponding to the abscissa of the point and the temperature that represented by the ordinate. It will also be seen that the lines joining the various freezing-points, viz., the lines AEB, CEF and EL, divide the whole area of the diagram into a number of separate fields or areas. If we look at the matter more closely we shall see that each of these areas represents a definite state of the alloys. Thus, if we take any point such as P, lying above the line AEB, the alloy corresponding to that point will be completely liquid ; any point lying above the line AEB represents an alloy at a temperature above that at which solidification can commence. Next, if we take a point Q lying within the lines AE, EC, CA, such a point must represent an alloy partly solid, partly liquid, and from what has been said above in describing the process of freezing of such alloys we see that the part which is already

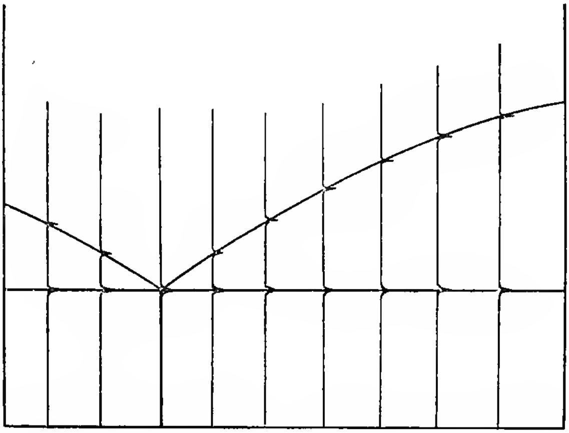

FIG. 31.—Diagram illustrating the relation between arrest-points on Thermal Curves and the lines of the Constitutional Diagram.

solid will consist of the pure metal A. The whole area or field AECA thus represents alloys consisting of mixtures of solid A with a residue of liquid, but it should be noted that the proportion of solid to liquid will vary very widely for different portions of this area. If now we take a point below the line EC, we find that the alloy must be completely solid, since the line EC passes through the points of final solidification, or freezing of the eutectic. The alloys in the region CEZX consist of a mixture of solid A with solid eutectic. Near the line CX the A constituent predominates, and the eutectic occupies only a small proportion of the whole volume, but, as the line EZ is approached, the eutectic is present in increasing proportions until, when the line EZ itself is reached, the entire alloy consists of the eutectic. This, of course, corresponds with the fact indicated by the meeting of the various lines in the point E, which indicates that for an alloy of this composition, *i.e.*, for the eutectic alloy, the temperature of the commencement of freezing is also the temperature of final complete solidification, the eutectic alloy having thus a simple freezing-point like that of a pure metal. The condition of the alloys corresponding to the remaining areas of the diagram will readily be understood on the basis of those already described ; the region BEDB corresponds to mixtures of solid B with liquid, and the region ZEDY to mixtures of solid B with solid eutectic.

A diagram of this kind is generally known as an " equilibrium diagram " of the system of alloys in question ; this name is applied to it because the diagram indicates the conditions which the alloys would assume for any given composition or temperature, provided that they were allowed to attain equilibrium. This latter proviso is very important, because in a great many cases alloys can be brought to temperatures and compositions indicated on such diagrams without assuming the conditions implied by the diagram. These other conditions are always of a more or less temporary and artificial nature—exposure to suitable temperatures which allow of more ready adjustments of molecular conditions always results in allowing the alloy gradually to revert to the condition of stable equilibrium. On the other hand, these other "meta-stable" conditions are of very considerable importance, since most of the metals in ordinary use are to some extent held in such a condition by the difficulty which their molecules experience in rearranging themselves at ordinary temperatures. A striking example of this class of phenomenon is found in hardened steel, and, indeed, all industrial steel comes under this description to some extent. The equilibrium diagram, however, shows the "natural" state of the alloys, *i.e.*, that state to which they revert whenever the opportunity is given them to do so. In many cases, however, where true equilibrium conditions are not thoroughly known or cannot be even approximately realised in the laboratory, the diagram represents partially meta-stable conditions and is better termed a "constitutional" rather than an "equilibrium" diagram.

Certain of the lines seen in the diagram of Fig. 31 have received names which it will be convenient to define here. Thus the lines AE, EB form the lower boundary of that region in which the alloys are completely liquid; they are sometimes called the "melting-point curve," but since most of the alloys do not possess a single "melting-point," it is preferable to adopt the Latin term "*liquidus*" for this curve. Corresponding to the line which bounds those regions of the diagram which represent entirely fluid alloys, we have a line which bounds those regions within which the alloys are completely solid, and this line is known as the "*solidus*" curve. In the diagram of Fig. 30 the *solidus* curve is represented by the simple straight line CED, but it must be remembered that this diagram corresponds to an ideally simple case, the diagrams of actual alloys being always much more complex. The above definitions, however, hold in all cases.

We have now to consider some of the complications which are introduced into both cooling-curves and constitutional diagrams when the simple, ideal condition laid down above—that the two metals shall be mutually completely insoluble in the solid state—is departed from in varying degrees.

When the state of mutual solution of two metals remains unchanged by the process of solidification, we have seen that the result, so far as the microscope is concerned, is the production of a homogeneous mass of crystals quite similar to the aggregate of crystals which constitutes a pure metal. Corresponding to this micro-structure we should expect the cooling-curve of such a " solid solution " to resemble that of a pure metal. To a certain extent this is true, but there is an important difference, and one which is very apt, unless extremely gradual cooling is resorted to, also to introduce a disturbing factor into the resulting micro-structure. Experiment soon shows that such solid solutions do not possess a simple freezing-point like that of pure metals, but that they show a " freezing range," *i.e.*, a range of temperature of definite extent over which the freezing process extends. If the cooling process were artificially arrested at any temperature lying within this range, the alloy would be found to consist of a definite proportion of solid and liquid—a proportion which would be quite fixed for any given temperature. The freezing process of a solid solution is therefore obviously different from that of a pure substance, and we must now examine this difference.

In the first place, the temperature at which freezing commences will, as a rule, be lower than that at which the pure metal would freeze, and we find, further, that while in the case of the pure metal during the freezing process the portion which has already solidified is exactly the same in composition as that which is still liquid, this is not and, indeed, cannot be the case where the formation of a solid solution is concerned. For if the part already frozen and the part still liquid were exactly alike in composition, their freezing temperature would also be the same, and the rest of the liquid would solidify without any fall of temperature ; this is exactly what does occur in a pure metal, but does not occur in a solid solution. Let us consider an alloy containing a small proportion of B dissolved in A. When freezing commences, the solid which separates first contains less B than the liquid alloy as a whole. The remaining liquid is thus left richer in B than it originally was, and it therefore possesses a lower freezing-point. As soon as the temperature falls, a further quantity of solid is formed, containing more B than the first portion of solid, but less B than the liquid from which it is deposited. At this stage, therefore, the alloy consists of cores of solid containing least B, shells of solid surrounding them containing rather more B, and a residual liquid still richer in B. This, however, is not the stable condition, for, if time be allowed, the composition of the whole solid will become the same, viz., like that of the fresh solid formed at the temperature in question; but this can only occur by the slow process of diffusion, some of the excess of B travelling from the liquid through the already solid shell richer in B to the core which contains the lowest proportion of B. The process of solidification, extended over a range of temperatures as thus indicated, continues until the whole of the alloy has become solid, provided that the composition of the alloy is such that the limit of solubility of solid B in solid A is not passed at any time. If time be allowed, as already indicated, the whole of the solid thus formed will attain one and the same composition, and an aggregate of homogeneous crystals will result. When, however, the rate of cooling has not been slow enough to allow the process of diffusion to equalise the composition, each of the crystals of the solid solution will consist at the end of the freezing process of a core of metal relatively poor in B, surrounded by successive shells or layers increasing in their content of B from the centre outward. When alloys of this kind, which have been cooled somewhat rapidly from fusion, are examined under the microscope, very distinct traces of the cores and shells just described are often found ; in some cases the changes of composition between adjacent layers are very strongly marked, and the alloy almost looks as if it possessed a true duplex structure, while in other cases the changes of composition are very gradual, and the cores then present a shadowy, ghost-like appearance which is very readily recognised whenever met with. An example of such a " core " structure has been shown above in Fig. 21, Plate VI.

The shape of the cooling-curve of an alloy of this kind is shown in Fig. 32. The commencement of freezing is well marked, but there is no definite arrest—the peak in the inverse rate curve is spread over a range, and, although the maximum departure of the curve is always found near the beginning of the process, the curve only returns to its normal position at a temperature at which the whole of the alloy has solidified. The precise position of the end of the freezing process, however, is not usually sharply defined on such curves. As in the case of the class of alloys formed by metals which are mutually insoluble in the solid state, the cooling-curves of a system of alloys of metals which are mutually soluble in the solid state can also be grouped together in the form of a constitutional diagram, although the shape of this diagram is not so well defined. A typical example is given in Fig. 33, which represents the alloys of copper and nickel.

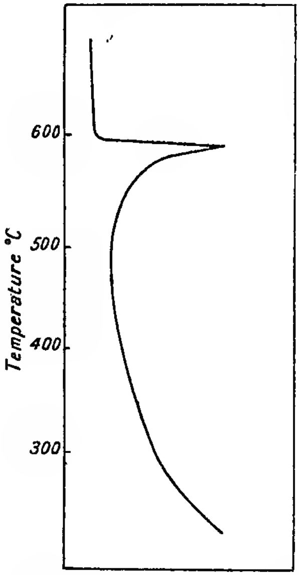

Fig. 32.—Cooling Curve showing the Freezing-Range of an Alloy forming a Solid Solution.

The line ACB is the "*liquidus*," forming the lower boundary of the region in which the alloys are completely liquid; the "*solidus*" is indicated by the line A*s*B, and the relations of the cooling-curves to the diagram are indicated by the dotted lines representing the inverse-rate cooling curves of a few of the alloys of the series. The shape of the *liquidus* curve in such a system of alloys, however, is not always of the kind indicated in Fig. 33. In certain cases the curve either droops or rises in the centre, although it is not quite certain whether in such cases special disturbing causes may be at work, such as the formation of a chemical compound between the two metals, the compound, however, being completely soluble in either of the constituent metals. With such questions we need not, however, concern ourselves here—the typical form of the *liquidus* curve of a series of alloys forming solid solutions is that of a smooth, continuous curve showing no sharp break or angle. With this continuous form of curve the properties of such alloys correspond very closely, also forming a continuous series without sharp breaks or changes of properties.

While the class of alloys consisting of metals entirely insoluble in one another in the solid state may safely be regarded as an ideal case never met with in practice, the class of alloys whose constituent metals are mutually soluble in all proportions in the solid state is met with in quite a number of cases of actual binary systems. In the greater number of cases, however, metals behave towards one another in an intermediate manner, the metals being soluble in one another in the solid state to a definitely limited extent. The behaviour of their alloys during freezing and the shape of their constitutional diagrams is, therefore, also of an intermediate nature. Alloys whose composition is such that their solidification implies no disturbance of the state of mutual solution of the two metals behave as if they belonged to class (*a*) described above, solidifying in the manner typical of solid solutions and exhibiting the corresponding cooling curve and micro-structure. Thus, if

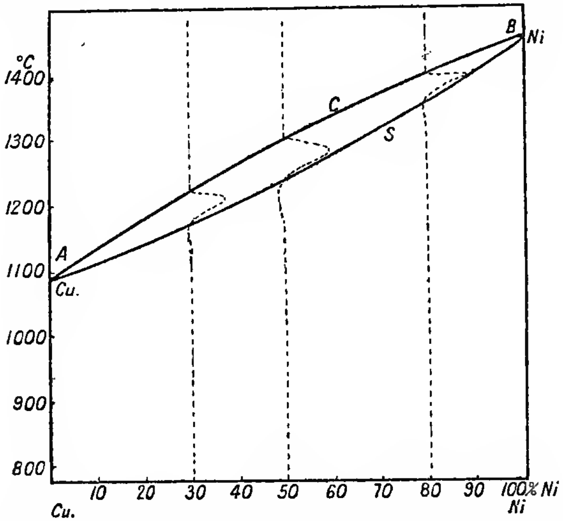

FIG. 33.—Constitutional Diagram of the Alloys of Copper and Nickel, typical of an uninterrupted series of Solid Solutions.

metal A is capable of retaining say 8 per cent. of metal B in solid solution, then alloys of A and B containing less than 8 per cent. of B will, at all events if slowly cooled, solidify as simple solid solutions. On the other hand, those alloys of the series whose composition places them beyond the limit of solid solubility of the metals at either end of the series behave in most respects in a manner very similar to alloys of class (*b*) described above. The only difference is that the solid which first crystallises is not pure metal, but the saturated solid solution of one metal in the other, according to the end of the series to which the particular alloy belongs. The cooling-curves of alloys belonging to this portion of the series are in every way like those of alloys of class (*a*), and the constitutional diagram is correspondingly similar. The diagram of the whole of such a system is, therefore, made up of three distinct portions—a central portion BC resembling the diagrams of class (*a*) and portions AB and CD at each end, typical of alloys of class (*b*). A diagram of this type is shown in Fig. 34. The

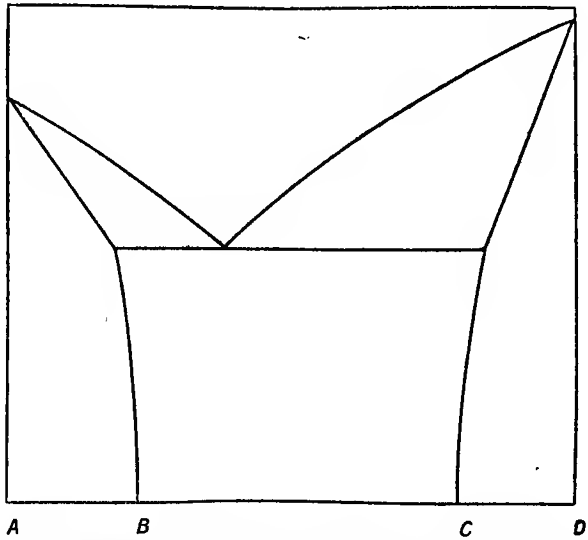

Fig. 34.—Constitutional Diagram typical of Alloy Systems partly eutectiferous but forming solid solutions at each end of the series.

alloys of silver and copper belong to this class. The *liquidus* is, in a general way, very similar to that of a system entirely belonging to class (*a*), but the *solidus* differs widely—the line of eutectic solidification does not extend to the two sides of the diagram, the *solidus* being completed by two curved branches leading from the end of the eutectic line up to the freezing-points of the two metals. The diagram is again divided up into fields which represent groups of alloys in different conditions, but we need not enumerate them in detail, since the reader will be able, by comparison with the two simpler cases, to discover the interpretation of each field, if it is not at once obvious to him from what has already been said.

A further class of alloys, possessing a somewhat different constitutional diagram from those already described, are those systems in which definite inter-metallic compounds are found. These, however, need but little separate discussion here, since the whole matter can be regarded in a very simple manner. From the point of view of cooling-curves and constitutional diagrams, as well as from that of micro-structure, any definite inter-metallic compound may be regarded as being simply another pure metal—it is in fact a pure substance of metallic character, so that this method of regarding it is by no means strained. If, however, this idea be kept steadily in mind, the facts concerning inter-metallic compounds are much simplified. A system of alloys of two metals in which such compounds occur is simply broken up into a series of systems. Thus, if the metals A and B form the compound A_mB_n, the series of alloys between A and B may be looked upon as two successive series, one consisting of the alloys of A with the compound metal A_mB_n, and the other of the compound and the metal B. Each of these systems has its own characteristic constitutional diagram, usually with series of solid solutions, a eutectic alloy, etc., and to obtain the complete diagram of the A–B system it is merely necessary to juxtapose these two diagrams. In doing this, we see at once that, since the compound A_mB_n forms the right-hand end of the first diagram and the left-hand end of the second (see Fig. 35, relating to the alloys of magnesium and tin), the *liquidus* and *solidus*[1] of both diagrams will meet at the point which represents the freezing-point of the pure compound A_mB_n, and—what is more—both *solidus* and *liquidus* fall away from the point corresponding to the compound. It is thus clear that in any complete constitutional diagram the presence of a pure compound will be marked by (1) a maximum point in the *liquidus*, and (2) a meeting-point of *solidus* and *liquidus*. Correspondingly, in the micro-structure we find the compound represented by the typical structure of a pure metal, viz., an aggregate of crystals all of one kind, although these, as we have already seen, are not always to be distinguished from the crystals of a slowly-cooled solid solution.

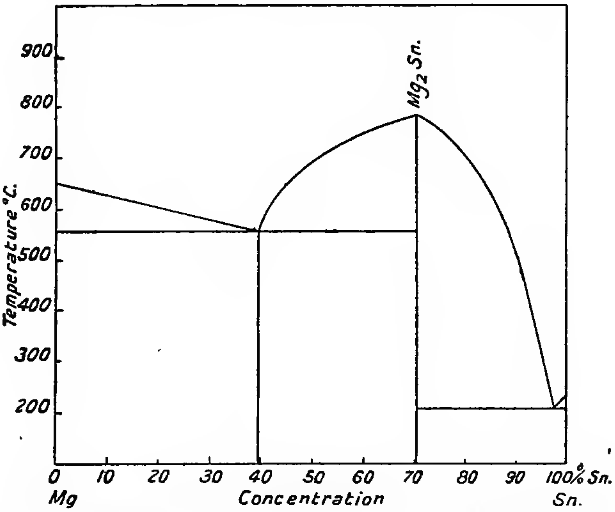

FIG. 35.—Constitutional Diagram of the Alloys of Magnesium and Tin, typical of a series forming a definite Inter-metallic Compound.

It may here be remarked at once that, from the point of view of the mechanical properties of alloys, inter-metallic compounds and alloys consisting to any notable extent of such compound bodies are entirely useless. It is a very striking fact that these compound bodies are always brittle and, as a rule, very weak mechanically. Their presence in small proportions in many cases serves to strengthen and stiffen metals or alloys which would otherwise be unduly soft, but as soon as a notable proportion of such a body is present the ductility of the alloys disappears. The same action, of course, also occurs where pure metals, or solid solutions of pure metals, of a brittle nature enter into the structure of an alloy, but the interesting fact at the present point is the almost universal occurrence of brittleness in the case of inter-metallic compounds.

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[1] The vertical part of the *solidus* in Fig. 35 should really be shown as two lines, very close together and sloping very steeply towards the maximum of the *liquidus*; they are shown merged into a single vertical line.

Another very important feature which is frequently met with on constitutional diagrams has yet to be discussed ; this feature is a horizontal line (or lines) representing a series of changes occurring in some (or all) of the alloys at a temperature below that of complete solidification. Such changes occur in many solid alloys, in some cases at moderately high temperatures, while in others the changes take place at quite low temperatures. When the cooling-curves of such alloys are followed to temperatures below the end of the freezing process, fresh evolutions of heat, represented by peaks on the cooling-curves, are met with. When these are observed in successive members of a series of alloys they usually lie on a horizontal line in the diagram, although in a certain number of cases curved lines are met with. In the great majority of cases, also, it is possible to trace some change of micro-structure which is associated with the evolution of heat. Such changes of structure are usually observed by means of a process known as "quenching." For this purpose small pieces of the alloy are raised to a temperature just above that at which the evolution of heat takes place and are kept at that temperature for a sufficient length of time to attain the condition of equilibrium which corresponds to that temperature. Then the specimen of alloy is cooled as rapidly as possible, usually by immersion in cold water. A special apparatus for effecting this operation without either removing the specimen from the furnace in which it has been heated, or exposing it to oxidising gases, has been devised by the author (5), and by its aid this operation can be effected with great precision. This apparatus is illustrated in Fig. 36, Plate VIII. The very rapid cooling undergone by the specimen of metal in these circumstances is intended to prevent the occurrence of the change which gives rise to the evolution of heat under study, and it is found in practice that, although as a rule such changes cannot be entirely suppressed even by the most rapid cooling, they are reduced to such an extent that a good idea of the true structure of the metal as it existed at the quenching temperature can be arrived at. A comparison with the micro-structure of a piece of the same alloy when slowly cooled, then serves to reveal the nature of the transformation which the metal has undergone in passing through the change accompanied by the heat-evolution. Photo-micrographs of an alloy of copper and tin containing 13·4 per cent. of tin, one slowly cooled, another quenched from a temperature of 700° C., and a third annealed at 480° C., are shown in Figs. 58, 59, and 60, Plate XII. Perhaps the best known of such changes are those occurring in carbon steels, but these will be dealt with in a later chapter.

The data for the establishment of a constitutional diagram which are furnished by heating and cooling-curves are not, however, exhausted when the temperatures of all the observed arrest-points are plotted on the diagram. The quantities of heat evolved or absorbed at each of these arrest-points are also of importance. Were it possible to measure these quantities with any great degree of accuracy they would furnish data of the highest importance, but in practice the quantitative indications of thermal curves must be regarded as decidedly approximate. Whether the simple duration of an arrest be observed, as has been done by Tammann (6) and his collaborators, or whether the more elaborate and accurate method of measuring the areas of the peaks of carefully determined inverse-rate or derived differential curves be adopted, as has been done by the author (7), no very high degree of accuracy can be attained, principally because the end-point of an arrest is never sharply defined, and also because the conditions of heating and cooling cannot be kept absolutely constant from one alloy to another. Yet even the approximate data are useful, provided that care is used in their interpretation; this is particularly necessary where there is any possible doubt whether the heat-evolutions which are being measured take place under conditions of equilibrium or whether the alloys are in a partially meta-stable condition. Where the latter is the case, the quantity of heat evolved or absorbed in a given instance may vary owing to causes outside those under immediate investigation, and false conclusions may be arrived at. With these difficulties in mind, the indications of a quantitative nature obtained from thermal curves may be utilised to determine the concentration at which a eutectic point occurs, since the heat evolved by the freezing of the eutectic will be at a maximum in a specimen containing nothing but eutectic, and will fall off regularly in alloys whose composition lies on either side of the eutectic composition. If the quantities of heat evolved during cooling are plotted as ordinates against the composition of the alloys as abscissæ the resulting curve shows a peak or maximum which indicates the eutectic composition, in the manner shown in Fig. 37. In the same way, the end of a eutectic line where it either abuts against a vertical line indicating a compound or a pure metal, or where it merges into the curved "*solidus*" of a series of solid solutions, as at F and H in Fig. 48, may be inferred by continuing such a curve as that of Fig. 37 to the point where it crosses the axis of composition, but this extrapolation is always rather uncertain. Similarly, where a compound is formed by a reaction between solid and liquid portions of an alloy, the composition of the compound may be determined by finding, much as in the case illustrated in Fig. 49, the composition corresponding to the maximum heat-evolution; but here it is particularly important to be certain that in every case the

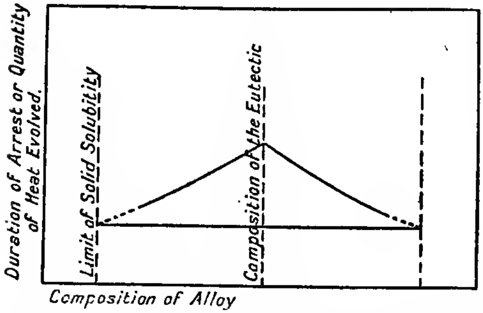

FIG. 37.—Diagram of Thermal Analysis Curves.

reaction has had time to complete itself, otherwise the quantity of heat evolved may depend more on the rate of cooling than on the true composition of the compound.

The constitutional diagram as discussed in the preceding pages would almost appear to be little more than a summary of the purely thermal data obtained from heating and cooling curves. Yet while these are extremely useful and important in assisting an investigator to establish such a diagram, they are not in themselves quite sufficient for that purpose, and their indications must be checked and amplified by microscopic research. In many cases this is merely a question of observing whether a new constituent appears where the supposed lines of the diagram would lead one to anticipate its coming, and whether the typical eutectic structure occurs, as the diagram would suggest. In other cases more elaborate investigation is required. The use of annealing at a temperature just above a line of thermal arrest-points, followed by quenching, has already been mentioned. In some cases, however, lines of the diagram cannot be located at all by the pyrometer and there microscopic research is the principal resource. For instance, since thermal curves only represent vertical sections of the diagram, these curves cannot be used to fix the position of vertical lines in the diagram. Where these lines indicate the limits of solid solubility their exact position can best be settled by means of a series of small specimens of the alloys ranging a short way on either side of the supposed line. These must then be " annealed " for a long period—in some cases amounting to many weeks—at exactly known temperatures, and subsequently examined with the microscope. Up to a certain limit in composition they are found to have become homogeneous—*i.e.*, after the prolonged annealing they consist solely of a single constituent. Beyond that composition no amount of prolonged heating will render them entirely homogeneous—*i.e.*, traces of the second constituent persist to the end. The limit of solubility is thus fixed at the boundary between these two different results. In the same way, quenching experiments often serve as the only true guide to the position of the " *solidus* " curve in a range of solid solutions.

We have already seen that thermal curves yield no satisfactory indication of the exact end of the process of solidification. This point can, however, be ascertained with considerable accuracy by quenching small specimens of suitably chosen alloys from a series of temperatures lying slightly above and slightly below the temperature at which the "*solidus*" is likely to be met. The specimens quenched from a temperature slightly above the *solidus* must contain, at the moment of quenching, a very small amount of liquid (molten) metal, and, during the rapid cooling which occurs in quenching, this liquid metal solidifies very quickly and thus produces minute regions of very fine structure. These "fusion spots" are readily noticed when the specimen is afterwards polished and etched, so that it becomes fairly easy to say which of a series of specimens have been quenched from temperatures above and which from below the "*solidus*."

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CHAPTER VI

THE CONSTITUTIONAL DIAGRAM AND THE PHYSICAL PROPERTIES OF ALLOYS

THE " Constitutional Diagram " has so far been considered almost entirely as a representation of the behaviour of the alloys at various temperatures so far as solidification and fusion are concerned, but the diagram in reality relates to all the physical properties of the materials—indeed, in the case of the lines of a diagram which relate to a transformation occurring in the solid alloys there is nothing in the nature of a change of state connected with the passage from one of the fields of the diagram to another. It is, however, a universal rule that passage across the boundary of any of the fields of a properly constructed constitutional diagram involves a change in most of the physical properties of the alloys—whether the transition from one field to another be due to change of temperature or change of chemical composition.

This connection between the constitutional diagram and the properties of alloys is, of course, not only useful for the purpose of forecasting the probable properties of an alloy of given composition from its position in the diagram, but it is also available in the reverse way, for by the study of the changes in physical properties of a group of alloys with changing composition and temperature, it is sometimes possible to fix with accuracy the position of certain lines of the diagram which are not readily ascertained by either microscopic or thermal methods. Almost every physical property, and even some essentially chemical or electro-chemical properties, have been utilised in this way, and although none of them have as yet proved as powerful for this purpose as the use of the pyrometer and the microscope, yet valuable results and confirmations have been obtained in this way.

It is not possible to enter into a detailed account of these varied investigations here, and little more than an enumeration will be attempted. The references to the literature will, however, enable the reader to follow up any of these paths of inquiry as far as it has hitherto been explored.

One of the most obvious physical properties which might be correlated with the constitutional diagram for the present purpose is the specific volume (1) or density of metals and alloys, and more particularly the changes which the specific volume undergoes as the alloy is heated and ultimately melted, or during the reverse process. This method has been employed by Charpy and Grenet (2) for the study of the critical points in steel, but it does not lend itself well to the exact study of changes involving fusion or solidification. The author has attempted an investigation of this kind for the more fusible alloys, such as those of tin and lead, and has developed a method of differential weighing against a "neutral" body for that purpose (3); unfortunately, however, the difficulty of finding a liquid in which the specimens of alloys could be weighed at temperatures up to and above their melting points has not yet been satisfactorily solved. A certain amount of work has, however, been accomplished on very fusible alloys—such as amalgams and alloys of the alkali metals—in Germany (4). The whole subject has been very fully reviewed recently by Guertler, who has worked out the theory of the whole matter very clearly. Mention must also be made of the efforts of Turner (5) and his collaborators (Murray, Ewen, Haughton, Chamberlain, and others) who endeavoured to trace the volume changes in metals and alloys by pouring the molten material into a sand mould of a T shape and following the movements of the "free" end of the metal by means of a delicate indicator or "extensometer." A very large amount of work has been done in this way and some interesting results have been obtained, but, unfortunately, the method is open to serious and fundamental objections, and it is now admitted that the results, although in certain cases they appear to be closely related to the form of the constitutional diagram, cannot attain a degree of precision sufficient to be of use in the determination of these diagrams.

The relationship between magnetic properties and the constitution of alloys is not as yet sufficiently well understood to allow of magnetic measurements being satisfactorily employed for the study of alloy constitutions, although, of course, the magnetic properties of iron and its alloys are often considered in discussions of their constitutional diagrams, particularly in relation to the much-discussed question of the " beta " phase in pure iron and mild steels. Although these magnetic properties have been very widely studied (6), it does not appear to the author that they can be very safely used as critical data in such questions; the magnetic behaviour of any given piece of iron or steel appears to be influenced in a very complex way by its entire past history—thermal, mechanical and even magnetic—on the one hand, while, on the other hand the magnetic properties would appear to be directly related to the nature of the atoms of the element rather than to the arrangement—crystalline or molecular—in which those atoms may be present at any given time. Apart from the alloys of iron there is only a limited range of metals and alloys in which magnetic properties are sufficiently strongly marked to invite careful study. Among these the alloys of copper with aluminium and manganese, and some allied materials, generally known as " Heussler alloys " (7), are of special interest since they constitute materials showing comparatively strong magnetic properties while they appear to contain no strongly magnetic element. The fuller study of these questions, however, has shown that several compounds of manganese behave as if that element were magnetic when present in a certain state of combination, and similar properties probably exist in other allied elements.

Another interesting feature which connects the magnetic properties of alloys with their constitution is the effect produced on the magnetic hysteresis of pure iron by the addition of various alloying elements in small quantities. It was thought at one time that all impurities or intentional additions to pure iron tended to increase its magnetic hysteresis, and for such purposes as transformer sheets the aim was to produce the purest possible commercial iron. In this respect the effect of impurities or additions would have been strictly analogous to their effect on the electrical conductivity of metals. This analogy, however, does not hold, since it has been found that the addition of certain elements, notably aluminium and silicon, so far from increasing the hysteresis, markedly reduces it (^{8}). Study of the matter has shown that the effect of an addition or impurity in this respect is a function of the relative atomic volume ; elements whose atomic volume is less than that of iron tend to increase the hysteresis, while those whose atomic volume is greater have the opposite effect. This observation has proved of considerable practical value in the production of sheet iron of remarkably low hysteresis for magnets and transformers, while it is also of considerable theoretical interest in connection with the theories of magnetism in metals, such as that of Ewing (^{9}), and the "magneton" theory of Weiss (^{10}).

The electrical properties are of far more immediate importance in connection with the constitutional study of metals and alloys. This method of investigation has now attained such a degree of importance that no investigation of the constitution of a system of alloys can be regarded as really complete until a study of electrical conductivities and their temperature coefficients has been carried out. A very full statement of the relation between these electrical properties and the constitution of alloys has been given by Guertler (^{11}) in a paper read to the Institute of Metals in 1910 and only a brief indication of the wider aspects of the subject can be given here.

In regard to electrical conductivity, observation has shown most definitely that the highest conductivity is always found in a pure metal, and that the presence of any alloying element reduces the conductivity very materially, particularly if the second element forms a solid solution with the pure metal. This occurs even in cases where the added metal itself is a far better conductor than the metal to which it has been added. A satisfactory physical explanation of these phenomena has not yet been put forward, although an attempt is made to account for the phenomena of electrical conductivity in metals by the electron theory which supposes that the electric current in a metal is constituted by a stream of moving electrons ; the electrical resistance of the metal then becomes a simple frictional resistance to the movement of these electrons, but it is not easy to see why the simultaneous presence of two or more kinds of atoms or molecules—all of whose attendant electrons are supposed to be alike—should produce such striking effects.

The correlation between the phenomena of electrical conductivity and the constitutional diagram of a system of alloys however, a very close one. If the specific electric conductivity is plotted for a binary system it is found that some very typical curves are obtained. Taking the various types of binary systems in the same order as before, we have first those in which there is a complete and unbroken series of solid solutions between the two metals. For such a system the curve of conductivities takes the form of a deep U, falling rapidly from the pure metals at the ends of the series and becoming more or less horizontal for the middle of the series. The depth of the U is, however, very great ; thus in the copper-nickel series, the alloy known as " constantan " has a conductivity of only one-thirtieth of that of copper, while it consists of 60 per cent. copper and 40 per cent. nickel.

In alloys of our second group, where no solid solutions are formed, and in which, with the exception of the pure metals forming the ends of the series and the eutectic alloy itself, all the members of the series consist, in the solid state, of crystals of one of the metals embedded in the eutectic, the curve of electrical conductivities assumes a very different shape. Here the two metals are present in a state of simple mechanical mixture or juxtaposition—there is no intermingling of the molecules, and thus each retains its original electrical conductivity unaltered, and the alloy exhibits a behaviour which is the arithmetic mean of its two constituents. The curve of conductivities is thus—if plotted in relation to composition by volume—a simple straight line joining the values for the two simple metals. Such an actual case is probably never met with in practice, and, indeed, it can be shown that there must be a slight degree of mutual solid solubility between any two metals—complete absence of molecular interpenetration cannot really exist.

Consequently, although several binary systems of alloys—such as those of cadmium and zinc, and of lead and antimony—closely approach the limiting case, in the majority of binary

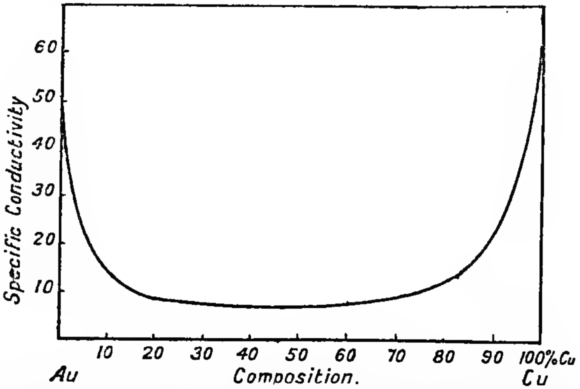

FIG. 38.—Curve of Specific Electric Conductivity typical of an unbroken series of Solid Solutions. (Alloys of Gold and Copper.)

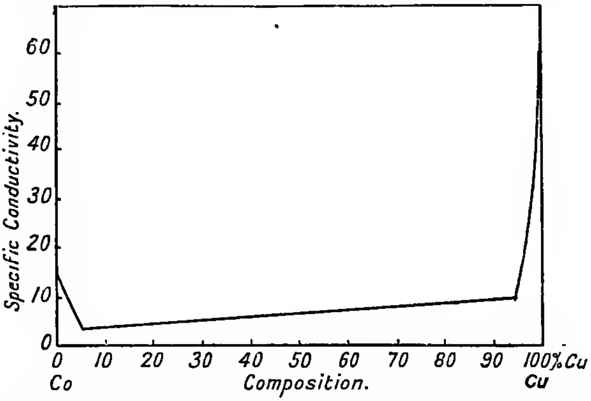

FIG. 39.—Curve of Specific Electric Conductivity typical of a Eutectiferous Series. (Alloys of Cobalt and Copper.)

alloys of the " eutectiferous " type, the curve of conductivity drops sharply at either end for a short distance and then becomes horizontal. This form is, of course, typical of the intermediate type of alloys in which there is a limited range in which the two metals form solid solutions, the remainder of the systems being eutectiferous. Here we have a drop of the conductivity curve at either end very marked, with a straight line forming the intermediate part. Typical curves of this kind are given in Figs. 38 and 39, representing data obtained from the alloys of gold and copper, which form an unbroken series of solid solutions, and those of copper and cobalt, which are eutectiferous over the greater part of their range. Reference to these figures serves to show that, where the measurements of electrical conductivity have been made on a sufficient number of alloys, it becomes possible to determine the type of the binary system in question from the shape of the conductivity curve. The reservation as to a sufficient number of measurements is essential, however, as with a few points only it would not be possible to distinguish between the "solid solution" and the "intermediate eutectiferous" types. This is illustrated diagrammatically in Fig. 40, where it is clearly shown how two different types of curve may agree in fitting points representing only a few determinations. The same remark also applies, by the way, to thermal and other data and, indeed, actual mistakes in laying down a constitutional diagram have been made in several instances owing to the fact that the observed

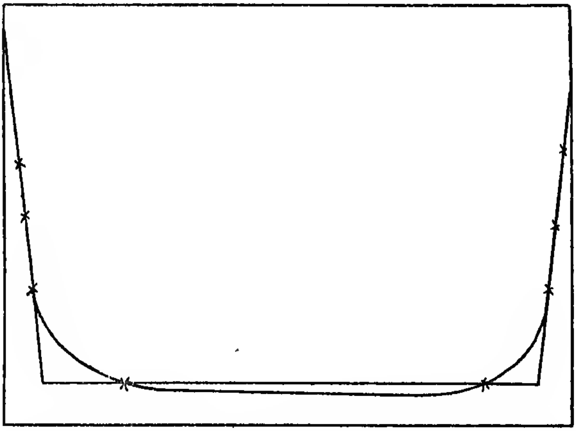

Fig. 40.—Diagram illustrating Need for numerous Observations in laying down Curves.

points were too far apart to indicate all the important features.

In the case of more complex alloys, containing either definite compounds or series of solid solutions which are based upon definite compounds, the conductivity curve assumes more complex shapes. In these alloys new solid constituents make their appearance at various points along the axis of concentration, and corresponding to these sudden changes in structure and constitution, the curve of conductivities generally, but not always, changes its direction. As a rule, therefore, a change of direction in the conductivity curve may be taken as indicating that one has passed into a new field or region of the equilibrium diagram, but it is not safe to conclude that, because the conductivity curve shows no deflection, no line of the diagram can have been crossed. Definite inter-metallic compounds resemble pure metals in their conducting properties to some extent—*i.e.*, they conduct better than either mixtures

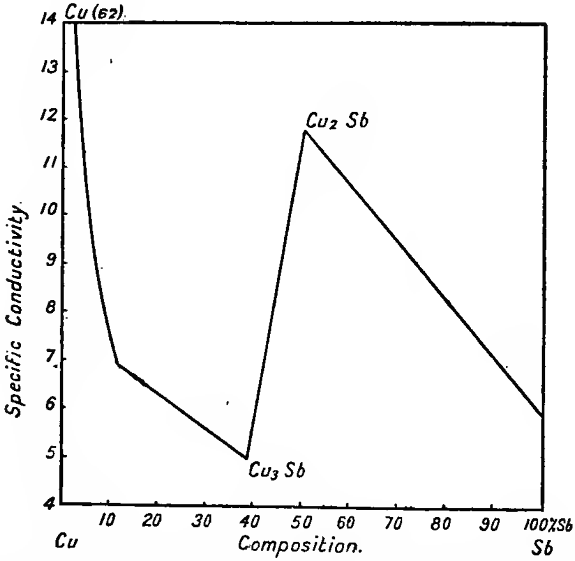

FIG. 41.—Curve of Specific Conductivity for the Alloys of Copper and Antimony, showing Discontinuities corresponding to definite Compounds.

or solid solutions containing them—but they do not conduct nearly so well as their component pure metals, nor does their conductivity bear any numerical relation to the pure metals and the proportions in which they are present in the compound. As a rule, but again by no means universally, the existence of a definite compound in a binary system is indicated by a break in the conductivity curve, as shown at P in Fig. 41, which relates to the alloys of copper and antimony, where two compounds are indicated. Where such a break is met with the existence of a corresponding compound can be inferred with certainty, but the absence of a break is no proof of the absence of a compound.

Beyond the study of the electrical conductivities of metals and alloys it has also been found interesting to determine the rate at which the conductivities change with variations of temperature. The conductivities of pure metals always decrease, in many cases with some rapidity, with rise of temperature, while in the case of alloys it is generally found that the "temperature coefficient" varies in accord with the electrical conductivity itself, so that a pure metal having a high conductivity exhibits a large temperature coefficient, while an alloy of the solid solution type which has a very low conductivity also shows a low temperature coefficient. Incidentally this property is of importance in connection with several well-known high-resistance alloys which possess the additional advantage of exhibiting only slight changes in resistance with variations of temperature. The alloy "Constantan," containing copper 60 per cent., nickel 40 per cent., which has already been mentioned, is a typical example. The use of curves representing the variation of the temperature coefficient of electrical conductivity or resistance in connection with the determination of the lines of constitutional diagrams has been suggested, and certainly possesses some important advantages.

Before leaving the subject of electrical measurements on alloys in connection with the establishment or interpretation of constitutional diagrams, the experimental aspect of the subject requires brief mention. Measurements of electrical properties, such as conductivity, resistance or temperature coefficient, require a knowledge of the actual dimensions of the specimen of metal employed. In the ordinary way such measurements are made on drawn wires, whose length and diameter can be readily measured to a high degree of accuracy. Even relatively short, thick rods can be used for this purpose, provided that the electrical instruments employed are sufficiently sensitive. In every case, however, the accuracy of the resulting measurement must depend upon the accuracy of the measurements of the dimensions of the test-piece and these in turn depend upon the regularity of the shape of the piece of metal. Where metals and alloys can be obtained in the form of drawn wires, or even of rods which can be accurately turned in the lathe, no difficulty need arise. In the middle regions of our binary series, however, the great majority of alloys are too weak and brittle, not only for the purpose of drawing into wires, but even to allow of being turned in a lathe. The attempt is sometimes made to make electrical measurements on such alloys on rods cast as nearly as may be to a circular shape. Sometimes special devices are adopted for this purpose, such as drawing the molten metal into a tube either by the application of suction or pressure. In most of these cases the degree of regularity attained is insufficient for exact work, principally because in a cast metal, and particularly if it is cast in the form of a thin rod, there is no guarantee that there may not be cavities or blow-holes, either of a relatively large size or of microscopic dimensions, and their presence would interfere vitally with the measurements. It would require an excessive amount of labour to determine by subsequent sectioning and microscopic examination that any given specimen had really been free from cavities. An accurate density determination is somewhat simpler, but is not quite conclusive, as no really reliable standard of comparison is available.

A number of other physical properties of metals have also been utilised in connection with the study of alloy systems. These can only be briefly mentioned. The mechanical properties, such as hardness, tensile strength, elastic properties, etc., are all closely related to the position of the alloy in the constitutional diagram, but, with the possible exception of hardness, these properties are not measured with sufficient ease and rapidity to invite their use in exploratory work. There is the further difficulty that the mechanical properties of any metal depend to a very large extent upon the mechanical and thermal treatment which it has undergone, so that numerous factors apart from chemical composition and constitution enter into these matters. The study of the mechanical properties has, therefore, been undertaken, in the great majority of cases, for the sake of the value attached to a knowledge of those important properties for their own sake rather than as a guide to the constitution of a system of alloys. This whole question is therefore treated in a separate chapter.

Other physical properties, such as specific heat, thermal conductivity, etc., have been employed for the study of metals and alloys, but not to an extent which would justify their treatment here. The measurement of thermo-electric power is a more promising method, but labours under certain difficulties which are likely to prevent its wide adoption. Rather more consideration must, however, be given to some electro-chemical and purely chemical methods of studying alloys.

The electro-chemical method consists in making determinations on a series of alloys of the electric potential which is set up when the specimen is used as an electrode in a specially-arranged voltaic cell. By this means a concentration-potential curve ([12]) can be set up, and it is claimed that on this curve the exact concentrations at which certain constituents appear or disappear are clearly marked, and that the existence or otherwise of definite compounds can be readily inferred. The method has not as yet been widely applied, but it appears to offer some advantages, although it suffers from one serious difficulty in that the potential observed in a given case must depend solely upon the constituents which are exposed, at the time of experiment, to contact with the electrolyte of the cell. If the alloy is of uniform composition and the structure is fine, then the surface in contact with the electrolyte is almost certainly adequately representative of the whole, but if the constitution is coarse in structure, and particularly if one of the constituents exhibits a tendency to be surrounded by or embedded in another, errors may arise.

The objection just raised applies with still greater force to the purely chemical method of studying alloys which consists in the endeavour to isolate the crystals of any definite compound which they may contain. It frequently happens that an inter-metallic compound is considerably less soluble in some reagent than the rest of the alloy, and prolonged exposure to such a reagent should produce a residue consisting entirely of the isolated crystals of the insoluble compound. This method was extensively used before the modern methods of thermal and microscopic analysis had been developed, and a very large crop of so-called " definite alloys " or compounds was obtained by the older workers. Lists of these may still be found in many of the older text-books of chemistry. The modern methods have, however, shown that the great majority of these compounds were entirely fictitious, and that no place for them can be found in any well-established constitutional diagram. This state of affairs has rightly led to the method being largely discredited, and the reasons for its failure are not far to seek. A study of the micro-structure of alloys containing compounds serves to show that we could not expect to separate them from the surrounding metal by such a process of differential solution. The crystals in many cases completely enclose particles of the matrix, which is thereby entirely protected from solution. In other cases, particularly where a chemical reaction occurs between the crystals first deposited from solution and the residual mother-liquor, the resulting compound or product forms a relatively thin sheath around a core of totally different composition. In still other cases, where an alloy consists of a solid solution which has not been given time to attain equilibrium during the cooling process, the outer margins of crystals may be more or less soluble than the cores, and this difference will vary with the size of each individual crystal. If an attempt is made to separate a " compound " from such a material a certain residue will be obtained, but its composition will not be that of any definite compound found in the alloys in question. The whole method is thus beset with serious difficulties and used by itself must be regarded as decidedly weak, although in careful combination with the study of the micro-structure valuable data can be obtained by its aid. The discovery of the composition of the carbide of iron known as "Cementite" by Abel, in 1885, was made by this process of residue analysis and must stand as a notable achievement to its credit.

Any general review of the subject of the constitutional study of alloys and of the construction of equilibrium diagrams would be incomplete without some reference to the thermo-dynamic principle of physical chemistry known as "the phase rule" (^{13}). This principle is sometimes employed as the basis for the study of the whole subject treated in the present chapter, but the writer has thought it preferable to approach the subject from the experimental and observational side rather than from a purely theoretical basis. The phase rule is a simple arithmetical formula, deduced from the first principles of thermo-dynamics, which enables us to state what will be the behaviour of a mixture of any kind under given changes of conditions. For this purpose the constituents of an alloy are classified as "phases," any constituent which is spacially distinct from the surrounding region being termed a "phase." Each phase within itself must be regarded as completely homogeneous and of one and the same chemical composition throughout. Thus in a liquid or molten alloy (except in the rare cases where two metals are present which do not mix when molten) the entire system consists of a single phase, viz., the liquid. A perfectly pure metal after solidification again consists of only one single phase; during the process of solidification, however, since both liquid and solid are present simultaneously, the system consists of two phases. But two phases present at the same time need not differ in their physical state; thus every eutectic alloy, containing juxtaposed crystals of two metals or of two solid solutions, consists of two phases, since the two kinds of crystals are spacially distinct from one another and are of different chemical composition. The "phase rule" tells us how many such phases can be present at any one time, when the alloys are in *complete* equilibrium, under given conditions. These "conditions" are determined by the three factors which affect the constitution of an alloy, viz., chemical composition or "concentration," temperature and pressure. If any one of these conditions can be changed without bringing about the complete disappearance of an existing phase or the appearance of a new phase, then the alloy is said to "possess a degree of freedom" in respect to that condition. An alloy can, at most, possess three degrees of freedom, *i.e.*, one with regard to each of the conditions "concentration," "temperature," and "pressure." If we denote this "degree of freedom" by the symbol f, the number of phases present by the letter p, and the number of component elements (*i.e.*, metals) as n, then the "phase rule" may be written

$$f = n - p + 2,$$

from which it will be seen at once that the greater the number of phases present the fewer will be the remaining degrees of freedom. It should also be noted at once that while the value of f can never exceed 3, it can also never become negative, *i.e.*, less than 0. This sets a limit to the possible number of phases which can ever be present in a mixture containing a definite number of components. In a binary alloy, where $n = 2$, p can consequently never be greater than 4.

In the special case of alloys, with which we are solely concerned here, one of the "conditions" may be disregarded, as we do not usually vary the pressure far from that of the atmosphere. When we consider the effects of stress, of course, this may no longer be true, but for purposes of equilibrium diagrams the pressure factor may as a rule be disregarded. If this is done the system can never have more than two degrees of freedom, and the formula of the phase rule becomes

$$f = n - p + 1.$$

For the simple binary system, where $n = 2$, p can consequently never exceed 3 when the alloys are in equilibrium. This number of phases, three, can, however, co-exist only when $f = o$ and that implies that a mixture of three phases in a binary system possesses no degree of freedom. and can, therefore, exist at one definite temperature and concentration only. In the equilibrium diagram this fact expresses itself in the circumstance that four regions or "phase fields" can only meet at a single point which represents a fixed temperature as well as a fixed composition or concentration. In a simple binary eutectiferous series the only point where three phases co-exist is at the melting-point of the pure eutectic, since there we have liquid in equilibrium with solid crystals of both component metals at the same time. In the case of a pure metal, where $n = 1$, f cannot exceed 2, and this number only occurs at the melting-point.

This subject need not be pursued further here, especially as its intricacies would require much space for their adequate elucidation. A tendency exists in some quarters to attach exaggerated importance to the "phase rule" as a guiding principle in the study of alloys, but, although of undoubted value, there are certain definite limitations. The greatest of these is that the rule is only fully applicable to alloys in complete equilibrium, and such complete equilibrium is rarely, if ever, strictly attained. If, therefore, observation indicates that the number of phases which appear in given circumstances is at variance with the deductions from the phase rule, the explanation is at once available that the alloys as examined are not in final equilibrium. As a rule it must be admitted that efforts to bring the alloys to a true equilibrium condition always show at least a tendency towards the elimination of one of these redundant phases. In practice, however, many of the most interesting, and also the most puzzling, features in alloy systems are associated with conditions of imperfect equilibrium. Indeed, it may fairly be said that all materials which find practical application in the arts depart more or less from a state of physico-chemical equilibrium. So well recognised has such a condition become that its persistence is admitted in the term used to describe it, viz.. "meta-stable." The alloys employed in a meta-stable condition include every kind of steel and almost all the more complex alloys. The persistence of these meta-stable conditions is, of course, due to the fact that most metals at the ordinary temperature are solid bodies possessing a high degree of rigidity or viscosity, *i.e.*, offering very great internal resistance to molecular re-arrangement of any kind. If, therefore, an alloy has once been cooled down to the ordinary temperature at such a rate that full equilibrium has not had time to establish itself during the cooling process—and excessively slow rates of cooling would in most cases be required in order to allow equilibrium to be attained—the molecules and atoms of the material are no longer sufficiently free to undergo re-arrangement and the alloy retains its condition of meta-stability. Examination of ancient metal objects, particularly of some from Egypt, indicates that this persistence of meta-stable conditions may last over many thousands of years and may for practical purposes be regarded as permanent. It is only by raising the temperature of the metal to a point high enough to afford the molecules sufficient freedom to undergo changes of arrangement, and maintaining the metal at such a temperature for a sufficiently long time—possibly many months—that equilibrium can be attained.

These considerations naturally raise the question whether our constitutional diagrams should rightly relate to these ultimate conditions, only attainable in ideal circumstances, of complete physico-chemical equilibrium, or to the practically far more important meta-stable conditions. There can be no doubt as to the answer : equilibrium diagrams must relate only to really stable conditions of complete equilibrium. This is necessary, since in those circumstances only is the constitution of an alloy a fixed and definite thing ; in the case of meta-stable conditions, however permanent they may be, there is no definitely fixed condition—the alloy will approximate more and more closely to the ideal equilibrium condition the slower has been the rate of cooling or the more prolonged the period of heating or annealing. Consequently, the true equilibrium diagram, indicating the final equilibrium condition, stands as the limit towards which the alloys tend and in terms of which it is alone possible to express or to describe their intermediate meta-stable conditions. Indeed, the skilful interpretation of any equilibrium diagram will serve as a guide to the structures and constitutions which the alloys are likely to assume in their more usual meta-stable state resulting from ordinary practical rates of cooling or even from intentionally accelerated cooling, such as quenching. An endeavour to put this interpretation of the equilibrium diagram upon a correct quantitative basis has recently been made by Gulliver (^{14}), and if his methods can be sufficiently simplified for practical purposes, they should lead to a still wider and more direct usefulness of the equilibrium diagrams.

Our consideration of the constitution of alloys has so far been confined, for the sake of simplicity, to binary systems—*i.e.*, to alloys of two metals only, In practice, of course, alloys only rarely belong to a simple binary system, since the majority of industrial materials contain three or four component metals or metalloids, in addition to impurities present in greater or lesser amount. From the scientific point of view also, the study of alloys must be pushed forward to include systems of three component metals (ternary alloys), and even of four or more. The difficulty, however, lies in the rapidly increasing complexity of all constitutional and structural conditions when the number of components is increased. For the ternary alloys we still have available a method of clear and comparatively simple graphical representation, but for alloys of four or more metals this aid fails us so far as any comprehensive view is concerned, and the representation can only be made piecemeal. In addition to this difficulty the fact must also be faced that for the study of a ternary system an enormously larger number of experimental determinations and observations must be made. If for the adequate investigation of a binary system the study of fifty separate alloys is found necessary, then a proportionately close study of a ternary system would require the examination of $\frac{50 \times 50}{2} = 1{,}250$ alloys—in itself a stupendous task. In spite of this difficulty the study of ternary systems is now being undertaken vigorously, but it must be admitted that the closeness of observations is still far behind that which has been found desirable in the best investigations of binary systens, so that the results on ternary alloys obtained by the majority of workers up to the present must be regarded rather as preliminary surveys than as exhaustive studies.

The graphical representation of the constitution of a ternary system of alloys is accomplished by means of a "constitutional model" in three dimensions in place of the plane constitutional diagram which suffices for systems of two components. Where the binary diagram is erected upon a single line as a basis, points along the line indicating the composition of the mixture, the ternary model is erected upon an area the points in which indicate the composition of the triple mixture. This can be most conveniently done by employing for the basis of the equilibrium model an equilateral triangle drawn to such a scale that its height is taken as 100. It is a well-known property of such a triangle that the sum of the perpendicular distances of any point within it from the three sides is equal to the height of the triangle and is, therefore, constant over the whole area of the triangle. These perpendicular distances may thus be used to indicate the percentage composition of every alloy of a ternary system. In the triangle ABC of Fig. 42

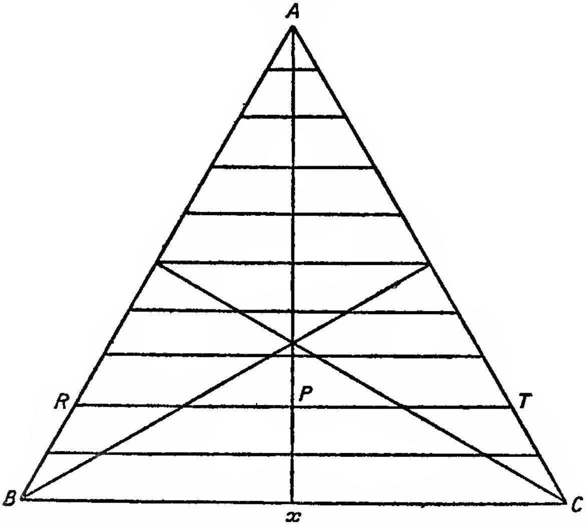

FIG. 42.—Triangular Diagram for Plotting the Composition of Ternary Alloys.

perpendiculars have been dropped upon the three sides from each of the three corners of the triangle, and each of these perpendiculars has been divided into ten equal parts. If now lines are drawn through each of these divisions they will mark all the points lying at equal distances of 10, 20, 30, etc., from one of the three sides. This distance in every case represents the percentage of that metal present in the alloy which is placed in the diagram at the opposite corner of the triangle. Thus the perpendicular A*x* dropped from the corner A upon the opposite side has its second division, representing 20 per cent., at the point P. The line RPT drawn through this point parallel with the side BC of the triangle thus connects all the points in the triangle whose composition is such that they contain 20 per cent. of the metal A. Similarly the lines drawn through other points of that perpendicular, or through corresponding points of the two other perpendiculars, connect all the points having a constant proportion of one metal. The outside lines of the triangle itself thus obviously represent the three simple binary systems formed by the three component metals taken two at a time, the corners representing the pure metals themselves, exactly as the end vertical lines of a binary diagram represent the pure metals.

Since the composition of every possible member of a ternary system can thus be represented by a point in an equilateral triangle, the constitution of the ternary system can be represented in exactly the same way as that which we have seen employed in the case of the binary systems, by the erection of verticals upon the points representing alloys which have been studied. In this way melting or freezing-points, eutectic points, transformations and, indeed, every feature in the equilibrium conditions of an alloy can be represented by vertical plotting above the point representing its composition. But while in the simple binary case these verticals were erected on a single line and could thus be shown on a single sheet of paper, in the ternaries the result will be a model in which surfaces take the place of the simple lines of the binary diagram. Thus we may erect verticals representing the temperature at which solidification begins, and the ends of these

tion of the ternary model in the first instance. Thus one might begin with a binary series of metals A and B and then determine a quasi-binary system—in reality a section of the ternary model—corresponding to the line of the triangle representing the system of A and B *plus* 5 per cent. of C, and following this throughout the whole system by successive lines lying parallel to AB. The data thus obtained will, of course, also make it possible to plot the sections of the model along lines parallel to either of the two other sides. The series of sections thus obtained may then be combined into a solid model; a very convenient method is to erect sheets of thin, clear glass or celluloid vertically upon a board graduated to represent the basal triangle and then to draw the successive sections upon the corresponding sheets of glass. The transparency of the whole is then sufficient to enable the observer to obtain a good idea of the true ternary equilibrium surfaces.

The apparent complexity both of these methods and of the resulting surfaces might perhaps be regarded with some misgiving from the point of view of the utility of such results, but fortunately in those cases hitherto investigated, and particularly in those relating to the more important alloys, considerable simplification is found applicable. We have already indicated that in binary alloys the more interesting and important members always lie near the two ends of the series. Similarly it is found that the majority of ternary and of complex alloys consist predominatingly of one metal, or at most diverge only slightly from a binary system. Within these limits it has been found that in the majority of cases the form of the ternary surfaces is fairly simple and of such a nature that the sections of the ternary model lying near the outer lines of the triangle are not very widely different from the constitutional diagrams of the limiting binary series. The actual temperatures of the various curves are, of course, altered more or less materially, and the various phase-fields are somewhat changed in shape and extent; but it is rare to find new phases entering into the constitution of such alloy groups. For that reason it becomes possible to regard these ternary alloys as modifications of the nearest similar binary alloys by merely applying certain modifications or "corrections" to allow for the effect of the third metal.

The conclusion to be drawn from what has just been said is that the detailed study of ternary alloy systems from the equilibrium point of view is not as yet of vital importance except from the purely theoretical point of view. It is, of course, far too early to suggest that the fuller study of the more complex systems may not reveal the existence of materials of unexpected interest. Indeed, some such materials have already been found, as, for instance, the Heussler magnetic alloys and—far more important—the whole series of ternary alloy steels. Where such interesting materials are to be met with, the full study of the ternary and even of more complex equilibria is urgently wanted. Thus our whole understanding of the alloy steels is at the present time vague and our knowledge scrappy for want of a complete and systematic series of investigations of these difficult ternary systems. The only reason why these investigations have not been undertaken hitherto lies in the fact of their great experimental difficulty and expense. The complete and accurate survey of such systems as iron-carbon-manganese, iron-carbon-nickel, and other similar ones would undoubtedly clear up many of the existing doubts and difficulties; it is, however, for those commercially interested in these materials to see that the necessary time and money are made available for their study.

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CHAPTER VII

TYPICAL ALLOY SYSTEMS

In the preceding chapters the constitution and structure of alloys has been treated in a very general way, with only passing reference to individual series of alloys for purposes of illustration. The whole subject will, however, be rendered much clearer by treating in somewhat greater detail the constitution and structure of a few selected systems. Not only will this serve to show the application of the principles and methods described in the previous chapters, but it will introduce the reader to some of the more important facts concerning those alloy systems with which the physical metallurgist is most frequently called upon to deal. If one were to select the alloy systems solely from the latter point of view, there can be no doubt that the alloys of iron and carbon would call for attention before any of the others. That particular system is, however, of a very complex kind, and for that reason it is preferable to postpone our detailed consideration of the iron-carbon alloys until a slightly later stage, when our acquaintance with other alloys will make it easier to follow the intricacies of that most important system.

The simplest type of binary alloy system, as we have seen in the last chapter, would be one of the purely eutectiferous kind in which the two metals are completely mutually insoluble in the solid state. The equilibrium diagram for an ideal case of this kind has already been given (Fig. 30, p. 91), and it is believed that the alloys of lead and antimony approximate very closely to this ideal limit. But even in those cases it is probably only a question of sufficiently close and accurate study to discover that the real case departs more or less widely from the ideal limit. In the older books and papers dealing with this subject it was customary to quote the alloys of lead and tin as typical examples of a binary series of this simple type. More careful study has, however, shown that at the lead end of this series at all events there is a considerable degree of solid solubility, lead forming with tin a series of solid solutions containing up to about 16 per cent. of tin (1). The earlier mistaken ideas about these alloys arose from the fact that when lead-tin alloys lying near the lead end of the series are allowed to cool from fusion even at a slow rate, both the thermal arrest due to the solidification of eutectic and the corresponding eutectic structure in the solid alloy can be detected. This, however, is solely due to the slowness with which these alloys approach their true equilibrium condition. In the author's experiments on this series it was found that heating at a temperature of 175° C. for a period of six weeks was required in order to bring the alloys approximately into their final state. The fuller study of the lead-tin series has also shown that the simple ideal diagram requires modification in yet another way. The alloys are found to exhibit an evolution of heat on cooling and a corresponding absorption of heat on heating at a temperature which lies, for alloys containing from 16 to 63 per cent. of tin, at 149° C. An explanation of this line of arrest-points has been put forward by Mazotto (2) to the effect that they are due to a species of " under cooling " in consequence of which the eutectic does not completely solidify at the true eutectic temperature, but remains in a meta-stable liquid condition until the limiting temperature of 150° C. is reached. It is difficult to see how such a process of under cooling can possibly account for the absorption of heat at the same temperature when the alloys are again heated, and there are several other vital objections to this view. In the same way the view of Degens (3) that a chemical compound is formed in the alloys at the temperature in question will not bear critical examination in the light of the data obtained by the author. If a compound were involved then the amount of heat evolved on cooling through this critical temperature would attain a maximum value for alloys whose composition approached that of the compound in question ; a maximum does occur, but the composition of the alloys near this maximum is not consistent with any rational formula for a compound. The only remaining explanation is that put forward by the author—that the critical temperature in question arises from a change in the metal lead which at that temperature alters in its power of dissolving tin in the solid state. This explanation is embodied in the constitutional diagram given in Fig. 45, which is slightly modified from that first published by the author and Tucker, in order to bring it nearer to the requirements of the phase rule. Further study of these alloys may well throw fresh light on these phenomena and result in a more satisfactory explanation, so that the diagram below the eutectic line must be regarded as somewhat tentative.

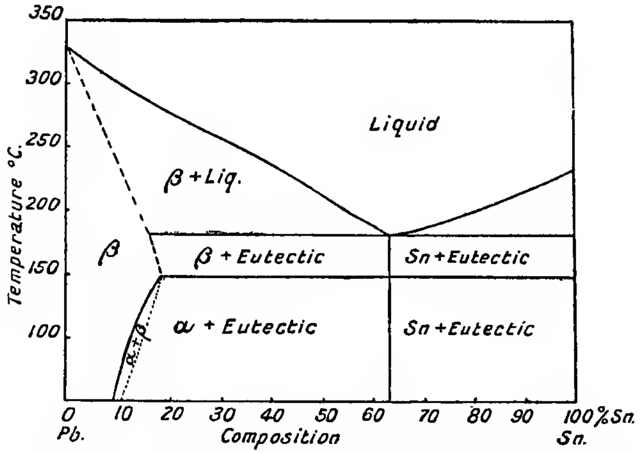

FIG. 45.—Constitutional Diagram of the Lead-Tin Alloys.

The micro-structures associated with the various fields of the lead-tin equilibrium diagram are very typical of the structures met with in all eutectiferous alloys. They have already been illustrated in Figs. 24 to 27. A further example of these alloys is given in Fig. 46 (Plate IX.), which shows one of the structures typical of the lead-tin eutectic, having the laminated character often associated with eutectics. This laminated character, however, although often beautifully marked, is not to be regarded as an essential feature of these substances. If a specimen of a well-laminated eutectic is heated for a long time to a temperature a few degrees below its melting-point, the structure gradually changes, various laminæ coalescing to form lumps or globules, and the result is a much coarser granular structure. Such a granular structure may also be obtained if the molten eutectic is very slowly cooled.

The eutectic alloy is the result, so far as its structure is concerned, of the simultaneous crystallisation or freezing of the two component metals. As a rule one of these acts as the "predominant partner," and its own crystalline form or habit determines the way in which the whole structure is arranged. It has been shown that eutectic alloys, like pure metals, consist of an aggregate of juxtaposed crystals. These crystals are, however, merely skeletons formed of one of the metals—the "predominant partner"—with the interstices filled in by the other metal. In the case of the lead-tin alloys the tin is the predominant metal, and each of the crystals of the eutectic is in reality a radiating structure, known as a "spherulite," of tin carrying the lead in its interstices.

The micro-structures illustrating the lead-tin series are typical of other similar alloys, such as those of lead and antimony. An interesting practical application of certain alloys of this latter series has recently been suggested by Hannover ([4]) in the production of porous metal, principally for use in the construction of electric storage batteries. For this purpose he utilises an alloy somewhat like that illustrated in Fig. 25 while it is at a temperature lying between the lines AE and CE of the diagram (Fig. 30)—*i.e.*, within the temperature range where the crystals of one metal (in this instance lead) are already solid but the eutectic is still fluid. By centrifuging the alloy at this temperature Hannover has found it possible to drive out the fluid eutectic, thus leaving behind a porous mass of lead.

The constitutional diagram of the lead-tin series is also of interest from the practical point of view, owing to the use of some of these alloys for soft-soldering. The most fusible and also the most homogeneous solder is formed by the eutectic alloy of the series, containing 37 per cent. of lead; owing to the high price of tin, however, solders nearer the lead end of the series are more frequently employed, and for certain purposes offer a decided advantage. The diagram shows that the eutectic alloy solidifies at a single definite temperature, but an alloy containing equal parts of lead and tin has a solidification range of 60° C. between the temperature at which crystals of lead first begin to separate and that at which solidification is completed by the freezing of the residual eutectic. In such work as the "wiping" of joints as practised by plumbers, this range of temperature, in which the alloy (or solder) is in a pasty stage, is utilised by the workman to bring the mass gradually into the desired shape around his joint.

From the lead-tin series of alloys a number of ternary and complex alloys are derived, some of which are of considerable practical importance. Among these are the alloys of lead and tin with antimony, which are largely employed for type-founding and for the production of bearing-metals. We cannot go into the structure and constitution of these ternary alloys in any detail, but it may be mentioned that these alloys containing antimony largely owe their value to the existence of a definite compound between tin and antimony, having the formula SnSb (5). This is a hard, brittle substance which appears in the alloys in the form of angular crystals. The presence of these hard crystals tends to make the alloys much stronger, stiffer and harder, but also more brittle. For type-metal it is necessary to secure adequate hardness and at the same time to have a metal which will fill the minute interstices of a mould with great accuracy. The actual composition of type-metal employed varies widely with the special purpose for which it is required and the consequent limitation which has to be imposed upon its price. This consideration governs the amount of tin which can be introduced. The structure of the alloy is always rather complex, but consists of primary crystals of either antimony or of the antimony-tin compound, embedded in two layers of eutectic. In the case of white bearing-metals the requirements are different—what is wanted is a metal sufficiently soft and plastic to accomodate itself to the inequalities of the moving parts and thus to afford them an even bearing, while it must also present a surface of sufficient hardness to prevent rapid abrasion. The crystals of the tin-antimony compound serve to provide the resisting hard surface, while the soft and plastic eutectics in which they are embedded yield to the pressure and adapt themselves to the needs of the bearing in question. The typical structure of an alloy consisting of the hard crystals of SbSn embedded in eutectic is shown in Fig. 47, Plate IX.

We now pass on to consider the constitutional diagram and the correlated micro-structures of a decidedly more complex system of alloys, viz., those of aluminium and zinc. This system still shows a well-defined eutectic, but at the one end of the series there is a long range of solid solutions, while the series also shows one definite compound possessing somewhat remarkable features. This series is of interest as forming the basis of what are probably the best available light alloys of aluminium, some of which combine a comparatively low density (about 3·25) with the strength and toughness of mild steel.

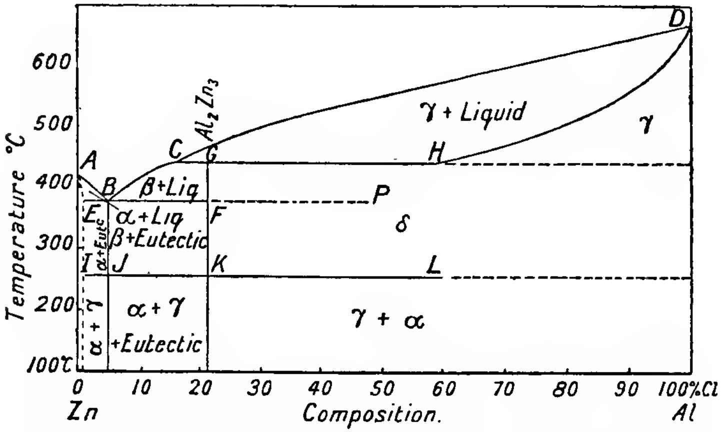

FIG. 48.—Constitutional Diagram of the Zinc-Aluminium Alloys.

The constitutional diagram is shown in Fig. 48. In this case also a much simpler diagram was for a long time generally accepted; the author and Archbutt (6), however, established the diagram here shown which is itself not quite complete in regard to the region occupied by the dotted continuations of the lines CGH and IJKL. The diagram consists first of all of the freezing-point curve or *liquidus* ABCD. Starting from the zinc end, this runs down to a eutectic point B at a concentration of about 5 per cent. of aluminium. From that point the *liquidus* runs up smoothly to the point C, where a small break or kink is found, and then again smoothly to the point D, corresponding to pure aluminium. The "*solidus*" or curve bounding the region in which the alloys are completely solid is given by the lines AEBFGHD. The curious feature in this curve is the sudden step-up at the point F corresponding to a concentration of about 78 per cent. of zinc and 32 per cent. of aluminium, which represents the compound Al_2Zn_3. The reason for this step-up becomes quite plain when the manner in which the compound Al_2Zn_3 is formed in these alloys, is understood. Along the branch of the *liquidus* between C and D the alloys begin to solidify, on cooling, by depositing crystals of a solid solution of zinc in aluminium, this substance being called γ in the diagram. As the alloys cool further they continue to deposit an increasing quantity of this γ body until they reach the temperature 443° C., which is indicated in the diagram by the horizontal line CGH. Alloys lying to the right of the point H, *i.e.*, containing more than 60 per cent. of aluminium, become completely solid before they reach this temperature, and in that case it is possible that no further change takes places in them, although the dotted continuation of the line GH is intended to suggest that something does occur even there. To the left of the point H, however, the alloys are still partially liquid when the temperature 443° C is reached and then a chemical reaction sets in, resulting in the absorption of the residual liquid and the formation of the compound Al_2Zn_3. This reaction may be written

$$\gamma + \text{Liquid} = Al_2Zn_3.$$

The crystals of γ, as a result of this reaction, become coated with a layer or sheath of the newly-formed compound, and as soon as such a sheath has become completed the reaction in the ordinary way comes to an end, even though the residual liquid is not used up. In this case the alloy remains in a meta-stable condition and cools down to the temperature of the line BFP, where the residual liquid solidifies as eutectic. This is indicated by the dotted line FP which was formerly regarded as the true eutectic line. If, however, these alloys are kept at a temperature just below 443° C. for a considerable length of time, the formation of the compound Al_2Zn_3 is completed, by the aid of slow diffusion, in spite of the protecting sheaths above described, and when an alloy so treated is further cooled there is no residue of liquid and consequently no further freezing takes place on the line FP.

This statement holds good for all alloys which contain less zinc than the quantity required to convert the whole of the alloy into the compound Al_2Zn_3—*i.e.*, for alloys lying to the right of the line FG. To the left of that line, however, there is an excess of zinc, and no amount of prolonged heating will cause the alloys to become completely solid at temperatures just below 443° C. In other words, even after the whole of the γ crystals have been converted into compound, a residue of liquid remains and this solidifies as a eutectic of zinc and the compound along the line BF. It is for this reason that the "*solidus*" steps up at FG from the line BF to the line GH.

The line GH really indicates the temperature which limits the stable existence of the compound Al_2Zn_3, so that when alloys cool down through that temperature the compound is formed, and when they are heated up through it the compound is again decomposed. At the point C this line cuts the *liquidus* curve and we see that to the right of C the compound has decomposed, on heating, before the alloys are completely liquid, while to the left of C the compound melts without having previously been decomposed. It follows that, conversely, on freezing, the alloys to the left of the point C begin to solidify by depositing crystals, not of the γ solid solution, but of the compound Al_2Zn_3. This difference accounts for the small break in the *liquidus* curve at C.

The diagram contains another horizontal line IJKL, lying at a temperature of 256° C. This line marks the lower limit of stability of the compound Al_2Zn_3. On cooling down past this temperature the compound breaks up into a duplex structure,

PLATE X.

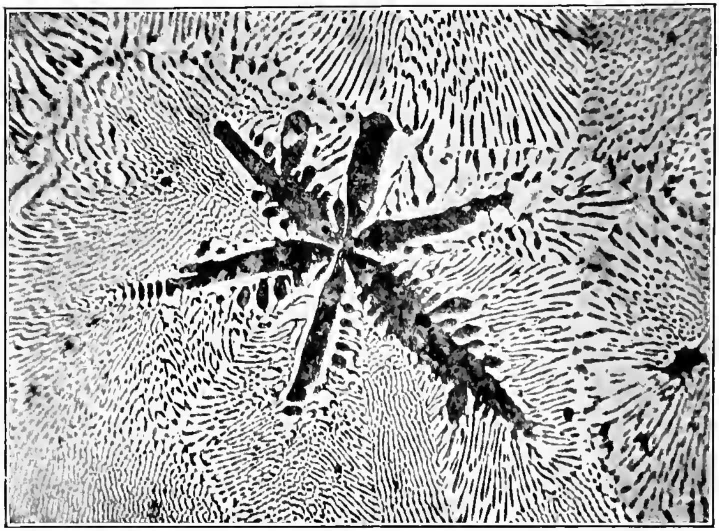

FIG. 51.

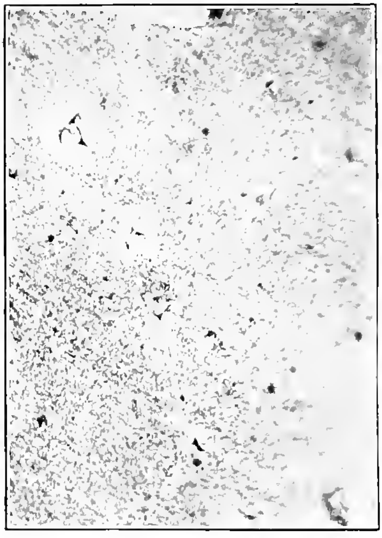

FIG. 52.

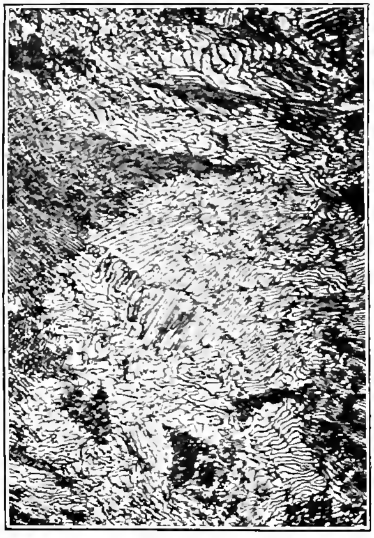

FIG. 53.

[*To face p.* 139.

sometimes finely laminated, consisting of crystals of zinc and of the saturated solid solution of zinc in aluminium which we have already called γ. Along this line there are very well-marked heat-evolutions in the cooling-curves of the alloys, and provided these have been so treated as to allow the reaction at the temperature of the line CGH to be completed, these lower heat-evolutions show a well-marked maximum at the concentration corresponding to the compound Al_2Zn_3. Conversely, in alloys so treated, the eutectic heat-evolution at 381° C. diminishes at such a rate that it would just vanish entirely at the concentration of the compound. The curves showing the relations of these heat-evolutions to the composition are reproduced in Fig. 49, since they serve as good examples of the way in which careful measurements of quantities of heat evolved may be used as evidence for the existence of a definite compound. In Fig. 50 are shown a few of the cooling-curves of typical alloys of this series, and the reader will find it instructive to correlate the various heat-evolutions indicated by the peaks on these curves with the lines of the diagram.

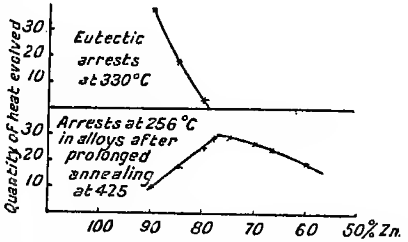

FIG. 49.—Thermal Analysis Curves of Zinc-Aluminium Alloys.

The micro-structures found in the alloys correspond exactly with the deductions from the constitutional diagram of Fig. 48. A few typical examples are shown in Figs. 51 to 53 (Plate X.). The first of these (Fig. 51, Plate X.) shows a six-rayed dendritic crystal of the compound Al_2Zn_3 embedded in eutectic; this corresponds to an alloy containing a little less zinc than the eutectic composition. The edges of this dendritic crystal show signs of decomposition, which has taken place while cooling through the line JK. This is more fully shown in the next two figures, which relate to an alloy lying just to the right of the line FG. In Fig. 52, Plate X., we see the blank, uniform structure of this alloy which, after prolonged heating at 440° C. in order to allow the formation of the compound to be completed, has then been quenched in order to avoid decomposition while passing through the line KL. The same alloy after re-heating to a temperature a few degrees below the line KL, in order to allow the normal decomposition of the compound to take place, is shown in Fig. 53, Plate X., where the laminated structure of the decomposition products is well shown. Alloys lying near the right-hand (aluminium) end of the series do not show these changes, and, if treated so as to attain their equilibrium condition,

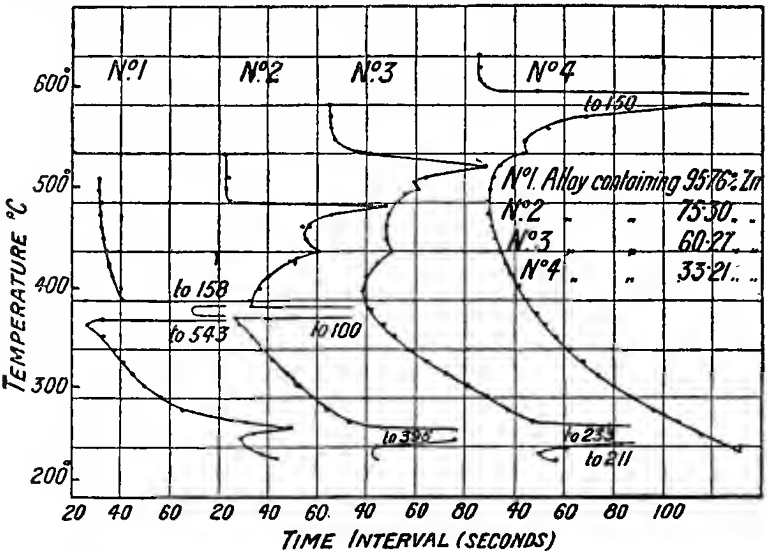

FIG. 50.—Typical Cooling Curves of Zinc-Aluminium Alloys.

exhibit the typical polyhedral structure of a simple metal or of a solid solution.

Having described thus briefly some of the principal features of the constitutional diagrams of two very typical systems, we now pass on to consider the diagrams and constitution of some of the more important alloys of copper which in industrial importance, at the present time, rank next to steel itself. The alloys of copper with zinc, tin and aluminium all afford examples of somewhat complex constitutional diagrams which it will not be possible to discuss in any detail in the present volume, and attention will be very largely confined to those regions of the diagrams which relate to the more important alloys of the series in each case. For fuller details reference must be made to special works dealing with each group of alloys.

The constitutional diagram of the alloys of copper with zinc is shown in Fig. 54. Essentially this is the diagram established by Shepherd (7) and practically universally accepted; a modification due to the work of Carpenter (8) on the β phase of these alloys has, however, been included, affecting the lines in the region occupied wholly or in part by the β phase.

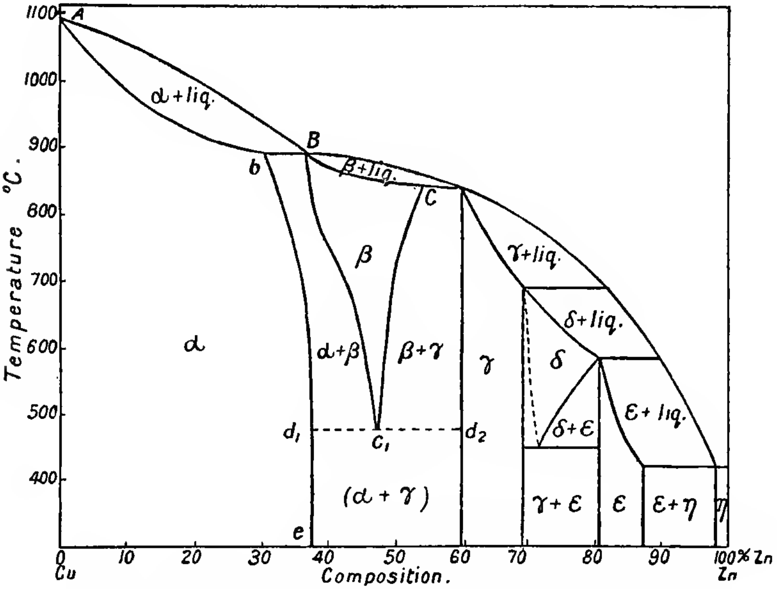

FIG. 54.—Constitutional Diagram of the Zinc-Copper Alloys.

The diagram shows in all six phases, but we shall only deal with the first three of these, viz., those denoted in the diagram by the letters α, β and γ. The first of these bodies is the α phase; this is a solid solution of zinc in copper, and may contain as much as 37 per cent. of zinc. The position of the point *b* in the diagram indicates the limiting composition of the alloys which never contain anything but the α body—*i.e.*, from the moment of incipient solidification down to the ordinary temperature, whether cooled slowly or quickly, the alloys containing less than 30 per cent. of zinc always consist entirely of the pure a body, but it does not follow from this that the alloys are necessarily entirely homogeneous in all circumstances. If we recall the process of freezing, as already described for a solid solution, we see that in the case of an alloy containing, say, 20 per cent. of zinc, the solid which first separates when the alloy *begins* to freeze will have approximately the composition 8 per cent. zinc, 92 per cent. copper. If the cooling at this stage is not slow enough to allow of the attainment of complete equilibrium, the central portion of each crystal, *i.e.*, the portion first formed, will remain to the end considerably richer in copper than the outer or later-formed portions of the crystals. Each crystal of metal of such composition will, in these circumstances, consist of a core which is richer in copper and an outer portion which is poorer in copper, than the average composition of the alloy. A quickly-cooled alloy in the cast condition thus shows an apparent duplex structure, although consisting of only one phase, for although the layers of solid solution of varying concentration which form these crystals are all forms of the same a phase, their different concentration renders them susceptible to the attack of etching reagents to different degrees; by most reagents the regions richest in copper are less attacked than those which contain a larger proportion of zinc. Since those portions of the crystals which are first formed consist of the dendritic arms and branches already described as occurring in the early stages of the freezing of a metal, the etched pattern of such an alloy reveals this dendritic structure, and in some circumstances this may be almost as clearly defined as if the outer regions of the crystals really consisted of a different phase. An example of this kind has already been shown in Fig. 26, Plate VII.

When, however, such an alloy is slowly cooled, or, after rapid initial cooling, is subsequently heated so as to allow of the attainment of equilibrium by the slow process of diffusion, the metal becomes entirely homogeneous, the dendritic cores disappear, and we have again the familiar aggregate of homogeneous crystals such as are seen in all pure metals. It should be noted that the mechanical work and subsequent annealing which occur in the working of brass as usually carried out are also sufficient to render the metal homogeneous in this sense, with the result that wrought brasses containing less than 30 per cent. of zinc do not as a rule show any trace of dendritic structure ; their structure in fact is very similar to that of pure copper when treated in the same way, *i.e.*, it consists of an aggregate of crystals whose size depends upon the manner of heating and working, but these crystals show the strongly marked characteristics of a freely " twinned " structure. An example is shown in Fig. 55, Plate XI.

When we pass beyond the range of alloys terminated by the point *b* of the diagram and examine alloys containing from 30 to 37 per cent. of zinc, we meet with a different state of affairs, as we have now entered a region in which the β phase plays a part. In these alloys crystallisation commences, on cooling past the line AB, in much the same manner as in the first class described above, but this only continues for a short time, until in fact the temperature of the line *bB* (about 880° C.) is reached. The solid which is formed above this temperature is still the a body, but at this temperature the remaining liquid freezes in the form of the second phase, β. While the a body, consisting as it does chiefly of copper in the free state in which a relatively small proportion of zinc is held in solution, retains most of the properties of copper, and is, therefore, a comparatively soft and very ductile body, which can be readily worked in the cold, the β phase is a much harder, stronger, but also much less ductile body, and its presence in the alloy at once makes itself felt by a decided increase in the strength and hardness, but also in an equivalent decrease in ductility, which soon makes cold working impossible. For this reason the subsequent cooling-process of this particular group of alloys is of special interest and importance. Owing to the shape of the line *be*, these alloys on cooling pass from the region in which both a and β can exist side by side into a region where a only is stable, and where, therefore, β either does not exist at all or only occurs as a meta-stable form, *i.e.*, a form which has been preserved in existence by cooling the alloy at a rate too rapid to allow of the completion of a change which is necessary for the attainment of equilibrium. In the present case the β body tends to change into the a body when the alloy passes through the temperature represented by that point on the line *be*, which concerns that particular alloy. If the alloy is slowly cooled this change takes place and the relatively hard β body disappears, and the alloy is reduced to an homogeneous aggregate of a crystals. If, however, the cooling is too rapid to allow this change to occur or to be completed, the alloy retains a certain amount of the β body in its constitution and is thereby rendered harder and more brittle. The annealing and subsequent cooling of such alloys is, therefore, capable of modifying their properties in a very decided manner.

When the proportion of zinc indicated by the point *b* is exceeded, *i.e.*, in alloys containing more than 37 per cent. of zinc, the β phase remains stable at all temperatures down to 470° C., and the slowly-cooled alloys possess a duplex structure which is well seen in ordinary Muntz metal (approximately 40 per cent. of zinc), as in Fig. 56, Plate XI. Rapid cooling from a suitably high temperature also affects the structure and constitution of these alloys, for rapid cooling from temperatures lying above the line Bc_1 will result in the suppression of the β to a change, and the alloys may even be obtained as a homogeneous mass of the β phase. Here, again, heat-treatment is capable of profoundly modifying the structure and constitution, and consequently the properties, of the alloys (9).

The region of true stability of the β body is confined, according to Carpenter (8), to temperatures above 470° C. At this temperature a line of small heat-evolutions occurs in the thermal curves of these alloys, and Carpenter considers that this indicates the decomposition of the phase into a and γ. In accordance with this view the lines of the diagram starting from the points B and C respectively are drawn to meet at the point c_1 on the line d_1d_2. The decomposition of the β phase which occurs along this line is not readily seen under the microscope, nor can the decomposition products of the pure β phase be caused to coalesce into lumps or laminæ visible under moderate magnifi-

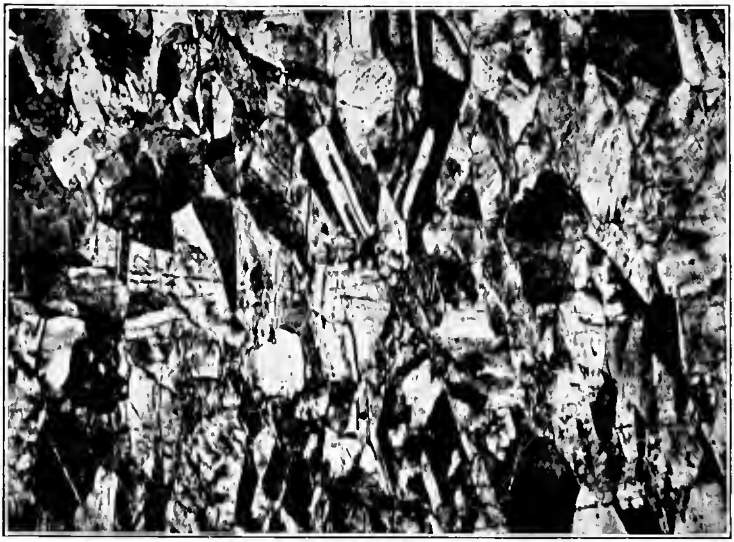

FIG. 55.

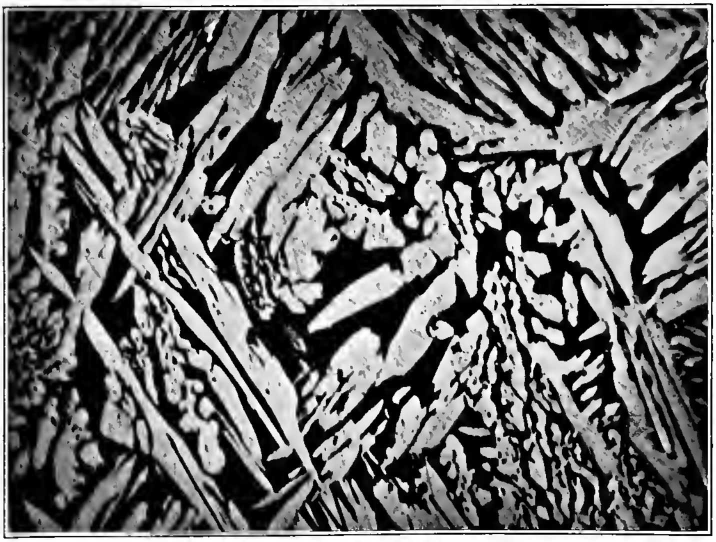

FIG. 56.

[*To face p.* 144.

cation, although such coalescence appears to occur in the presence of certain third elements. How far this supposed decomposition of the β body affects the mechanical or other physical properties of the alloys is also not yet ascertained, although it has been suggested that it plays a part in the spontaneous cracking of certain brass articles. Further evidence must, however, be awaited before much weight can be attached to this whole matter.

In the region of the diagram enclosed by the lines BC, Cc_1, c_1B, the alloys consist entirely of the β phase, and it is interesting to note that it is this phase which, while comparatively hard and brittle in the cold, lends itself to hot rolling and forging, while the α phase, which is soft and ductile at the ordinary temperature, is generally regarded as being too weak and friable when hot to withstand hot working.[1] At the ordinary temperatures the alloys lying between the points d_1 and c_1 appear to consist of a mixture of the α with the β body, while those between the point c_1 and d_2 appear to consist of a mixture of the β and γ phases. This latter phase is exceedingly hard and brittle and its presence in the alloys renders them useless for any purpose where strength and toughness are required.

This is a typical example of a law very widely applicable to alloys, viz., that those phases of a binary system which contain the two elements in anything like equal proportions are hard and brittle, only the alloys near the ends of a series being as a rule sufficiently strong and ductile to be of practical utility. We have already seen that the β phase is harder and more brittle than the α, so much so that the best brasses, in which strength and ductility are of importance, are generally made with a zinc-content of approximately 30 per cent., this being the cheapest alloy which does not contain the β phase. For many purposes the 60/40 brass (Muntz metal) is still sufficiently ductile, but with the appearance of the γ phase the strength of the brass diminishes rapidly and its ductility is still further reduced, so that brasses containing such large proportions of zinc are of little importance for engineering purposes. It is perhaps worthy of notice at this point that the zinc-copper alloys are particularly noticeable on account of the wide range of composition over which they show useful mechanical properties. In the tin-copper and aluminium-copper series a content of 15 per cent. of the added metal is sufficient to destroy the ductility of the alloys. The fact that zinc is itself a cheap element, and the further unique fact that 30 per cent. of it can be added to copper before a second phase makes its appearance, act together to bring about the wide utility and numerous applications of the brasses as compared with all other copper alloys. The shape of the constitutional diagram has thus a most direct practical bearing on the scope and utility of the system of alloys which it represents.

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[1] The author has recently seen a 70/30 brass hot-rolled quite successfully, and it therefore seems that the hot-shortness of the brasses may not be an inherent property of the alloys.

The micro-structure of the zinc-copper alloys has already been referred to in describing their constitution, and the structure of the α alloys has been illustrated in the cast "cored" condition and in the worked and annealed condition in Figs. 21 and 55, Plates VI. and XI. The duplex structure of the alloys corresponding to the fields of the diagram in which the α and β phases appear together is shown in Fig. 56, Plate XI., which is typical of Muntz metal, zinc 40 per cent., copper 60 per cent. The β shown in this micrograph is, of course, "apparent β," and, according to Carpenter's view, would consist of an almost ultra-microscopic mixture of α and γ.

We now pass on to the consideration of the constitution and structure of another important group of the alloys of copper, viz., those with tin. The constitutional diagram of this system has been very carefully worked out by Heycock and Neville (10) in a classical research, but their diagram was admittedly incomplete, and it has to a certain extent been modified by the subsequent work of Shepherd and Blough (11), and of Giollitti (12). Even now it is doubtful whether the intricacies of this complex system have been completely worked out. The diagram as given in Fig. 57 also embodies modifications suggested by Hoyt (13), but our discussion of the alloys must again be confined to those near the copper end of the series, which are the most important for all practical purposes.

These may be taken as having a tin-content of less than 20 per cent.

In these alloys, according to the diagram, we shall only meet with three constituents, viz., those denoted by *α*, *β*, and *δ*. The very complex changes undergone by the alloys ranging from 20 to 40 per cent. of tin do not extend to the range of bronzes ordinarily employed for engineering purposes. The transformation which occurs along the line PQ is, however, of great imporance in regard to all bronzes containing more than 12 per cent. of tin.

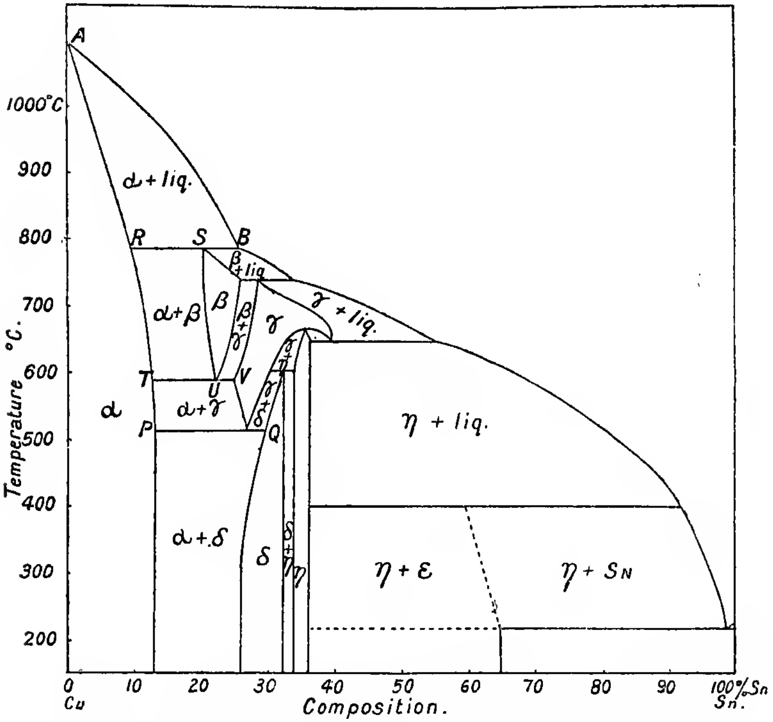

FIG. 57.—Constitutional Diagram of the Tin-Copper Alloys.

The micro-structure of tin-copper alloys containing less than 10 per cent. of tin is very simple and exactly similar to that of the corresponding zinc-copper alloys, being that of a simple solid solution of a tin-copper compound in copper. When rapidly solidified these alloys exhibit the dendritic structure characteristic of solid solutions which have not attained equilibrium, but slower freezing, or subsequent annealing at a high temperature, obliterates the differences of composition which exist between the cores and the peripheral regions of the crystals, and results in the formation of the uniform crystalline aggregate with which we are already familiar. This change, however, very materially affects the strength and other properties of the metal—the rapidly-cooled material being very much superior from the mechanical point of view to that obtained by slow cooling. Hot rolling, of course, further improves the strength of the material. Cold working—in these as in other metals—hardens the material, increasing its ultimate strength, but seriously reducing its ductility. In the case of bronzes, with the exception of those containing very little tin, the hardening effect of rolling in the cold is much more marked and rapid than is the case with copper-zinc alloys. Bronzes somewhat richer in tin cannot be rolled or worked to any considerable extent in the cold. The analogy between the a body of the tin-copper series and the a body of the zinc-copper alloys is in many respects very close; under the influence of mechanical work and annealing *both* these bodies assume the rectilinear forms characteristic of twinned crystals, such as that illustrated in Fig. 55, Plate XI. The a body of the aluminium-copper series behaves in a similar manner.

Alloys lying in the short range between the points R and S in the diagram correspond to the second group of the zinc-copper alloys to this extent, that while their solidification begins by the deposition of the a body, it is completed, along the line RS, by deposition of β. Only those near the point R, however, lying vertically above the curve RT, are completely transformed into a, even by very slow cooling. Those lying to the right of the composition corresponding to the point T undergo a transformation whereby the β originally present is transformed finally into a mixture of a and δ phases. According to the diagrams of Heycock and Neville, and of Shepherd and

PLATE XII.

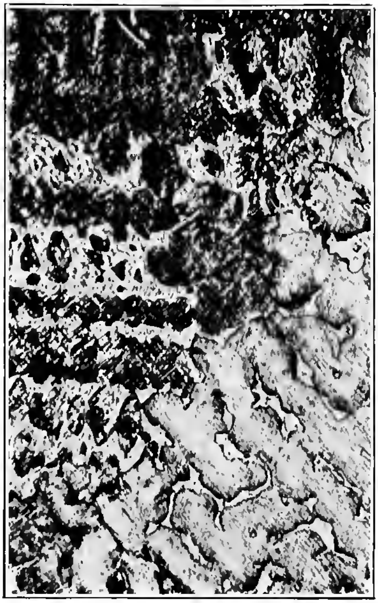

FIG 58.

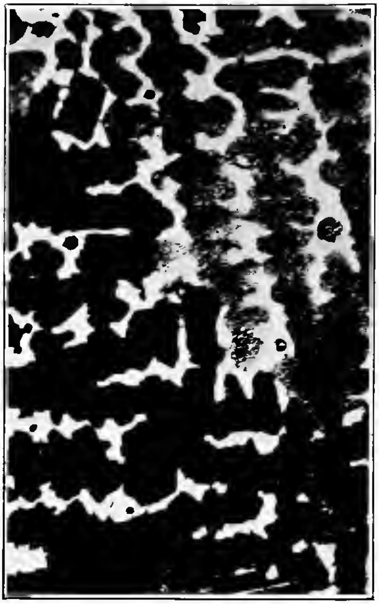

FIG. 59.

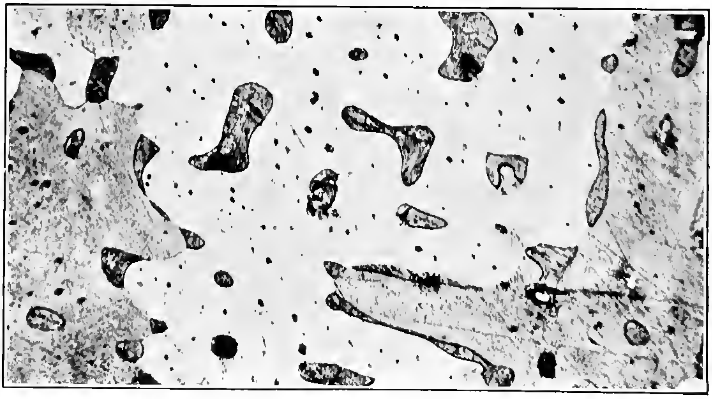

FIG. 60.

[*To face p.* 149

Blough, this is a direct transformation at the temperature of the line PR according to the equation

$$\beta = a + \delta.$$

Hoyt, however, has found evidence for the existence of an intermediate transformation along the line TU, where β is transformed into an intermediate phase, γ. In either case the finally resulting phase, δ, is much harder and more brittle than β, so that the mechanical properties of the alloys are improved by quenching in such a way as to retain the β phase. The various conditions of micro-structure found in an alloy of this group are illustrated in Figs. 58, 59 and 60, Plate XII., which represent the structure of an alloy containing 18 per cent. of tin in various conditions, as slowly cooled in the ordinary way, Fig. 58, Fig. 59, as annealed at 750° C. for thirty minutes and quenched (thus being in the $a + \beta$ state), and Fig. 60 after annealing at 450° C. (just below the line PQ) in order to complete the transformation, thus bringing the alloy into the $a + \delta$ condition.

The alloys richer in tin, particularly those covering the intricate part of the diagram relating to alloys containing between 20 and 40 per cent. of tin, although of great theoretical interest, cannot be dealt with here, as a discussion of their constitution and micro-structure would occupy too much space. Such a discussion is further rendered difficult by the fact that the exact details of the constitution are not yet definitely settled. Only one point of particular interest must be mentioned ; this relates to the fact that owing to the peculiar form of the constitutional diagram the alloys containing from 33 to 37 per cent. of copper exhibit a very unusual behaviour, which consists in first undergoing solidification in the usual manner, but afterwards—on cooling to a lower temperature—again becoming liquid, and only then undergoing final solidification at a still lower temperature. Such behaviour can, of course, only be explained by the occurrence of a chemical reaction as the result of which the crystals of a solid solution are transformed into a compound—or a solution of a compound in an excess of one of its constituents—which is more fusible than the original solid solution, with the result that the formation of the compound on cooling through a critical temperature is accompanied by the fusion of the alloy which had just previously solidified.

In the preceding sections the constitution and structure of typical members of the two binary series—zinc-copper and tin-copper—have been very briefly discussed. A very large number of important alloys, however, although closely related to these two series, are essentially ternary alloys in which both zinc and tin are present. In view of the complexity of both the two binary systems, it might be anticipated that the ternary equilibrium would be excessively complicated. Actually the systematic investigation of these ternary alloys has only been undertaken quite recently by Hoyt (13), but although that author has obtained interesting and valuable data, it cannot be considered that these alloys have been fully explored as yet, As far as it goes, Hoyt's ternary diagram is reproduced in Fig. 61. The diagram relates only to the corner of the ternary triangle representing the alloys rich in copper ; the figure shows

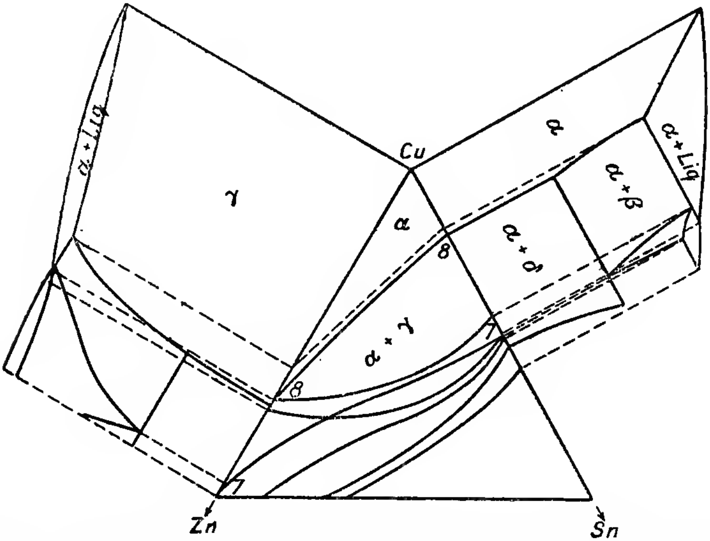

FIG. 61.—Diagram of the Constitution of the ternary alloys of Tin, Zinc and Copper, rich in Copper.

the binary diagrams of the zinc-copper and the tin-copper systems folded down to either side of the triangle, while the manner in which the various regions of the binary diagrams are connected in the ternary diagram are shown by the lines drawn on the ternary triangle. From these it will be seen that there is a large area, marked *a* in the diagram, in which the alloys solidify as a simple *a* solid solution, whose structure and properties resemble those of the *a* constituent of either of the two binary systems, the tin and zinc simply replacing one another, although this replacement is not without influence on the mechanical properties. This field is marked *Cu* 8, 8 in Hoyt's diagram. Next to this lies the region 8, 8, 7, 7, in which the alloys contain two phases, one the solid solution, and the second the γ phase, which is similar to the corresponding phase of the zinc-copper system. Within this region, however, the structures of the alloys vary according to their mode of solidification and subsequent transformations ; in those near the line 7, 7, and particularly near the zinc-copper side of the diagram, a duplex structure, consisting of the *a* and γ phases, is found, and this is regarded as the product of decomposition of the β phase of the zinc-copper system, this decomposition being rendered more evident by the presence of tin.

The ternary system just described is by no means the only one which is of interest and importance in connection with the alloys of copper, but the matter cannot be pursued here. It should be pointed out, however, that the influence of a third metal or metalloid on a system of alloys cannot be fully understood until the constitution of the ternary system formed by that third element with the primary system has been studied and elucidated. As an approximation, it is sometimes sufficient to determine " the effects of small additions " of the third element to the binary system, but this is in some cases an unsatisfactory proceeding, chiefly because traces of new constituents which may appear are likely to be overlooked or their true significance misunderstood if only the alloys lying very close to the true binary system are studied. It is to be hoped, therefore, that the difficult and tedious exploration of ternary systems will be steadily pursued.

Mention may be made here of certain alloys which belong really to the class of ternaries just referred to, but whose true constitution is not yet fully worked out. Their practical importance, however, demands some reference to them.

The addition of phosphorus to copper ([14]) and its alloys is well known to improve the mechanical qualities of the metal, particularly if the quantity is carefully adjusted. This is not in reality due to the formation of any new alloy, since the phosphorus serves simply to remove the oxides present in the molten metal, the phosphoric oxide passing into the slag or scum on the surface. When melted in the ordinary way, copper and its alloys are always more or less seriously contaminated with oxides. In the case of copper the presence of the oxide is easily recognised under the microscope ([15]), and its influence on the properties of the metal is well known. For electrical purposes the presence of oxide is particularly undesirable, but the use of phosphorus for its removal is not satisfactory, owing to the fact that any slight excess of the metalloid remaining in the copper would seriously affect its conductivity and its mechanical properties. For that reason a more satisfactory deoxidiser for copper has been sought, and it is believed to have been found in the substance known as boron sub-oxide ([16]). In the zinc-copper and the tin-copper alloys oxide is also habitually present. In the tin-copper series it can be readily detected both analytically and under the microscope, as Heyn and Bauer ([17]) have shown very clearly. In the zinc-copper series its detection by either method is very difficult. The use of phosphorus for the removal of oxide is principally practised in the case of the tin-copper alloys. When the quantity of added phosphorus—which is usually introduced in the form of either a phosphorus-copper or a phosphorus-tin alloy—is so adjusted that the phosphorus is entirely or almost entirely oxidised, the resulting material is not really a ternary alloy, but merely a purified tin-copper alloy, which is, therefore, somewhat misdescribed by the term "phosphor bronze" ([18]). When larger quantities of phosphorus are introduced, the metalloid is found in the resulting alloy in the form of a definite compound, a phosphide of copper, which is hard and brittle. The presence of this substance in the alloys, where it is readily distinguished under the microscope, renders them much harder and stiffer than the pure tin-copper alloys, but at the same time renders them comparatively brittle. As a consequence, these alloys—containing up to 1·5 per cent. of phosphorus—are employed principally for bearing-metals, where the copper-phosphide plays much the same part which the tin-antimony compound plays in certain white-metal bearings.

Metallic manganese may also be employed as a deoxidising agent in copper alloys, and although it is a less active reducing agent than phosphorus, it has the considerable advantage that if used in excess it does not render the alloys hard and brittle. Manganese does not form any definite compounds with copper, the copper-manganese constitutional diagram being that of an unbroken series of solid solutions, although this particular system exhibits a minimum in the *liquidus* which somewhat recalls a eutectiferous system. The presence of small quantities of manganese in alloys of copper with zinc or tin, therefore, does not as a rule give rise to the formation of any new constituents ; the manganese enters into solid solution, and merely adds its quota to the hardening effect of the dissolved metals.

A more powerful deoxidising agent than manganese is furnished by aluminium, but this differs from manganese in two vitally important respects. In the first place, the oxidation product of aluminium is a particularly refractory substance —alumina—which has a strong tendency to remain in the molten metal in suspension as fine particles. These, of course, tend to lessen the strength and toughness of the alloy. Beyond this, aluminium exerts a very powerful hardening effect on copper, owing to the fact that it enters into chemical combination with that metal. Both these reasons militate against the use of aluminium as a deoxidising agent for alloys of copper, although it is employed for that purpose in the metallurgy of steel.

Returning to the binary alloys of copper, those with aluminium remain to be considered. These are of interest in several directions ; their constitutional diagram presents a number of peculiar features, some of which have not yet been fully elucidated, although the subject has received much study at the hands of Carpenter and Edwards (19), Curry (20), and others (21). A constitutional diagram based on their results is reproduced in Fig. 62, but this must still be regarded as somewhat tentative. From the point of view of practical application the alloys at the copper end of the series, containing up to 10 per cent. of aluminium, are of considerable interest, both on account of their valuable mechanical properties and also on account of their marked powers of resisting corrosion. Certain difficulties which have been experienced in their use and working are likely to be overcome when their advantages are fully realised. At the other end of the series is a group of light alloys consisting principally of aluminium, but containing up to 4 or 5 per cent. of copper, which are of interest, not so much for their own sake, as on account of an important alloy which is derived from them. This alloy, known by the trade name of "Duralumin," will be referred to again in connection with the ternary system manganese-aluminium-copper.

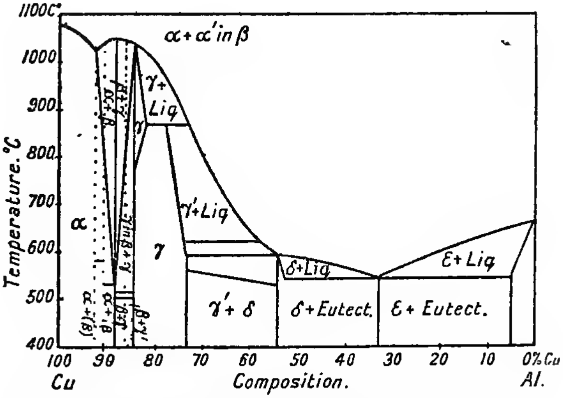
1100C°
1000
900
800
700
600
500
400
Temperature. °C
α + α′ in β
γ + Liq
γ′+ Liq
α
γ
α + β
β + γ
γ in β + γ
γ′ + δ
δ+Liq
δ + Eutect.
ε + Eutect.
ε + Liq
β + γ′
100
90
80
70
60
50
40
30
20
10
0% Cu
Cu
Composition.
Al.

FIG. 62.—Constitutional Diagram (tentative) of the Aluminium-Copper Alloys.

At the other end of the series we will again confine our attention to the alloys containing less than 10 per cent. of aluminium. Up to an aluminium content of slightly more than 7 per cent.

the alloys are simple solid solutions consisting entirely of the *a* phase, which is very similar in character and appearance to the *a* phase of the zinc-copper or the tin-copper system. Like the two latter the *a* body of the aluminium-copper series readily undergoes twinning when subjected to plastic deformation followed by annealing. In its mechanical properties, however, the aluminium-copper *a* phase differs widely from that of the other copper alloys. This series of solid solutions, however, exhibits one peculiarity; it will be seen from the diagram that, unlike the two other copper systems discussed above, there is no long freezing-range for the *a* phase; indeed, the *solidus* and *liquidus* lie so close together that it is difficult to distinguish them from one another. It is a direct consequence of this circumstance that the portions of the *a* body which crystallise first do not differ very much in composition from the portions which solidify last, and as a result the cast alloys do not exhibit that well-marked structure of dendritic cores which is so frequently met with in solid solutions. This range of pure *a* alloys corresponds to the first branch of the *liquidus* curve, AB of the diagram. At the point B a definite minimum in the *liquidus* is reached and in the majority of cases such a minimum is associated with the formation of a definite eutectic alloy. In the aluminium-copper system, however, this is not the case, and the minimum seems to be analogous to that which occurs in the manganese-copper series, being simply formed in an unbroken series of solid solutions. It would, however, probably be more correct to draw the curve continuously through this minimum rather than to show a definite cusp.

From this minimum the *liquidus* curve rises to a maximum at D, which corresponds to the definite compound Cu_3Al. Corresponding to this new branch of the *liquidus* there is a striking change in the micro-structure of the alloys, which now becomes duplex. Since the field of the *a* phase is bounded by the sloping line BO, it will be seen that an alloy whose composition lies just to the left of the point P (*i.e.*, containing about 12·5 per cent. of aluminium) should still be homogeneous when in a state of equilibrium. The change from *β* to *a* in

material which can be readily broken to powder, and is consequently very useful in the preparation of alloys in the foundry, as it can readily be weighed out exactly to the desired quantity. If a small ingot of this alloy be allowed to set superficially, and if the skin is then broken and the residue of liquid metal is poured off, a mass of beautiful interlacing crystalline needles is left behind. These, although they consist of equal proportions of copper and aluminium, are of a brilliant white colour and extremely brittle.

The ternary alloys of aluminium and copper with other metals have received a good deal of attention. Edwards and Andrews ([22]) have studied the equilibria of the aluminium-tin-copper system, while the author and Lantsberry ([23]) have investigated the ternary system containing manganese. The relationships found are, however, too complex to be described here, and reference for particulars must be made to the original memoirs. One or two points of interest may, however, be mentioned. The addition of manganese to the aluminium-copper system, so far as the alloys near the copper end of the series are concerned, appears to result in a slight increase of strength without any reduction of ductility, provided that the manganese addition is small or that the alloy in question lies well below an aluminium content of 10 per cent. Apart from this effect, however, these alloys containing manganese appear to possess a still greater resistance to corrosion than the binary aluminium copper alloys, and they are also peculiarly resistant to abrasion, so much so that they excel tool-steel in that respect. This combination of properties offers some advantages in certain branches of instrument construction, particularly where the use of non-magnetic material is essential. When severely cold-worked these alloys attain a very high degree of strength and hardness, so that it has been possible to make cutting tools of these materials which are quite capable of cutting wood and even stone.

In the light alloys containing less than 4 per cent. of copper the addition of manganese was found to be an advantage, but the quantity that can be added is limited by the fact that aluminium and manganese form the definite compound Al_3Mn, which is a hard and brittle body, and one, moreover, which—if present in any large proportion—tends to cause the alloy to fall to pieces spontaneously. Additions of manganese are therefore confined to 2 per cent. The alloy of aluminium with copper 3 per cent. and manganese 1 per cent. was at the time when it was investigated the best light alloy known, and by the addition of 0·5 per cent. of magnesium it is converted into the alloy already mentioned, known as "Duralumin."[1] The presence of this small percentage of magnesium appears to confer on this material, and indeed upon any alloy consisting largely of aluminium, a peculiar property of hardening slowly in the course of several days after it has received an appropriate heat treatment (^{24}). The exact nature of this hardening process is not understood, but it results in very nearly doubling the tensile strength of the alloy without very seriously reducing its ductility. This remarkable behaviour constitutes one of the most striking unsolved problems in present-day Physical Metallurgy.

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[1] A group or range of alloys is known under the trade name "Duralumin"; the composition stated above is typical of *one* of these.

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CHAPTER VIII

THE IRON-CARBON SYSTEM

On account both of their intrinsic importance and of their complexity of constitution and structure, the iron-carbon alloys require treatment in a special chapter. Such separate treatment must not, however, be taken to indicate that iron and steel differ in any fundamental way from other alloy systems. Such an idea appears to have been prevalent in the minds of some of the earlier workers (1) in the subject, and even now there is an unfortunate tendency to discriminate too strictly between " ferrous " and " non-ferrous " metallurgy or metallography. It is, therefore, well to emphasise that iron and steel are alloys subject to precisely the same laws and to be studied in exactly the same way as other alloy systems. A good deal of the difficulty and confusion which has at times clouded the view of the constitution of the iron-carbon system has, indeed, arisen from the circumstance that this subject has often attracted workers who came to it without previous acquaintance with the more general methods of studying alloys, and often even without an adequate knowledge of the fundamental principles of physical chemistry. On the other hand, the iron-carbon system has probably been subjected to more minute study than any other series of alloys ; now, as each binary system is more closely studied, it is found that constitutional diagrams which on first investigation appeared to be simple have turned out to be more and more complex. The complexity of the iron-carbon system as we know it to-day may thus simply be the result of this minute study, so that even in this respect the system does not differ very widely from other alloy series.

An approximate constitutional diagram of the iron-carbon system is given in Fig. 64. This is not, strictly speaking, an equilibrium diagram, since it represents what is probably merely a very persistent meta-stable system. The diagram of the completely stable system is not, however, thoroughly known and is of minor importance, since it deals with conditions never met with either in practice or in the laboratory. So far as it is known it is given in Fig. 65.

The constitutional diagram of Fig. 64, while, strictly speaking, representing only the author's views on the constitution of iron and steel, is very similar to the diagram which is accepted by the great majority of physical metallurgists, and is practically identical with that published by the International Testing Association in connection with the Report of the International Committee on the Nomenclature of the Microscopic Constituents of Iron and Steel in 1912 (²). Some minor points on which differences of opinion exist will be mentioned as the details of

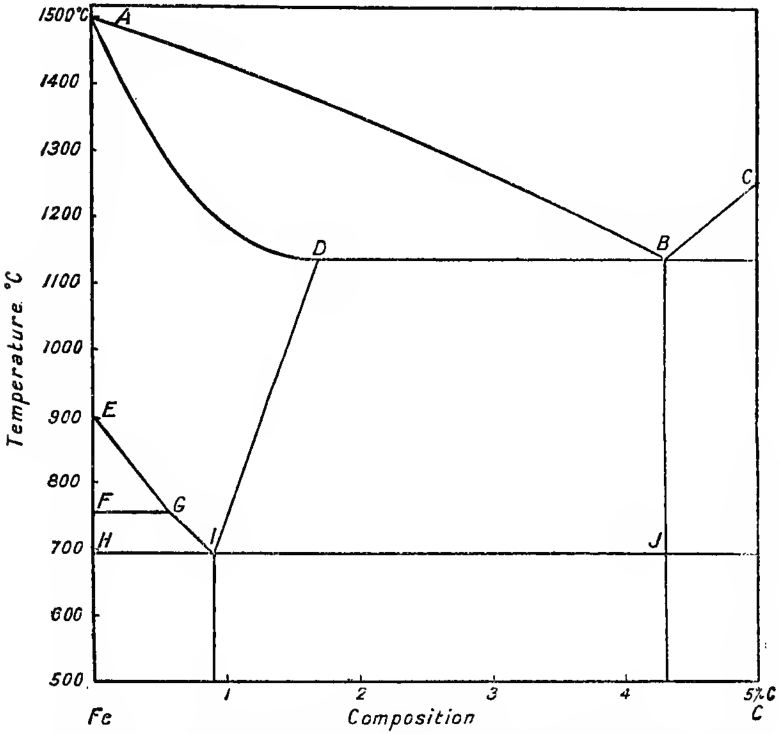

FIG. 64.—Constitutional Diagram of the Iron-Carbon System.

the diagram are discussed. The diagram as a whole—broadly speaking—may be regarded as accepted by all but one small and isolated group of metallurgists, who have not, however, put forward an alternative diagram for discussion. Beyond the present warning that such a group exists, therefore, their peculiar views will not receive further consideration here.

The constitutional diagram of the iron-carbon alloys, as shown in Fig. 64, is peculiar, in the first place, on account of the fact that it does not extend beyond a carbon concentration of 6 per cent. A few alloys of rather higher carbon content have been prepared experimentally by the aid of the electric furnace, and attempts have been made to carry the diagram somewhat further to the right (3), but in the introductory treatment of the subject which is contemplated here that region of the diagram will not be considered. The reason why the diagram is not continued to the full extent on the carbon side lies, of course, in the fact that the system in question is one of alloys between a metal and a metalloid, the latter—carbon—being, moreover, a substance which cannot be melted in any ordinary way. We find similar limitations in the alloy systems of other metalloids, such as those of copper and arsenic, where the volatility of the arsenic limits the diagram to the vicinity of the copper end. In reality the "iron-carbon" system is the "iron-cementite" system, the name "cementite" being given to the definite iron-carbon compound having the formula Fe_3C, and containing 6·6 per cent. of carbon.

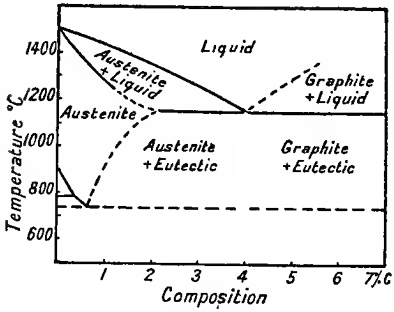

FIG. 65.—Constitutional Diagram (tentative) of the Iron-Graphite System.

The *liquidus* of the iron-carbon diagram is given by the lines ABC in the diagram (Fig. 64). The branch AB represents the deposition from the molten alloys of a solid solution of carbon—or more probably of iron carbide—in iron. The branch BC corresponds to the solidification of crystals of iron carbide (cementite), but the formation of such crystals from fusion is frequently accompanied or very shortly followed by their decomposition into iron and graphite. This change is in reality a transition from the meta-stable system iron-iron carbide to the stable system iron-graphite. It is of great importance in connection with the structure and constitution of cast iron, and will be referred to in that connection.

The point B of the diagram is obviously a eutectic point similar to those found in the lead-tin and aluminium-zinc systems ; in the present case the eutectic is that of the solid solution mentioned above—which we may refer to as the γ-iron solid solution—with cementite. Here also there is reason to believe that there is an alternative mode of solidification according to the stable iron-graphite system, a eutectic of that kind being indicated by the lines of the diagram of the stable system in Fig. 65.

The *solidus* of the iron-cementite system is given by the lines AD, DB, the point D indicating the limit of solid solubility of cementite in iron at a temperature of about 1,135° C. The system thus belongs to the general type, in which there is a considerable range of solid solubility between the two components, with a central eutectiferous range. The eutectic temperature in this case lies at or near 1,135° C. The position of the *solidus* between A and B cannot be ascertained from the data derived from thermal curves, and its position as given in the diagram is based on the work of Gutowsky (4), who determined the position of the *solidus* by the method of quenching small specimens of steel of various composition and thus ascertaining by the microscope at what temperatures the first traces of the presence of liquid could be discovered. This work is the best as yet available on this line, and it is probably sufficiently accurate to warrant the general shape and position of the line AB as drawn in the figure, but confirmatory work of the most exact nature is required in order finally to fix this important line.

Like all binary diagrams of this type, that of the iron-carbon system must possess a line limiting the region of the stable existence of the γ-iron solid solution which is formed by the final solidification of the alloys along the line AD. This line must start from D, the point at which, under conditions approximating to equilibrium, the eutectic first makes its appearance, and run downward to the base of the diagram. If the limit of solid solubility of cementite in γ-iron were the same at all temperatures, this bounding line would be a simple vertical. Actually, however, the amount of cementite which γ-iron can retain in solid solution decreases with falling temperature, and consequently the line DI slopes backwards towards the iron end of the diagram. This is in itself an unusual feature in alloys, as the bounding line of the region of the *a* phase in both the zinc-copper and the tin-copper systems slopes away from the copper end of the diagram. The line DI also exhibits another peculiarity in that it does not extend to the base of the diagram. This arises from the circumstance that the γ-iron solid solution does not exist at the ordinary temperature in a state approaching equilibrium, but undergoes decomposition at temperatures lying on or above the line HIJ (near 700° C.). The line DI, therefore, ends where it cuts the line HIJ, that being the limit of existence of the γ-iron phase.

In one sense the line DI may be regarded as strictly analogous to one branch of a "*liquidus*" curve in an ordinary eutectiferous alloy system. Such a branch of a *liquidus* curve indicates the temperatures at which the *liquid* solution of two components begins to deposit crystals of one of them, *i.e.*, the limit of solubility of the one component in the liquid solution of the two. Similarly the line DI indicates the temperatures at which the *solid* solution, γ, begins to deposit crystals of cementite, which is one of the components of the solid solution. Now if we pursue this analogy a little further we shall expect to find that, just as a downward sloping branch of a *liquidus* generally meets another downward sloping branch at a eutectic point, so the line DI, representing the temperatures at which the γ solid solution deposits cementite, should meet, at a point corresponding to a eutectic point, a branch or curve corresponding to the deposition from the solid solution of the other component, viz., iron. This branch is found in the diagram in the shape of the two lines EG and GI. The fact that there are two lines instead of a single one arises from precisely the same kind of cause as that which produces a break in the *liquidus* curve of the aluminium zinc alloys at the point C of that diagram (Fig. 48), or at the point B in the zinc-copper diagram (Fig. 54) —it is simply that the phase deposited from the solution along the branch before the small break is different from that which is deposited along that part of the curve lying beyond the break. At all events, we certainly have at I a point corresponding, for the decomposition of the γ solid solution, to the eutectic point of a liquid solution, while the lines EGI and ID, which meet at this point, I, correspond to the two branches of a *liquidus* curve in the case of an alloy solidifying from fusion. The point I is consequently called the " eutectoid " point, and the body formed along the line HIJ is known as a " eutectoid."

The region in which the γ solid solution is stable is thus bounded by the lines AD, DI and IGE. We may now follow somewhat more closely the manner in which this solid solution undergoes decomposition. As we have already seen, along the branch EGI we may expect to find that the solid solution deposits crystals of iron, while along ID it deposits crystals of cementite or iron carbide. The question naturally arises, why should the γ-iron solid solution deposit its burden of dissolved cementite, or its excess of iron at certain temperatures, instead of carrying them permanently in solution as the a phase in most of the copper alloys carries the zinc or tin or aluminium with which it is associated? Here also the analogy with the liquid solution of two metals, *i.e.*, with a molten alloy, will aid us in understanding what takes place. The deposition of a solid metal from a liquid solution is intimately connected with the natural freezing-point of the metal in question. In the pure metal itself, solid crystals are deposited from the liquid (*i.e.*, from the molten metal) at one definite temperature, which we call the freezing-point of the pure metal. Now that branch of the *liquidus* which relates to the deposition of crystals of that metal from the liquid alloy starts from the freezing-point of the pure metal and slopes downward to the eutectic point. The whole of such a branch of the *liquidus* may, therefore, be regarded as representing the depression of the natural freezing-point of the pure metal by successively increasing additions of another metal. What is really happening along such a *liquidus* curve is thus simply the freezing of the metal, modified, principally in regard to temperature, by the presence of the second element. If the analogy between the decomposition of the γ solid solution and the freezing of a series of alloys is correct we should expect to find that the decomposition of the γ solid solution is a phenomenon which we could trace as something analogous to a change of state in the pure metal, *i.e.*, in iron itself. And this is actually the case. The curve EGI starts from a point in pure iron itself—a point which does not, it is true, represent the passage of the material from the liquid to the solid state, but which indicates a profound change taking place in the iron, and accompanied by evolutions of heat on cooling and absorptions of heat on heating which are comparable with those which occur on freezing or melting. In the case of a change of state—*i.e.*, a change from liquid to solid or from liquid to gas—we see a phenomenon which involves a profound change in the arrangement of the molecules of the substances. In the gas the molecules are free from one another and move about unrestrictedly in all directions ; in the liquid state the molecules are much less free to move, although still comparatively free in contrast to the relatively rigid manner in which they are arranged in the crystalline system of a solid substance. We now come to the conception that, within the range of the solid state, there may be, and indeed there are, various possible arrangements of molecules, or even of the constituent atoms of a molecule, correspondin to differences almost as great as those between two different "states." Such different conditions are known as "allotropic" conditions or modifications, and their existence is well known in such elements as carbon, where graphite, diamond and "amorphous" carbon are recognised as allotropic modifications of one another. So also in sulphur, selenium, oxygen, tin, antimony and many other elements, well-known allotropic varieties exist. The occurrence of well-defined heat evolutions on cooling and heat absorptions on heating even in the purest obtainable iron are in themselves strong evidence that iron is capable of existing in at least three diverse or "allotropic" conditions. These are generally known as the γ, β and α forms of iron, and they have formed the subject of much controversy. This has, however, principally turned upon the question whether one of these modifications was in itself extremely hard, and whether its existence could adequately account for the hardness of hardened steel. That question does not concern us here, and it may fairly be said that the existence of two allotropic varieties of iron (the γ and the α) is universally accepted. The β form is still the subject of discussion, but the question of its inclusion or otherwise only leads to a very slight modification of the constitutional diagram. The main point which is required for the comprehension of the constitutional diagram is that γ-iron in the pure state undergoes an allotropic transformation at a temperature close to 900° C., marked by the point E in the diagram of Fig. 64. In consequence of this transformation the iron, now in the α or the β state, can no longer hold any appreciable amount of carbide in solid solution. Accordingly, along the line EGI, the solid solution deposits crystals of practically pure iron free, or almost free, from carbon. The deposit of such iron crystals, however, produces upon this solid solution precisely the same result as the deposition of crystals of lead, for example, produces upon a liquid alloy of lead and tin—the residual solution becomes impoverished in lead (or iron), and the temperature at which further deposition takes place thus corresponds to a point a little further down the line of deposition. Right down to the temperature of the line HIJ, therefore, there will always be a residue of γ-iron solid solution, and the amount of this residue will be greater the nearer the alloy under consideration lies to the point I. When the alloy finally reaches the temperature of the line HIJ, the residual γ-iron solid solution undergoes transformation *en masse*, and the "eutectoid" body known as "pearlite" is formed, with a large evolution of heat.

The precise meaning of the portion of the constitutional diagram of the iron-carbon system relating to the group of alloys generally known as "steel," which may be taken as lying to the left of the point D in the diagram, will be best understood by following a few typical alloys through the cooling and heating

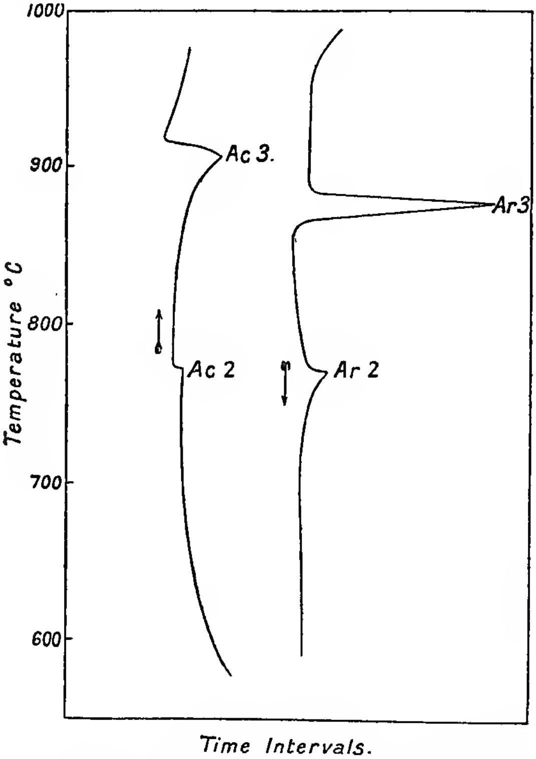

FIG. 66.—Typical Inverse-Rate Heating and Cooling Curves of Pure Iron (Burgess and Crowe).

processes. At the same time the micro-structure of these alloys can be considered.

We shall begin with pure iron. A typical set of heating and cooling curves of this material, reproduced from the work of Burgess (^{5}), is shown in Fig. 66. It will be seen that there are two peaks on both the heating and the cooling curves. On cooling we commence with the iron in the γ state, and nothing occurs until the point E of the diagram is reached, at or near 900° C. At this point there is a marked evolution of heat on cooling, and the heating curve shows a corresponding absorption of heat on heating, but at a slightly higher temperature. It has been shown that the exact interval between the temperatures at which this transformation occurs on heating and on cooling depends partly upon the rate of heating and cooling and on the maximum temperature which has been attained; but even when these factors are allowed for there probably remains a certain "lag" between the two, representing the tendency of an existing state to persist for a short distance on either side of its true equilibrium temperature. This is a species of under-cooling or of super-heating which is of constant occurrence. Phenomena of under-cooling are frequently met with in the crystallisation of salt solutions, and in that case it has been shown that below the true freezing-point there is a limiting range within which the solution can be made to crystallise instantly if it is brought into contact with a solid crystal of the same kind to act as a nucleus. In the absence of a nucleus, however, spontaneous crystallisation only occurs after the limit referred to has been passed. Now in a solid solution no nuclei can be introduced, and consequently it is not perhaps surprising to find that transformation does not occur until some corresponding limiting temperature has been passed, this limit lying very slightly above the true equilibrium temperature on heating and considerably below it on cooling. There is, however, no rise of temperature during the transformation, such as occurs when an under-cooled liquid freezes. This may, however, be due to the fact that the total quantity of heat evolved is much smaller, and also that the circumstances of the change, occurring as it does in a fairly rigid solid, do not permit of rates of transformation sufficient to bring about an actual rise of temperature.

On further cooling below the point E, the pure iron exhibits another "critical point" or evolution of heat on cooling, with a corresponding absorption on heating at the point marked F. This is a much smaller point than the one at E, and attempts have been made to discredit its existence (6) in pure iron.

According to the views of Benedicks (7), this thermal point does not represent an allotropic transformation of iron at all, but merely indicates the final disappearance of γ-iron molecules from the metal. This idea is based upon the assumption that the whole of the γ-iron is not at once transformed into another modification at E, but that a certain number of γ-iron molecules persist in a state of solution in the other form of iron, and that the last of these undergo sudden transformation at the point F. This view is stated here in the desire to represent current opinion in as fair a manner as possible, but the author believes that all the weight of evidence—into which it is not possible to enter here—goes to show that a β phase of iron, intermediate between the γ phase, which exists above the point E, and the α phase, which exists below the point F, really exists. Not only is there a definite thermal point at F, but it persists through the range of steels between F and G, and there is a slight break in the line EGI at the point G. There are also some small but very definite discontinuities in the physical properties of iron corresponding to the temperature of the point F, the most important of these being the sudden disappearance of ferro-magnetism at that temperature. Another is a sudden change in hardness or tenacity at that temperature, as shown by the author and Humfrey. Provisionally, at all events, we may, therefore, think of iron passing from the γ to the β state at or near 900° C. on cooling, and from the β to the α at or near 750° C. Pure iron undergoes no further transformations on cooling down to the ordinary temperature.

The question now arises whether any changes of micro-structure can be correlated with the two allotropic transformations of iron. As a rule, changes which occur at high temperatures can be more or less completely inhibited by sufficiently rapid cooling, *i.e.*, by quenching. That this is not the case for iron is at once obvious from the fact that while iron above 750° C. is practically non-magnetic, no known method of quenching pure iron renders it non-magnetic after cooling. As regards micro-structures, it must be remembered that we are dealing with a pure metal and that pure metals of most widely divergent properties still show practically identical micro-structure. It is not surprising, therefore, to find that iron quenched from temperatures above 900° C. does not differ markedly in micro-structure from the same material slowly cooled. That the mechanical properties also remain practically unaffected is more remarkable, since it is not likely —even if we had not definite proof to that effect—that γ-iron should resemble α-iron in that respect. The inference which we are forced to accept is that in pure iron the allotropic transformations cannot be prevented by rapid cooling or quenching. There is, however, good evidence to show that the properties of iron do undergo marked changes on passing through the critical temperatures, but this will be referred to, in connection with the effects of plastic strain on metals, in Chapter XI.

The cooling and heating curves of really pure iron, free from carbon, as reproduced in Fig. 66, show no sign of any thermal change corresponding to the point H of the diagram of Fig. 64. This is, of course, in accordance with the indications of the diagram itself, since the reactions represented by the line JIH are due to the presence of the dissolved carbide in the γ-iron of steels ; as the pure iron end of the series is approached, these reactions diminish in intensity and disappear entirely in pure iron itself.

We may next consider the case of an iron-carbon alloy or steel containing about 0·2 per cent. of carbon. In the γ region this is a homogeneous solid solution, and decomposition only begins, by the deposition of crystals of β-iron, when the alloy cools down to the temperature of the sloping line EG. We have thus a first arrest or critical point, on cooling, corresponding to the commencement of the deposition of iron, in the β condition, from the solution, at a temperature which for a 0·2 per cent. carbon steel lies at 840° C. As the alloy cools further, the quantity of β-iron separated from the solid solution steadily increases until the line FG is crossed at a temperature near 750° C. Here all the free β-iron present in the steel is transformed into the α form and, whereas above the line EG we had a mixture of residual γ-iron solid solution with crystals of β-iron, below the line EG we have a mixture of residual γ-iron solid solution with crystals of α-iron. With further cooling, the quantity of the α-iron crystals increases steadily until the temperature of the line HIJ is reached; there the residual γ-iron solid solution is transformed into the eutectoid mixture of α-iron and cementite. In this steel we thus have three thermal critical points indicated by absorptions of heat on heating and evolutions of heat on cooling. These "arrest-points" have received special names derived from their relative position, counting from the ordinary temperature upwards. The point connected with the line HIJ is called the first arrest, or "A_1," the one which occurs on the crossing of the line FG is the second arrest, or "A_2," and the arrest related to the sloping line EG is the "third arrest," or "A_3." Now in these steels, as also in pure iron, as has already been indicated, the temperature at which these transformations take place on cooling are not identical with those at which they occur on heating, and the arrest-points on heating and cooling are, therefore, distinguished by writing "Ac" for the points on heating and "Ar" for the points on cooling. Thus "Ac_3" is the arrest observed on crossing the line EG on heating, while "Ar_3" is the arrest obtained when the line EG is crossed on cooling. These special terms are convenient in use, but introduce an additional complexity into a nomenclature already somewhat needlessly involved. In the case of the metallography of steel, the analogy with petrography has been followed all too closely, so that names—and often personal names—have been given to everything. The equally complex metallography of the tin-copper system is quite as clear without the use of such names, while in steel the use of personal names has undoubtedly introduced an element of personal acrimony into what should be purely scientific discussions.

The micro-structure of a steel of 0·2 per cent. carbon content is found to be quite in accordance with the indications of the diagram and of the cooling curves. When slowly cooled in the ordinary way, such steel is found to possess a duplex structure, such as that shown in Fig. 67, Plate XIII., where the light areas represent the crystals of iron, while the dark areas are the eutectoid body formed at the line HIJ.

The simple white constituent is readily seen to be identical with the crystals of pure iron, and is consequently known as "ferrite." In commercial steels, however, the "ferrite" always holds some silicon and phosphorus in solid solution. The eutectoid is known as "pearlite" owing to the fact that it frequently exhibits a finely-laminated structure like that of mother-of-pearl and, under suitable illumination, displays an iridescent lustre of the same kind. That this body is typically laminated is illustrated in Fig. 68, Plate XIII., which represents such pearlite as seen under high magnification. In this respect the eutectoid "pearlite" bears out its analogy with the normal eutectics, which are also typically laminated. Both kinds of bodies, however, can easily be obtained in a non-laminated state, so that the laminated structure must not be regarded as a fundamental characteristic of eutectics or eutectoids.

The fact that the laminated eutectoid body—pearlite—is really formed on crossing the line HIJ is readily proved by quenching experiments. Such steel quenched from a temperature lying between the lines HI and EG still exhibits a typical duplex structure, one of whose constituents is ferrite, but the area of ferrite is markedly less than in the slowly-cooled sample, particularly if the quenching temperature lies near the line EG. The second constituent, however, is seen to be fundamentally different in character from the pearlite of the slowly-cooled material. The second constituent still appears darker than the ferrite when etched with the usual reagents, such as picric acid, but under moderate magnifications it appears to be perfectly homogeneous, and only under the highest magnification can any structure be found in it—but this is not a lamination or granulation, but a tracery of interlacing needles. If the quenching temperature is taken still higher, *i.e.*, above the line EG, then the whole—or very nearly the whole—area of the specimen is found to be covered by the darker-etching constituent having the faint acicular structure. We thus recognise in this constituent the representative of the γ-iron solid solution which exists in these steels at the moment of quenching. That this constituent is not really the solid solution itself preserved unchanged by the act of quenching is shown by several considerations, which, however, are best discussed in relation to steels of higher carbon content. The results of quenching experiments on this grade of steel, however, are obviously sufficient to justify the existence of the various lines of the diagram, with the possible exception of the line FG. whose influence on the structure has not so far been established. Additional evidence in support of the correctness of the diagram is also afforded by the work of Baykoff (9), who succeeded in etching specimens of steel at high temperatures by the action of hydrochloric acid gas. This method, even more definitely than the earlier efforts of Saniter (10) at hot-etching by means of fused calcium chloride baths, reveals the fact that, at temperatures above the line EG, the steel has a structure of simple polyhedra, such as those which we are accustomed to meet in homogeneous solid solutions.

Turning now to a steel of slightly higher carbon content, such as 0·6 per cent., we find a somewhat simpler type of thermal curve. On cooling, the lines GI and HI are successively crossed, and the steel thus shows only two Ar points. The lowest of these is obviously identical with Ar_1 as we saw it in the steel of 0·2 per cent. carbon ; the higher one was originally regarded as being the result of the merging of the Ar_3 and Ar_2 points of the lower carbon steels, and the point is consequently known as Ar_{23} or Ac_{23} respectively. This nomenclature is not, however, consistent with the constitutional diagram. If we accept the existence of the β phase in the region EFG, then the line GI represents a transformation—from the γ to the a state direct—which is not present in either Ar_3 or Ar_2, while, if we deny the existence of the β phase, we must also wipe out the break in the line EGI at the point G, and in that case the point corresponding to the line GI should be simply Ar_3. In any case, therefore, the term Ar_{23} is illogical, but, since it is frequently used, some reference to it was essential at this point.

As we have already remarked that the line FG is without any apparent influence on the micro-structure of steel quenched above it or below it, the absence of this line from the portion of the diagram relating to the steel now under discussion (0·6 per cent. carbon) will not affect the range of micro-

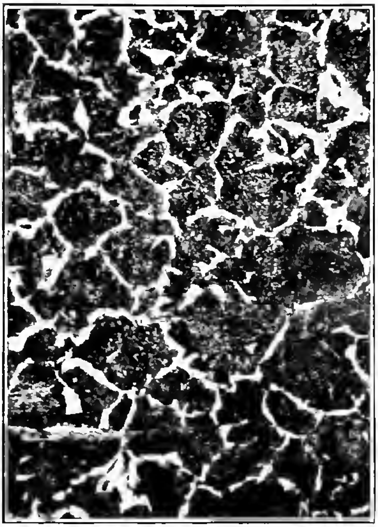

FIG. 69.

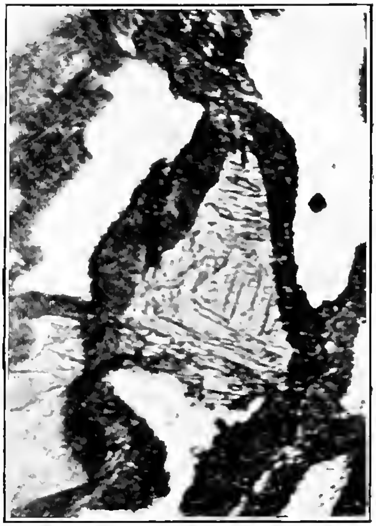

FIG. 70.

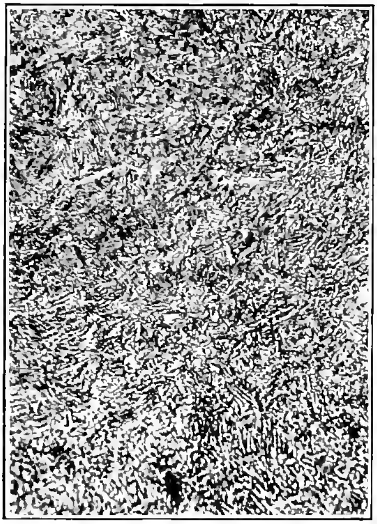

FIG. 71.

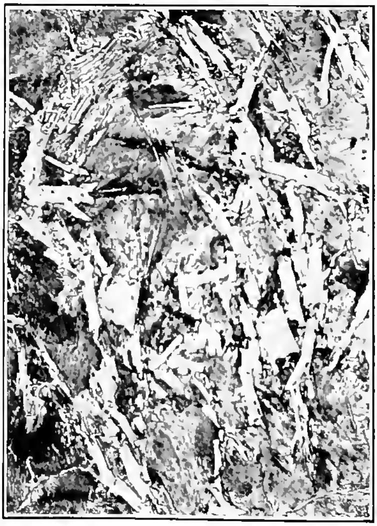

FIG. 72.

structures met with in this steel as compared with one of lower carbon content; only, in accordance with the indications of the diagram, the higher-carbon steel will, when slowly cooled, contain a much larger proportion of the eutectoid pearlite than is the case with a lower carbon content. This is well brought out by comparing Fig. 69, Plate XIV., relating to this steel, with Fig. 67, Plate XIII., relating to the other. On quenching at higher temperatures, the features met with in the milder steel are largely reproduced, again with the modifications due to the larger proportion of the γ-iron solid solution and the smaller excess of free α-iron or ferrite. The higher carbon content also seems to favour the development of the acicular structure of the quenched solid solution, which is much more marked in the present steel than in the previous one. There features are shown in the photo-micrograph (Fig. 70, Plate XIV.), which shows the structure of this steel after quenching from 750° C.

We now have to consider the steel of eutectoid composition—a point determined by Arnold (11) as lying at a carbon content a very little below 0·90 per cent. of carbon. This figure, however, will vary very perceptibly if any other elements, such as silicon or manganese, are present to an appreciable extent. Such a eutectoid steel will, in accordance with the diagram, exhibit only a single arrest-point on either heating or cooling. Following the somewhat illogical method already referred to above, this point is called Ac_{123} and Ar_{123} on heating and cooling respectively. It is a very strong evolution or absorption of heat—so strong, indeed, that if a piece of such steel is allowed to cool in air, when the evolution of heat which occurs at the transformation of the solid γ-iron solution to the eutectoid pearlite takes place the steel is seen to glow visibly. This phenomenon received the name "recalescence" long before its true nature was understood, and the thermal curves of steel are for that reason sometimes called "recalescence curves"—a misleading term whose use is to be deprecated.

Microscopically, steel of approximately 0·9 per cent. of carbon consists, when slowly cooled, entirely of the pearlite constituent, thus corresponding to the pure eutectic of ordinary binary alloys. Immediately above the temperature of the line

HIJ, however, such steel consists entirely of the homogeneous solid solution of cementite in γ-iron. Ordinary quenching is obviously unable to retain this homogeneous solid solution completely unchanged, for the acicular constituent, and frequently some other forms, make their appearance. A typical structure is shown in Fig. 71, Plate XIV. This is, of course, a steel hardened by quenching, for while even mild steels, containing as little as 0·2 per cent. of carbon, are, in the strict sense of the word, " hardened " as the result of quenching from temperatures above the line EGI, this hardening is very slight until a carbon content of 0·6 per cent. is reached, and it only attains its full value at or near the eutectoid composition.

For carbon contents beyond the eutectoid composition, an upper thermal point, corresponding to the crossing of the line ID, again makes its appearance, and the structure of the slowly-cooled steel again shows two well-defined constituents. One of these consists of angular crystals of an obviously hard material which lie embedded in the pearlite. We have here crystals of cementite separated from the γ-iron solid solution on crossing the line DI, embedded in the pearlite resulting from the decomposition of the residual solid solution on crossing the line IJ. A typical example of this structure is shown in Fig. 72, Plate XIV. If such a steel is quenched from a temperature above the line ID, provided that time enough has been allowed for the somewhat slow solution of the free cementite in the solid solution, we should expect to obtain a homogeneous mass of the unchanged γ-iron solid solution. In the quenching of lower carbon steels this has never been attained, the incipient decomposition or degradation typified by the acicular structure being always found. In these higher carbon steels it appears that a portion of the γ-iron solid solution is actually retained in its original homogeneous state, and we find streaks of this entirely unchanged solid solution lying among the acicular degradation product. This gives to severely-quenched high-carbon steels a very striking appearance, which is illustrated in Fig. 73, Plate XV.

The account of the micro-structures and constitution of the iron-carbon alloys up to a concentration of about 2 per cent. of carbon might be regarded as adequately concluded at this point, at all events for the purposes of an introductory survey, were it not for the fact that the importance of hardened and tempered steel lends very great interest to the structures met with in quenched steel. It has already been indicated that quenching never quite results in the retention of the structure as it exists at the instant when rapid cooling is begun, but that the very changes which it is intended to inhibit always occur to a small extent—the actual extent depending upon the circumstances of quenching and on the nature of the metal in question. In the case of steel the products of the incipient decomposition which takes place in these circumstances are particularly complex and interesting, although it is probable that similar complexity could be discovered in other alloys if they were studied in the same way.

At any temperature and composition corresponding to the area ADIGE of the constitutional diagram the alloys consist of the simple, homogeneous γ solid solution, having, as we have seen, the typical polyhedral structure of a "simple" alloy. The character of this γ solid solution, however, must vary from one side of this region to the other, owing to the difference of carbon content—the γ phase being pure iron in the γ condition at one side of its range of existence, and a solid solution containing as much as 2 per cent. of carbon at the opposite extreme. Its behaviour on quenching is, therefore, correspondingly different, but these differences may be readily understood if it is realised that the presence of the carbon or iron carbide in solution must materially affect the manner, and still more the rate, at which the solid solution can undergo transformation. Where there is little or no carbon present, the γ-iron molecules, in becoming transformed into the other allotropic form, have merely to re-arrange themselves *in situ*—there is no need for any transportation of matter through relatively considerable distances. Where the solid solution contains carbon, its normal decomposition involves the special separation of a carbon-rich constituent (pearlite) from a constituent free from carbon (ferrite), and this means that the carbide molecules must undergo a definite change of place, so that this decomposition implies the movement of matter (iron carbide) through distances which are very large compared with molecular dimensions. Such movement necessarily requires time, and we consequently are led to expect that while it is difficult to inhibit the transformations of pure iron by quenching, yet the rate of cooling attained by such means is sufficient to prevent the completion of the transformation in the presence of carbon, and more completely the higher the carbon content. This conclusion is in striking accord with the observed facts. While even the most severe quenching produces little effect in pure iron, it produces very marked effects in high-carbon steels and effects of intermediate intensity in steels of intermediate composition. We thus meet with a series of intermediate stages, between the theoretical limit on the one side—never attained in practice—of the complete preservation of the original γ-iron solid solution, and the complete and unhindered transformation of pure iron. These intermediate or transition products have a special interest on account of their typical occurrence in hardened and tempered steels, and have, therefore, received much special attention and a series of personal names.

The complete preservation of the γ-iron solid solution by quenching is, as already indicated, never attained in pure carbon steels. In steels of the highest carbon content, quenched violently from very high temperatures, traces of the undecomposed γ solid solution remain as white, structureless streaks running across the acicular constituent already mentioned. This structure has received the name of "Austenite," and by that term, as adopted by the International Association, we now understand the γ-iron solid solution when preserved as such down to the ordinary temperature—either as the result of quenching or by the presence of a third alloying element, as described below.

The first stage in the decomposition of the γ-iron solid solution consists in the formation of the acicular constituent already described and illustrated (see Figs. 70 and 71, Plate XIV.). This constituent has received the name of "Martensite," and much speculation has been offered as to its true nature. It is undoubtedly the hardest constituent of hardened steels, but it varies very widely in the details of its structure. When steel has been quenched from very high temperatures, the Martensite is found to occur in large grains showing a rather coarse acicular structure. When, on the other hand, a steel of eutectoid composition is quenched at a temperature just above the critical point Ar_1, then the structure of the resulting Martensite is exceedingly fine—so fine, indeed, that some workers, not perhaps provided with the best of microscopic appliances or employing unsatisfactory etching methods, have failed to detect the acicular structure, and have claimed that the best hardened steel contains a structureless "Martensite," which they have sometimes distinguished by the term "hardenite"—a purely local term whose general use is not to be recommended. The careful examination of samples of the best and most carefully hardened steel, however, has convinced both the author and the majority of impartial observers that Martensite can always be shown to

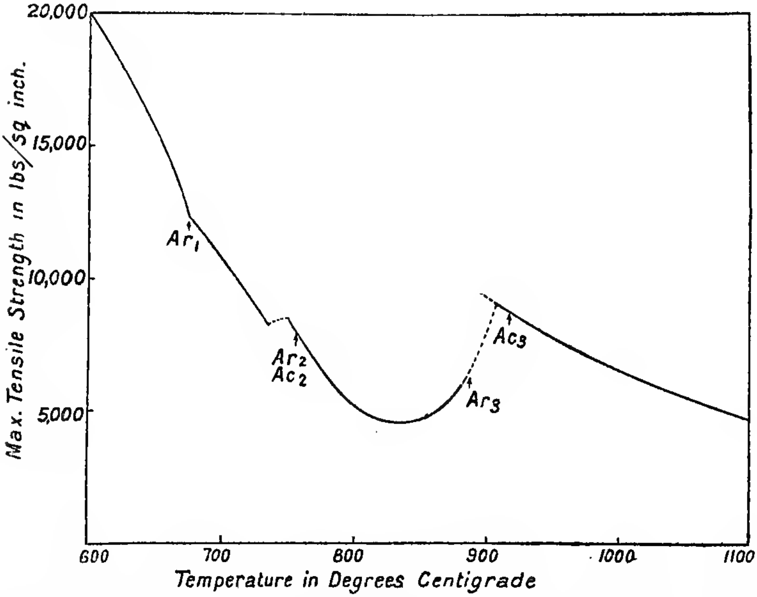

FIG. 74.—Temperature-Tenacity Curve for very Soft Steel at high Temperatures.

have an acicular structure, although in "properly hardened" steel that structure is exceedingly minute.

The question, "What is Martensite and to what is its great hardness really due?" cannot as yet be answered quite conclusively, particularly as several rival views are in the field. These may, however, be briefly indicated. The first and simplest is the purely "allotropic" view according to which the hardness of Martensite is due to the presence in it of a notable proportion of "hard" β-iron. Although attempts have been made to discredit this view recently, there is still much to be said in its favour. Thus it has been shown that the transformation from α to β-iron in nearly carbonless iron is accompanied by a sudden step-up in strength. This is indicated in Fig. 74, which reproduces one of the temperature strength curves of an iron containing 0·1 per cent. of carbon from the work of the author and Humfrey (^{8}). This step-up is not so large as the author had at one time supposed, but its existence is none the less significant, and is quite consistent with the view that, if it could be retained in that condition down to the ordinary temperature, β-iron would be very hard indeed. On this view, then, the acicular structure of Martensite would be due to the formation, on the cleavage planes of the original homogeneous γ-iron solid solution, of needles of β-iron. Normally such β-iron would be obliged to expel the carbon which it had held in solution before the transformation, but, during quenching, time for such separation would not be available, and the β-iron would be compelled to retain in "forced solution," or in very fine suspension, the carbon thus unavoidably retained *in situ*. It may well be that the presence of this "retained" carbon is the real cause of a development of great hardness in the Martensite, and in that case the transformation of the γ-iron might be regarded as taking place direct to the α form without reference to the occurrence of the β phase, whether hard or otherwise.

An alternative theory of hardening, which may be briefly termed the "amorphous" theory, has recently gained much ground. Like the β-iron theory, it explains the hardness of quenched steel by postulating the existence of an intrinsically hard but unstable transition product, which is formed when the transformation of the homogeneous γ-iron solid solution into ferrite and carbide is hindered by quenching. Instead of identifying this hard substance with β iron, which has only a short range of stability in pure iron and low-carbon steels, the new theory ascribes hardening to the presence in the steel of amorphous layers similar to those which are believed to be the cause of the strain-hardening of ductile metals. This hard amorphous phase has, of course, no stable existence below the *solidus* curve of the alloy system, but if its existence is admitted it serves to explain the phenomena of hardening in a very simple manner and to correlate the hardening of steel by quenching with the hardening of ductile metals by plastic deformation.

On the question of the manner in which amorphous layers are formed in steel during quenching, several rival views have been put forward. The first ascribes the genesis of the amorphous metal to the same cause as that which is operative when metals are strained ; it has been suggested that the interlacing needles of Martensite are merely extremely fine twin lamellæ and that Austenite and Martensite are merely the twinned portions of the same constitutent. This view meets with the insuperable difficulty that although quenching does set up very severe internal *stresses* in steel, it does not cause any serious internal flow or movement. The strain-hardening of metals, however, only becomes marked when severe plastic flow has occurred, and the conclusion is unavoidable that the deformations which occur during the quenching of steel are altogether too minute to produce the severe straining required to render the metal partially amorphous.

A more rational view is that the γ-iron crystals in passing through the transition temperature break up, leaving the molecules temporarily in a chaotic (amorphous) condition pending their re-organisation into crystals of α-iron and cementite, and that it is only this re-arrangement which is stopped by the rapidity of cooling. The present author is inclined to accept this view, which has been put forward by Humfrey, with the modification that the breakdown of the

γ-crystals only occurs in thin films around the boundaries of growing crystals of α-iron. This modification avoids the necessity for assuming that there are at any time present in the steel considerable quantities of the essentially unstable amorphous phase. According to this view, which can as yet only be regarded as a working hypothesis, the γ-iron solid solution on reaching the temperature of Ar_3 begins to undergo decomposition, by the formation of a large number of minute crystals of α-iron. These minute crystals will be formed on the planes of slip and of cleavage of the γ-crystals, as some little movement must take place at these points, thus causing disturbance which is favourable to transformation. Each of these extremely numerous but very minute α-crystals will be surrounded by a film of amorphous metal which is at any moment in the act of passing to the growing α-crystal and is continuously renewed from the mass of the surrounding γ-crystals. By rapid cooling, however, the growth of these α-crystals is stopped at a very early stage and the quenched steel is arrested in a condition in which it consists of numberless minute α-crystals surrounded by layers of hard and strong amorphous metal and possibly embedded in some unchanged γ-iron. The hardness of the quenched steel is then ascribable to the presence of an extremely minute network of amorphous layers. The amorphous material of these layers will not only possess the hardness of amorphous iron, but will be rendered still harder by the presence of carbide in a high state of concentration. The minute α-crystals, as they are formed, must reject the carbide which was present in solution in their γ-iron mother-crystals and this carbide will be rejected into the surrounding amorphous film. This film, being in character identical with the liquid phase, will take up all the carbide that is thrown out, and will retain it on subsequent cooling and congealing, so that the crystals of α-iron will be surrounded by films—not of amorphous iron, but of an amorphous iron-carbide solution. The amorphous theory as thus outlined, affords explanations of many of the more important phenomena connected with the behaviour of quenched steels and of alloy steels, but the matter cannot be pursued here, partly because

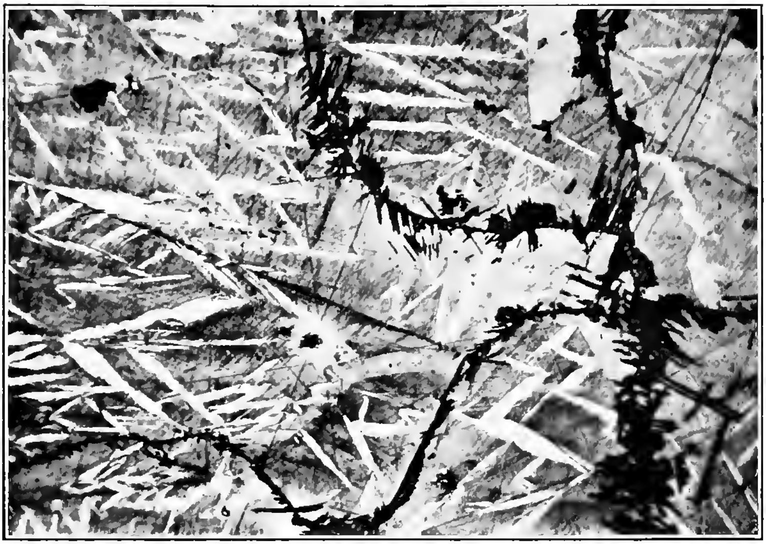

FIG. 73.

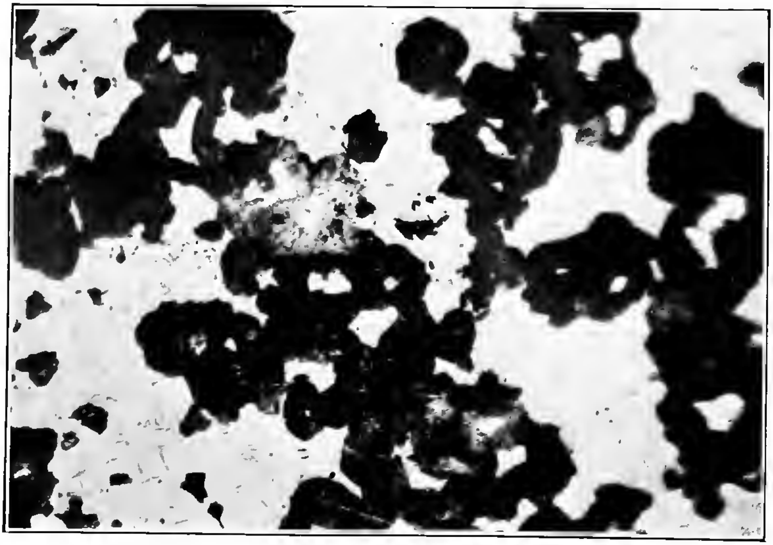

FIG. 75.

[*To face p.* 182.

the whole conception is still so new that opinion upon it must necessarily remain tentative for some time to come.

The Martensite stage found in quenched carbon steels, although theoretically of the greatest interest, is by no means the last of the transition stages met with. If the rate of cooling is rather slower, we find that the edges of the Martensite grains, more particularly where they border upon ferrite, in steels containing less than the eutectoid proportion of carbon (sometimes called hypo-eutectoid steels) appear to have undergone a further change. Instead of the faintly-coloured interlacing needles, this part of the structure appears, under most etching reagents, very deeply coloured and shows characteristic rounded or " woolly " outlines. By a suitable rate of cooling, or by subsequent re-heating to a suitable temperature—*i.e.*, by " tempering "—the whole of the Martensite can be transformed into this very dark-etching constituent to which the name of " Troostite " has been given. Controversy has turned a good deal upon the constitution of this " constituent " also, but we cannot enter into that question here. It is sufficient for our present purpose to regard Troostite as a further step in the degradation of Austenite into ferrite plus pearlite. The dark colour on etching appears to be due to the condition of the carbon in this stage; the separation of the dissolved carbide from the iron must have begun as soon as the first particles of γ-iron became transformed into the β or α condition. In the Martensite stage this separation only makes itself felt very slightly by the small differences of colour between the various systems of interlacing needles. When the Troostite stage is reached we are probably dealing with a material in which the separated iron carbide is present in slightly larger masses. According to Benedicks (12), the carbide in Troostite is present as a colloidal suspension, and it is quite probable that Troostite only differs from Martensite by the slightly greater segregation of the carbide particles. Troostite, at all events, is most frequently found in association with Martensite; its typical appearance is shown in Fig. 75, Plate XV. When the rate of cooling is further lessened or the temperature of re-heating or tempering is further increased, the steel is permitted to progress somewhat further towards the final state of ferrite plus cementite. Instead of the Troostite described above, we find a constituent still devoid of any visible detailed structure under the highest available magnifications, but not etching to such a deep colour as Troostite and without the peculiar rounded outlines. This is often called "Sorbite," but it may be regarded as simply a variety of pearlite in which the two constituents are still so finely divided that they cannot be microscopically separated. The dividing line between pearlite and Sorbite, indeed, is simply a question of microscopic resolving power. As between Martensite and Troostite on the one side and pearlite and Sorbite on the other, however, there is a very important distinction; the two former are found essentially in steels quenched from temperatures above the line HIJ, while the latter are only met with if the rate of cooling through that temperature has not been unduly accelerated. Troostite is most readily obtained by oil-quenching from temperatures just above HIJ, or by water-quenching while the steel is actually in the critical range Ar_1. Rapid air-cooling of steel specimens from temperatures above Ar_1 is sufficient to produce Sorbite, which merges into pearlite as the rate of cooling is decreased. Sorbite is as typically associated with pearlite as is Troostite with Martensite, although under special conditions all four may be met with in a single piece of steel.

Having dealt with the theory of hardening steel and with the micro-structures obtained by quenching, a few words may be said at this point on the practical bearing of the constitutional diagram and our interpretation of it on the hardening operations which are so widely employed in practice. In the first place, it is evident that in order to harden a carbon steel it must first be heated to a temperature high enough to ensure the entire passage of the steel beyond the line HIJ. In the case of steels lying near the eutectoid composition it is safe to go a little further and to state that, for satisfactory hardening, the passage of the entire steel into the region of the γ-iron solid solution is desirable. For this purpose the steel must be heated high enough to pass through the critical points Ac_1 and Ac_{23}, which in steels used for hardening generally lie close together.

It must not be forgotten, however, that the temperature of Ac_1 is from 30° to 40° C. higher than that of Ar_1, so that the indications of heating curves rather than of cooling curves must be followed in deciding the temperature to which the steel must be raised. Next, for reasons which will be explained in the chapter on heat-treatment, the steel must not be kept at this maximum temperature longer than is necessary to ensure its complete transformation. The steel must then be allowed to cool down, the rate being moderate, until it reaches a temperature just above that at which the critical change Ar_1 would take place, and then it must be quenched. Exactly at what temperature above the critical point quenching must take place will, of course, depend upon the size and shape of the object and the nature of the quenching bath. For small tools, good results are generally obtained by first heating to 760° C. and then cooling down and quenching in water from a temperature of 700° C. The resulting steel should consist of fine-grained Martensite and should be fully hardened, *i.e.*, in the condition sometimes described as "glass hard." Such steel then requires "tempering" by re-heating to various temperatures, generally below 400° C., resulting in the transformation of more or less of the Martensite into Troostite with a corresponding softening and toughening effect. The treatment depends, of course, upon the purpose for which the steel is required.

While this method gives very good results, it still exposes the steel, in most cases, to unnecessary strain by allowing it to be first hardened fully, *i.e.*, to a degree not required for the final purpose. Now hardening involves a risk, owing to the fact that rapid cooling sets up severe internal stresses in the steel, and these may, and frequently do, lead to cracking and warping, particularly in objects of considerable size or complicated shape. For that reason it is found desirable to quench in the first place from the lowest temperature which will ensure the attainment of full hardness, *i.e.*, just above Ar_1. Where a lower "temper" is sufficient, however, the same object can be attained by cooling from that temperature (just above Ar_1), but not by the vigorous method of quenching in a large bath of cold water. A slower rate of cooling, which allows the steel to acquire the desired temper at once without re-heating or "letting down," can be secured by the use of oil, or of hot water, or even by quenching in measured small quantities of water which reach the boiling point a certain short time after the steel has been immersed in them. Such methods, if carefully applied, not only reduce the risk of loss from cracking or warping, but also save the time and cost of subsequent tempering.

The constitutional diagram of the iron-carbon system has so far been considered only in regard to alloys whose composition places them to the left of the point D. We have now to consider the remainder of the diagram, relating to the alloys richer in carbon. Very roughly speaking, the alloys so far considered may be classed together as "steel," while the remaining members of the system include principally those materials known as "cast-iron"—but the division is by no means accurate or satisfactory, since the essential difference between "steel" and "cast-iron" is not one of carbon content.

From the discussion of the diagram already given, the constitution of the various phases found and, consequently, the micro-structures of the alloys lying to the right of the point D, can be to a large extent inferred.

The slowly-cooled alloys of concentration lying between the point D and the line BJ should consist, according to the diagram, of crystals of cementite embedded in pearlite. This cementite, while not primarily formed by crystallisation from the molten metal, is derived from the eutectic which forms along the line DB, and also from the solid γ-iron solution which has formed the primary crystallisation, but which, during the range of cooling from DB to IJ, has rejected some of the cementite which it originally held in solution. The cementite thus rejected from the solid solution would, with moderate rates of cooling, aggregate itself about the cementite crystals of the eutectic in such a way that these would grow at the expense of the crystals and lamellæ of the solid solution. What finally remained of this solid solution would decompose at the temperature of the line IJ, and the cementite of the alloy would thus be surrounded by pearlite. This structure is not often met

PLATE XVI.

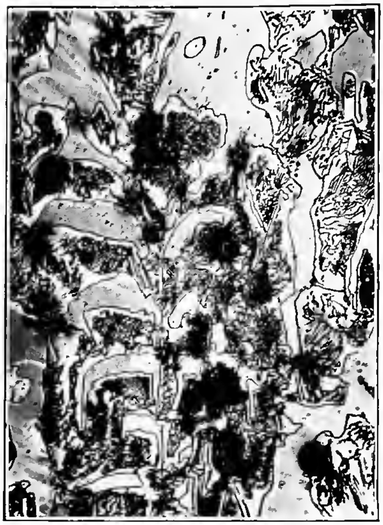

FIG. 76.

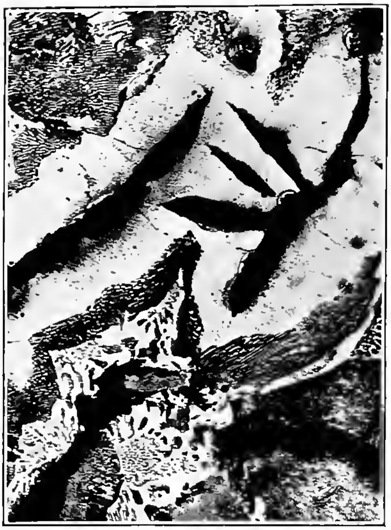

FIG. 77.

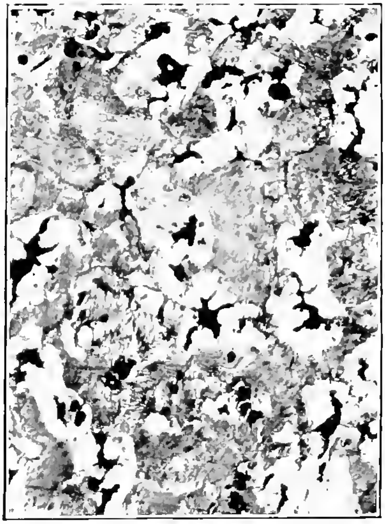

FIG. 78.

FIG. 79

[*To face p.* 187.

with in actual samples, since " a moderate rate of cooling " generally results in a partial reversion to the mode of crystallisation of the stable system, with the resulting formation of graphite. On the other hand, perfectly " white " irons, both of this group and of the final group lying to the right of the line BJ, can be obtained by fairly rapid cooling, and these consist of cementite and pearlite, as indicated by the description given above. An example of this structure is given in Fig. 76, Plate XVI. If, however, the cooling has been somewhat more rapid, the decomposition of the solid solution along the line IJ may be more or less completely prevented, and the resulting structure is then a mixture of Martensite, or of the transition forms, such as Troostite, with cementite.

With regard to the highest carbon alloys lying to the right of the line BJ, it need only be said that the tendency to graphite formation decidedly increases with the carbon content, and these irons can only be maintained in the " white " condition, *i.e.*, free from graphite, by very vigorous chilling or rapid cooling from the molten state. When obtained in the graphite-free condition their structure consists of crystals of cementite embedded in a matrix derived from the solid solution which formed one of the constituents of the eutectic formed along the line DB. This may take any form ranging from the Martensite-Austenite structure of quenched high-carbon steel to that of pearlite.

As has already been indicated, there is a strong tendency in the alloys richer in carbon to follow, in part at least, the mode of solidification of the stable iron-graphite system indicated in the diagram of Fig. 65. This appears, however, to affect only the regions of higher temperature in the diagram ; it would seem that the formation of graphite in the earlier stages of solidification practically results in the formation of an alloy of much lower carbon content—corresponding to the carbon removed in the form of graphite—which then follows the meta-stable mode of further cooling and transformation of these lower-carbon alloys. The result is that the structure of grey iron—as graphitic iron is generally called—is practically that of steel with which a certain amount of graphite appears to be mixed as a species of impurity (in addition to other impurities frequently present). It is not strictly correct, however, to regard these irons simply as impure steels, for the reason that the presence of the graphite plays an important part in the behaviour of these materials when heated, affecting the results of such operations as annealing and quenching, while, of course, it also reduces the strength and destroys the ductility of the material to a very considerable extent. For the purposes of describing the micro-structure of the slowly-cooled iron, however, the similarity to steel mixed with a certain proportion of graphite is very useful.

The grade of steel to which any given specimen of cast-iron or pig-iron corresponds when examined under the microscope depends on its initial carbon content, and also upon the amount of graphite which has been deposited in the earlier stages of cooling. Generally speaking, the irons containing the lower proportions of carbon tend to resemble the lower carbon steels, while the irons richer in total carbon tend to resemble the high-carbon steels, but this rule is subject to very wide variations according to the rate of cooling and to the presence or absence of impurities—such as silicon and sulphur—which affect the tendency of the metal to deposit graphite. The final structure will accordingly depend upon the amount of "combined carbon" present in the iron.

Slowly-cooled iron containing less than 0·9 per cent. of combined carbon will, on the basis of the analogy with steel which has been stated above, consist of a mixture of ferrite and pearlite, graphite being interposed in plates or nodules according to circumstances—an example of this kind of structure is given in Fig. 77, Plate XVI. An iron containing more than 0·9 per cent. of combined carbon, on the other hand, will consist of cementite and pearlite mixed with graphite, but it sometimes happens that the pearlite—as a result of slow cooling—separates out into very widely-differentiated layers or bands, so that the ultimate structure is really better defined as ferrite and cementite mixed with graphite.

The structures just described result from slow cooling carried on from the molten state down to the ordinary temperature;

if the cooling is rapid throughout, the meta-stable system will be followed and no graphite will be formed, but a further condition of the iron must be considered which results from subsequent re-heating of iron which was originally cooled rapidly.

The re-heating of white iron consisting of cementite-pearlite, if carried to a sufficient temperature, always results in the liberation of carbon in the free state—really a form of graphite although it is generally known as " temper-carbon." This free carbon is, of course, derived from a partial transition of the alloy from the meta-stable to the stable system, some of the cementite being broken up into ferrite and carbon. As a " phase " this carbon is identical with graphite, but, being formed in the solid metal, it occurs in a very finely-divided condition which reveals itself in a very characteristic manner when such iron is dissolved in certain reagents. The microscopic appearance of " temper-carbon " is shown in Fig. 78, Plate XVI., which shows the structure produced in a perfectly white cast-iron by heating to 900° C. for several hours *in vacuo*.

The fact that the heating in the above example took place *in vacuo* is of importance, since the phenomenon in question is liable to be masked by others if the iron is heated in an oxidising atmosphere or in other oxidising surroundings. The result in the latter circumstances is a tendency for the iron to become more or less decarburised by the oxidation of the carbon which it contains. The first effect of such an oxidising annealing process is probably the conversion of combined carbon into temper-carbon or finely-divided graphite, but, either by the penetration of gases or by the diffusion of solid oxides of iron and their re-action with the finely-divided temper-carbon, the latter is oxidised and removed from the metal. If this process is carried far enough, the structure of the resulting iron is simply that of comparatively pure steel (ferrite and pearlite) with a few patches of temper-carbon. This process is used to a considerable extent in the production of " malleable castings "—the castings in question are produced from cast-iron in the ordinary way, but they are subsequently packed in oxide of iron and exposed to a high temperature for a long time—the resulting decarburised iron is thus brought to a condition more or less resembling that of very mild steel, and it is thus rendered much softer and more ductile than the original cast material, but its strength cannot and does not become equal to that of actual steel, more particularly of worked or forged steel. There are two reasons for this difference; in the first place, the material is in a condition of crystallisation formed by casting alone and without that refining which results from forging or rolling, and this relatively weak and coarse structure is further inevitably affected in an unfavourable manner by the prolonged heating to which the castings are subjected. In the second place, it must be borne in mind that the removal of the temper-carbon or graphite is never complete and the residual graphitic areas diminish the strength of the material. Further, the chemical composition of a malleable casting, particularly as regards the impurities which are generally kept within very low limits in the case of steel—such as sulphur, phosphorus and oxygen—is rarely such as to conduce to favourable mechanical properties in these decarburised castings.

The process of decarburising cast-iron by prolonged heating in oxidising conditions is that known as Réaumur's; in modern practice, however, there is a tendency to prefer the American or "black heart" process. In this there is no real decarburisation; all the carbon originally present in the castings is precipitated as temper-carbon, whose presence gives these "malleable castings" their characteristic black fracture. This process has the advantage that oxidation is avoided and some surprisingly good results have been obtained, where pure materials are treated in carefully-controlled stoves.

The process whose theoretical foundation we have just mentioned, *i.e.*, the softening or rendering malleable of hard iron castings by heating under oxidising conditions, finds an exact converse in the widely-used process of "case hardening," or cementation, by which a soft low-carbon steel is rendered hard by the addition of carbon resulting from prolonged heating in carburising surroundings. Such carburising surroundings may consist merely of an atmosphere of carbon monoxide gas, or the steel may be packed in a carbonaceous powder, although it has been found that the process is always facilitated by the presence of nitrogenous matter, the gas cyanogen being particularly powerful as a carburising agent. The process of case hardening consists in the absorption of carbon by the outer layers of the steel, thus forming a coating or "case" of high-carbon steel. When the piece thus coated is subsequently quenched at a suitable temperature, the low-carbon core is but little affected thereby, while the high-carbon case is left in the Martensitic condition and is therefore exceedingly hard. Provided that the transition from the one region to the other is not unduly abrupt, the two portions of the piece support one another very well, and a very valuable class of article is produced. The absorption of carbon by heated low-carbon steel can, of course, only occur when the steel is at a temperature above Ar_1, and it does not occur readily until the whole of the steel is in the condition of γ solid solution. In that condition the steel readily takes up carbon, which slowly diffuses inwards. The complete cross-section of a steel rod case-hardened in this way is shown in the frontispiece of this volume, which is taken from a composite photograph built up of some 140 separate photographs. The dark ring surrounding the mild-steel core consists of the high-carbon "case." The transition from "case" to "core" in a hardened steel is shown in Fig. 79, Plate XVI.

In concluding this chapter it must be pointed out that the constitution and structure of the iron-carbon alloys have only been very briefly surveyed, and that many matters of fundamental importance have either been barely mentioned or have not been dealt with at all. Some of these, such as the effects of both good and bad heat treatment, are closely related to that aspect of Physical Metallurgy which is treated in the second part of this book, viz., the relation between micro-structure and mechanical and other physical properties, so that their consideration is left to that part of the book. Another matter of fundamental practical interest, although of comparatively little direct interest from the point of view of general principles, is the nature, manner of occurrence and influence of impurities—not only in the iron-carbon alloys, but in the pure metals and in all systems of alloys. To a slight extent this question is dealt with in the chapter on the defects of metals, but for fuller treatment reference must be made to separate treatises dealing with the various groups of alloys.

It must be further pointed out that our treatment of "steel" has been confined to a very brief consideration of the pure or nearly pure binary alloys of carbon. The ternary and quaternary alloys of this system, including all the "special" or "alloy" steels whose introduction into metallurgical and engineering practice has constituted the greatest of recent metallurgical advances, cannot well be treated, even superficially, in an introductory volume such as this. Their adequate treatment requires, not a separate chapter, but a separate volume.

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PART II.

THE PROPERTIES OF METALS AS RELATED TO THEIR STRUCTURE AND CONSTITUTION

CHAPTER IX

THE MECHANICAL TESTING OF METALS

In our brief survey of the constitution and structure of some of the important and typical alloy systems, references to the physical properties of the materials, and particularly to their strength and ductility, have frequently been made. Since the large-scale production of metals depends essentially on their engineering uses, those properties which are of primary importance for the use of metals or alloys in structures or machines are also of the highest importance in the production of the metals. Weak and brittle alloys have, in special cases, found uses of more or less importance for special reasons and for special purposes, but these uses are insignificant compared with the engineering uses of steel or even of brass or bronze.

The methods of ascertaining the mechanical properties of metals are, therefore, of the highest interest alike to the metallurgist and the engineer. These methods have, however, been very largely developed by the engineer for the purpose of controlling the products of the metallurgist and of ascertaining how the materials sold to him are likely to behave in actual use. It will probably be readily admitted that the only completely reliable test for that purpose is actual use itself, and it is upon the results of that very exhaustive test that engineers endeavour to base their future specifications. The test of actual use has, however, the serious disadvantage that it is generally slow and always extremely expensive—indeed, in the majority of circumstances where tests are called for in order to ascertain the quality of a given material, that test is totally inapplicable. As a result, engineers have elaborated various systems of tests intended to furnish the information as to how the material will behave in practice by means of simple experiments which can be completed in—at most—a few hours.

A test of this kind is frequently intended to imitate the conditions of actual service. Where such an imitation can be attained on a small scale very valuable results are found by its aid. The testing of ship-models in modern ship-tanks, or of aeroplane or airship models in wind-channels constitute favourable examples of this kind, but their nature also illustrates the limitations of such a method. This limitation may be readily expressed by saying that the small scale model will give a reasonable result if the law of similarity is observed. Whether this condition is fulfilled can be ascertained in most cases by varying the scale of the experiments ; if the results have a real meaning it should be possible to arrive at concordant results for the behaviour of the full-size object from the data of experiments, whatever the actual scale of the experiments may have been, within reasonable limits. Applying this criterion leads to the conclusion that in a mechanical test the results should either be independent of the actual dimensions of the test-piece, or at least related to those dimensions by some simple geometrical law.

If this criterion is applied to the majority of the more empirical tests sometimes advocated in the testing of metals, the results of the tests frequently fail to come up to the requisite standard. The reason is not far to seek. In the conditions of practical use engineering materials are exposed to complex conditions and to forces whose combined eeffcts it is not generally possible to calculate. When experiments or tests are devised to imitate these complex practical conditions the imitation is never perfect and only rarely " to scale." Usually it is necessary to reduce the time factor in the experiments, and in order to do this—*i.e.*, to secure the fairly rapid failure of the test-object in the experiment—some other factor must be enormously exaggerated. Where the material might, if unsatisfactory, fail in actual service in the course of months or years, in a test it must be made to fail in a few hours or at most a few days. The difficulty lies in bringing about such rapid failure without radically altering the conditions under which the material works. Beyond this difficulty lies the fact that in these "imitation" tests the conditions of the material under the test itself are ill-defined or incompletely known or understood. The consequence is that even duplicate apparatus fails to give strictly comparable results, and comparability is entirely lost if the size of apparatus or test-piece is changed.

A recognition of these difficulties leads, fortunately, to a very clear and simple principle which is coming to be recognised and appreciated in the science of mechanical testing—as it has long been recognised and followed in all other scientific measurement. This is that, in order to obtain results which have a definite meaning, we must measure one property of our materials at a time. This is simply the principle of isolating the various factors of a problem and dealing with them one at a time, which has long been followed in all other branches of science. A single, definite physical quantity is chosen for measurement and the conditions of the experiment are carefully designed, so as to eliminate, as far as possible, the influence of any other factors. In this way measurements are obtained which can not only be accurately repeated at any time and place by any suitable instrument, but the values found are quite independent of the size of test-piece or other incidental circumstances.

Two difficulties arise in the application of this principle to mechanical testing. The first is that the various physical properties which constitute "strength" are not yet fully understood and analysed, so that it is not as yet easy to say which and how many physical properties are of direct importance from the point of view of the engineer. Once the correctness of the principle is appreciated, however, this analysis will rapidly follow—the accumulation of really accurate and definite data will make it possible to unravel the physical relations involved in "strength" under various circumstances. Meanwhile, the criterion that the results must, subject to a simple formula ,be independent of the dimensions of the test-piece and of the testing apparatus, affords a guide in the whole matter. The second difficulty arises from the fact that in many cases the results of tests made on the principle here advocated are likely to furnish data which the engineer is not easily able to translate into practice. The answer is that such an objection really applies with far greater force to the vague and often meaningless results of some of the current "imitation" tests. Even among existing and well-established tests the engineer is only able to interpret those whose indications he has, through long experience, learnt to correlate—however imperfectly—with the results of actual use. If future development along the line here indicated takes place, the same process must be gone through—the results of tests must be correlated as accurately as possible with the data of experience; if the tests are in themselves based on a sound principle and determine the really fundamental properties of our materials, however, this correlation is bound to be far more satisfactory than can be the case with tests which are in themselves vague in their indications, owing to the complex mixture of properties which determine their results.

Although the adoption of the principle of determining the individual fundamental properties of metals has been referred to above as forming the basis for future development in the science and art of testing, this must not be regarded as implying that there are not, among the tests at present habitually employed, a number which conform to this principle. The process of natural selection has, in fact, been at work and, in spite of frequent voluntary departures from the guiding principle recognised above, those methods which have stood the test of time and have shown that they can and do yield really valuable and reliable data, have permanently established themselves in the favour both of practical engineers and of those concerned with the investigation of metals. In this and the following chapter we shall briefly describe and review the principal forms of mechanical test now in use or contemplated, and we shall see how far these tests follow or depart from our fundamental principle. No attempt will be made to give working details of the numerous testing appliances which are now in use all over the world—experimental details will only be considered as far as they are essential to a discussion of the results yielded by any form of test.

The best known and most widely used of all mechanical tests is undoubtedly the tension test, in which a piece of metal of known dimensions is firmly held at the two ends and exposed to a tensile force which is increased until rupture occurs. So firmly is this test established that for a time there was a strong tendency on the part of engineers to rely upon it exclusively; more recently, however, a strong movement has made itself felt in the direction of requiring, in addition to the tension test, some form of test in which the metal shall be subjected to shock, vibration or "fatigue." That movement has so far justified itself that few will be found at the present time who do not admit the need for some form of "dynamic" test, but the exact form of test to be adopted is still a matter for wide divergence of opinion.

In accordance with what has been said above, the permanence of the tension test, and the favour which it has found in engineering practice, leads us to anticipate that its results have a definite physical meaning and that the test is sufficiently simple at least to approximate to our fundamental criterion of measuring one single property of the material. It is quite true that, within the elastic range, mathematical analysis shows that a tensional stress is equivalent to a pure shear *plus* a negative hydrostatic pressure, but it is doubtful how far that analysis really applies to the important stages of a tensile test which occur after the metal has passed the elastic limit and is extending plastically. Not only that, but the component stresses of tension—shear and hydrostatic pressure in the negative direction—are not readily realised in any form of testing apparatus, although approximately pure shearing tests can be made. Therefore, although a tensile test may not be quite strictly a test of a single isolated physical property—*i.e.*, the property of resisting a simple statical stress—yet it is a test under a very simple combination of stresses and for that reason may with some precautions be made to yield results having a very definite meaning and comparable between different machines and different sizes of test-pieces.

The machines used for the purpose of tensile testing are very varied in form and size, the latter ranging from a "toy" machine, such as that employed in the research of the author and Humfrey (1) for measuring the tensile properties of thin little strips of red-hot steel, up to huge machines capable of exerting tensile forces of several thousand tons. All these machines, however, work to a certain extent on one common principle in that they possess three main organs; the first of these serves to apply to one end of a test-piece of suitable shape the force required to produce the desired tensile stress. The second organ serves to "take up" the extension in the length of the test-piece which occurs when large stresses are applied to it; in the case of ductile metals this extension may be very large indeed, and the machine must be capable of maintaining the load on the test piece in spite of these large extensions. Finally, the machine must possess an organ or apparatus for measuring the force applied to the test-piece in an accurate and reliable manner. As a rule, the first and second organ are combined by the use of an hydraulic ram, which applies the desired load and at the same time takes up any extension of the test-piece. The various types of testing machine differ principally in regard to the third organ, *i.e.*, the apparatus by which the tension or load on the test-piece is measured. Broadly speaking, there are only two ways in which this is done, viz., by direct counterpoise through the medium of one or more levers and weights, and by some form of hydraulic pressure measurement. In this country the lever and weight form of testing machine is almost exclusively used, a result of the refusal of the Board of Trade to recognise tensile tests made upon any other type of testing machine. This is, however, a restriction no longer justified by facts, and one which therefore cannot long be maintained in view of the circumstance that the lever type of machine has been entirely superseded in Germany by one of the other types, which owes its great development largely to Martens (2). In

America, also, the splendid Emery (^{3}) machines do not depend upon direct lever counterpoising.

What we may term the "English" type of tensile machine is shown diagrammatically in Fig. 80. In that figure the test-piece, T, is attached to the two shackles or holders, S S′. The upper shackle hangs vertically downward from a stirrup, R, which rests, by a knife-edge, K, on the lever, L. This lever is free to turn in a vertical plane on the knife-edge, I. On the lever, L, runs the jockey-weight, W, which is so adjusted that, when in the zero position, at the left-hand end of the lever, it just counterpoises the weight of the lever itself. As the weight is run out to the right it can thus be made to counterpoise the pull of the test-piece, T, acting through the shackle, S, and the stirrup, R. The lower shackle, S′, is attached to an hydraulic ram, P, which, by the application of water pressure, derived either from the mains or from a special pump, can be caused to move downwards and thus to apply the load to the test-piece. If the test-piece stretches, the ram, P, will

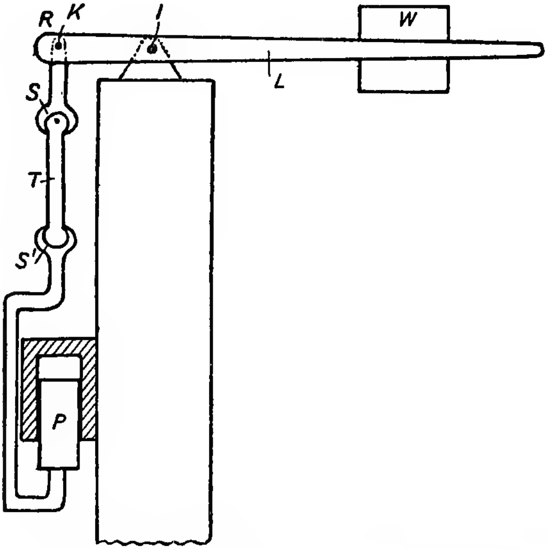

FIG. 80.—Diagram of the Single Lever Tensile Testing Machine.

simply descend under constant pressure and take up the stretch before applying additional load, unless the water is supplied to the ram so fast that the stretch of the test-piece cannot keep pace with it ; in that case the pull on the test-piece may increase, even while fairly rapid extension is taking place.

The necessity for the use of the lever in this type of testing machine, for the purpose of measuring the pull or load on the test-piece, is due to the fact that this pull cannot be directly deduced from the water pressure acting on the hydraulic ram. This discrepancy arises from the very large amount of friction which exists between the ram and the cup-leather which is used to make a tight joint between the ram and the cylinder in which it moves. The lever, however, although convenient in many ways, also possesses several serious disadvantages. In the first place, the knife-edges require care and attention at intervals because they are necessarily exposed to severe stresses and even to shocks when a strong test-piece breaks suddenly. Next, the lever—if a single lever is used—is long and heavy and occupies much space. The whole machine, indeed, is bulky and costly. A photograph of a 100-ton tensile testing machine of this type, as installed at the National Physical Laboratory, is shown in Fig. 81, Plate XVII. In this machine the hydraulic cylinder and ram are in the pit below the floor level, while the hydraulic pump and accumulator are in another part of the building, so that the machine as shown in the picture is only a part of the whole installation. A further disadvantage of the lever and jockey-weight is that they possess a considerable amount of inertia, and may thus momentarily exert forces far larger than the scale-reading of the jockey-weight would indicate. Particularly when a test-piece is stretching rapidly this factor may introduce serious errors, especially if measurements of a more delicate type are to be made.

The hydraulic measuring type of tensile testing machine is a much simpler and more compact apparatus than the lever type ; like the other it possesses, as a rule, an independent hydraulic ram for the purpose of exerting the loading pull and of taking up the stretch of the test-piece, but the load on the test-piece is transmitted to a second hydraulic apparatus,

PLATE XVII.

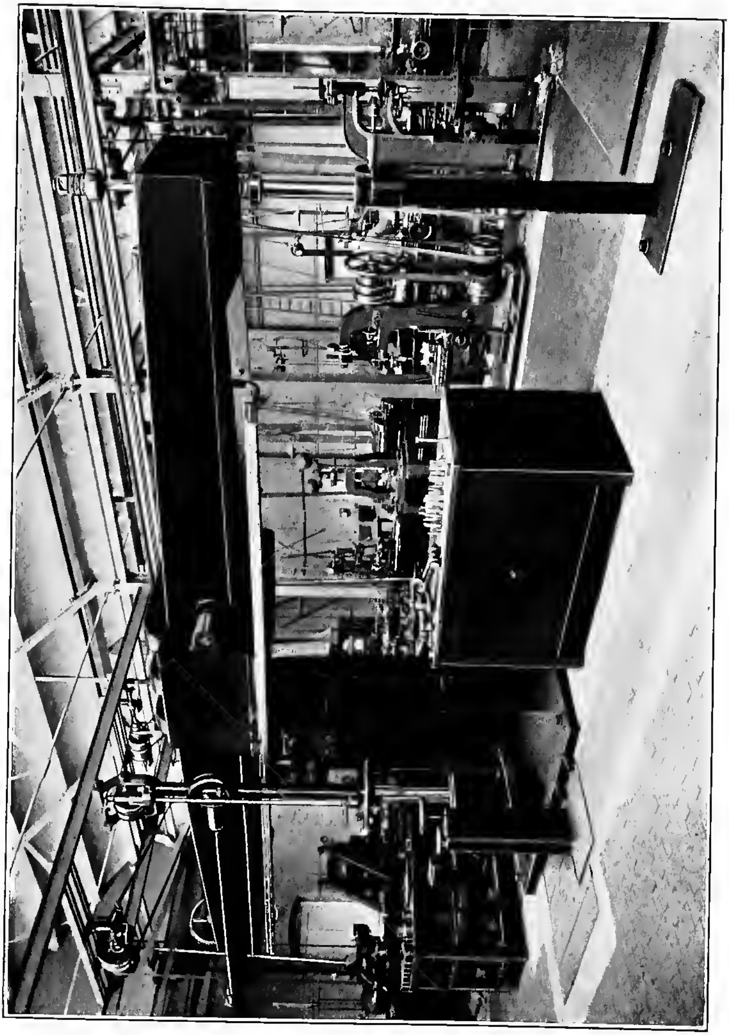

FIG. 81.

[*To face p.* 200.

which serves solely for the purpose of measuring the amount of pull exerted at any moment. This is accomplished by an appliance developed largely by Martens, and known in German as the "Mess Dose" or "hydraulic measuring box." In this appliance the pull of the specimen is transmitted to one side of a chamber which is partly composed of a flexible diaphragm. This chamber is completely filled with water, which is in communication with a sensitive pressure gauge. When the test-piece exerts the pull on the movable side of this chamber the pressure within the chamber rises until the pull of the test-piece is exactly counterpoised, and the pressure then recorded by the gauge measures the pull of the test-piece, being, of course, proportional to the area of the movable side of the box. In this way the actual pull can be very much magnified, and the scale of the pressure gauge, in terms of tons, can be made very open. This arrangement has the great advantage of compactness and cheapness and the total absence of serious inertia. The results, however, necessarily depend upon the accurate calibration of the measuring box and pressure gauge and upon the constancy of these two. The latter has, however, been amply established by the continued re-calibrations undertaken at the Material Prüfungsamt, at Lichterfelde, Berlin, and there can be little doubt that for accuracy and reliability this hydraulic measuring type of testing machine compares favourably with the lever types.

Another simple type of testing machine, which also depends upon the hydraulic measurement of the load applied to the test-piece, is that developed by Amsler in Switzerland. In this type of machine the ram which applies the testing load also serves to measure it. For that purpose the ram is made a slightly loose fit in its cylinder and no cup-leather is used. The pressure is applied by means of oil, fed from a high-pressure pump, and a thin film of this oil is continually allowed to leak past the ram and to return to the reservoir. In this way the friction of the ram is reduced to negligible proportions and maintained at a very constant value. The pressure of the oil behind the ram is then used as a measure of the load on the test-piece, and for that purpose a very simple and accurate form of direct gravity pressure gauge is employed, in which the oil pressure is measured by the deflection of a heavy pendulum. This type of machine is found to give very accurate and reliable results, if properly calibrated and kept in the requisite good order. In use it is decidedly more convenient than the lever type ; it occupies much less space and is free from inertia errors. Fig. 82, Plate XVIII., shows an example of this type of machine, both the high pressure pump and the pendulum manometer being shown.

Quite recently Dalby (^{4}) has perfected a new type of instrument for the autographic recording of the indications of a testing machine when employed for tensile work, which is self-contained, in the sense that it obviates the need for any means of stress-measurement on the part of the testing machine proper. This result is achieved by the use of what is termed a " weigh bar," which is simply a piece of steel of high " elastic limit " through which the pull of the machine is transmitted to the test-piece. Such a " weigh bar " is in reality a very stiff but perfect spring, since its elastic extension is always strictly proportional to the load upon it. The Dalby instrument, which will be referred to in greater detail when the determination of " stress-strain diagrams " is considered, measures the extensions of such a weigh-bar and thereby determines the load on the test-piece. It is, of course, essential that the weigh-bar should be very much larger in cross-section than the test-piece, so that the latter may be broken before the elastic limit of the former shall be passed. For the calibration of the weigh-bar itself—*i.e.*, for the purpose of determining once for all what load is required to produce various elastic extensions in the weigh-bar—the use of some accurate form of testing machine of the ordinary type, or working by direct dead-weight loading is, of course, required—but one standard machine could readily supply calibrated weigh-bars for any number of simple machines having no separate measuring appliances.

Leaving aside the question of the experimental details of testing machines as unsuited to the scope of the present book, we may now turn to a consideration of the nature of the data which are derivable from a tensile test. In order to understand

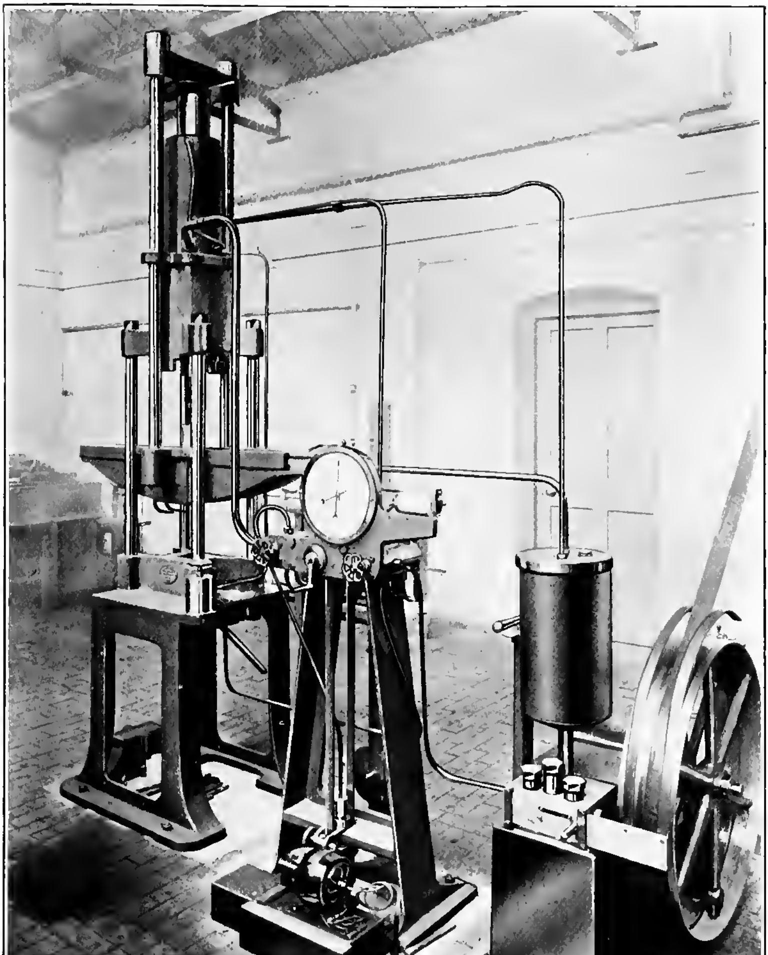

FIG. 82.

[*To face p.* 202.

these we must briefly describe the course of events which take place when a specimen of metal is broken in a tensile test.

As the load is gradually applied there is first a period in which no visible change occurs in the specimen—assuming, for example, that we are dealing with a material like mild steel. Delicate measurements show, however, that even in this stage the metal undergoes a measurable amount of stretching. This stretch, however, is temporary or "elastic" and disappears almost entirely when the load is removed. It is found, too, that during this period the amount of extension is strictly proportional to the applied stress, thus following the well-known law of Hooke, that (elastic) strain is proportional to stress. The actual amount of elastic stretch which occurs under a given stress varies very considerably with different materials. This amount is generally expressed in the form of the elastic constant, known as "Young's modulus," which is calculated, from measured loads and extensions, as the load in pounds per square inch which would suffice to stretch a piece of the material—if elastic stretching of such an amount were physically possible—to double its initial length. The same thing may be put rather more rationally by saying that Young's modulus is 1,000 times the stress, in pounds per square inch, which is sufficient to cause a test-piece to stretch by one thousandth of its original length. In mild steel this constant has a value of the order of thirty millions, or 3×10^6 pounds per square inch. In other materials it varies from such a value as twelve millions for some light aluminium alloys to eighteen millions for bronze or brass. The value of this constant, curiously enough, is very little affected by such processes as cold rolling or drawing, so that it appears to depend upon the nature of the atoms present in the material rather than on their arrangement.

The measurement of the elastic stretching of metals under tensile loading is a matter of some delicacy, as the changes of length to be determined are very minute. Instruments for this purpose, known as extensometers, have been designed in various forms, but only two need be mentioned here. In one of these, designed by Ewing (^{5}), clips are attached to two points of the test-bar a known and definite distance apart—usually eight inches. From the upper clip a rod is suspended, to which is attached a microscope; in the field of view of this microscope is a piece of glass engraved with a very fine scale, and this piece of glass is attached to the lower clip on the test-bar. The arrangement is diagrammatically shown in Fig. 83. The small glass scale moves with the lower clip, while the microscope moves with the upper, and the relative movement of the two shows the extension of the test-piece between the clips, the movement being, however, magnified in the first place by the system of levers which constitute the supports of the microscope and the scale, while the principal magnification is obtained optically in the microscope. With this instrument changes of length of $\frac{1}{50,000}$ of an inch can be measured.

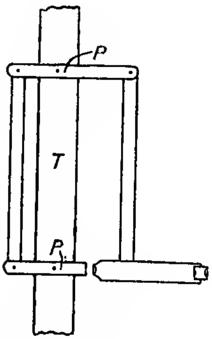

FIG. 83.—Diagram of the Ewing Extensometer.

Even more delicate, but less convenient, is the instrument employed by Martens (6). In this type of extensometer a clip is again attached to the one end of the test-bar; from this clip rods pass down the sides of the test-bar and parallel to the face of the bar—shown as RR in the diagram of the arrangement given in Fig. 84. At the point P, corresponding to the lower clip position in other extensometers, small rectangular prisms or double knife-edges are placed between the test-piece and the rods in such a way that the opposite knife-edges, E in the diagram, bear upon a rod and the test-bar respectively. If now there is any movement of the rod relatively to the bar, the little prism will be slightly tilted. In the Martens extensometer this prism carries a mirror, whose angular movements are measured by means of a telescope and scale. These give readings proportional to the minute extensions of the test-bar, since the test-bar will move relatively to the "idle" rod when the former undergoes elastic extension.

These and other extensometers serve to determine the curve of elastic stretching and the value of Young's modulus, as well as for the determination of what is known as the " elastic limit " or sometimes, perhaps more correctly, the " limit of proportionality." Suppose that the load on a test piece is increased step by step and the extension is read with a suitable extensometer. If the values of stretch thus obtained are plotted against load as abscissæ, a curve is obtained which represents the behaviour of the metal. A curve of this kind, on which the observed points are marked, is shown in Fig. 85, which is typical of mild steel. There is first a considerable range within which the observed points lie on a sloping straight line. This is the elastic range in which stretch is proportional to load, and the slope of the line merely indicates the value of Young's modulus —*i.e.*, how much the material stretches for each increment of load. After a certain point, however, which in this example lies at a stress of eight tons per square inch, the observed points visibly fall away from the straight line. This means that the material has ceased to obey Hooke's Law, the stretch is no longer strictly proportional to the load and the " limit of proportionality " has been passed. This " elastic limit " is a very important point in the behaviour of metals, but we shall see later that, as determined by a simple tensile test, its position is much influenced by the treatment which the metal has previously undergone. The " primitive " elastic limit, as this point is sometimes called when it is desired to point out that we are dealing with a simple determination upon a material in its " primitive " condition, may be displaced in either direction by means of mechanical treatment—it is raised by tensile over-strain, cold rolling or drawing, or any other mode of cold working which causes an extension of the material. If, on the other hand, the metal has previously been compressed longitudinally, or treated in such a manner as to produce diminution

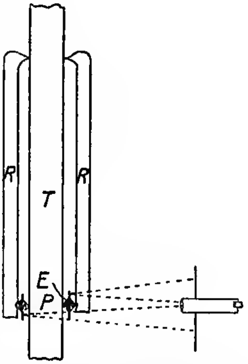

FIG. 84.—Diagram of Martens' Extensometer.

of length, then the " primitive " elastic limit will be displaced downwards from its true position. Unless, therefore, the material has been treated in such a way as to remove the effects of previous mechanical treatment, the determination of an elastic limit by extensometer is not very reliable. Bairstow (7) has shown that, however much the apparent or " primitive " elastic limit may have been displaced by mechanical treatment it can be brought to its normal position by first subjecting the material to a series of loadings in opposite directions, *i.e.*, compressions alternating with tensions, or even by repeatedly loading and unloading in tension alone. This phenomenon will be considered further when we deal with the question of "fatigue" in metals, but it is mentioned here in order to show that, unless we are dealing with " normalised " material, the term " elastic limit " has no very definite meaning.

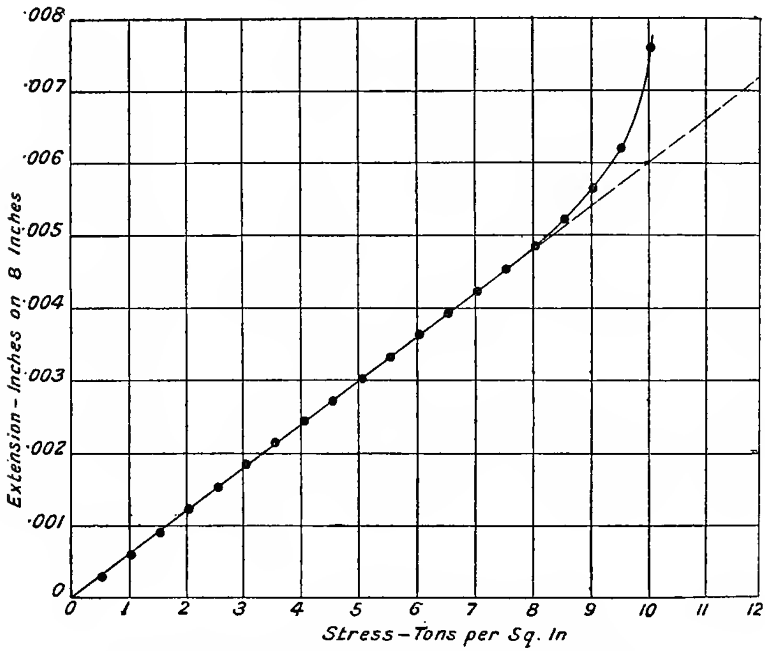

FIG. 85.—Stress-Strain Curve showing Elastic Limit.

The falling-away from the exact elastic curve, as indicated by the delicate extensometer, is not in itself visible or notable by an observer watching a tensile test without the aid of such delicate measuring instruments. When the load is, however, increased a little further, a very striking phenomenon makes itself felt in such materials as wrought iron or mild steel. This is generally known as the "yield-point," and indicates the end of the elastic stage of the test and the commencement of large permanent or "plastic" extensions. If one is working with a lever testing machine, this stage is announced by a sudden dropping of the beam, and the hydraulic ram must be lowered a considerable distance before the beam can be made to float again. The test-piece is seen to undergo a visible change; if it is a rough piece with the scale still on it, this is seen to flake off, often in regular lines lying at 45° to the length of the bar. A bright machined surface cannot show scaling, but it becomes dulled or "frosted" in appearance, the change commencing at one point and spreading steadily along the bar.

At the yield-point, as will be seen from autographic diagrams described below, there is in mild steel a sudden sharp drop in the load which the material will bear; the steel then stretches to a considerable extent at a constant load, and then slowly takes up a gradually increasing load. Up to a certain point this continues, the load growing steadily while the steel continues to extend, but at last a stage is reached where the extension of the steel bar becomes unstable and local necking occurs. At one or sometimes at two points the steel begins to constrict locally, much as a jet of liquid does when it is about to break up into drops. The constricted portion at once experiences an increased stress, and rapid local extension with growing contraction occurs until, finally, fracture supervenes.

It is evident that this process, with its various well-marked stages, is capable of graphic representation in the form of a curve representing the relation of extension of the test-bar to the stress applied to it. This is the well-known "stress-strain" diagram. Such a diagram can be constructed, so far as its general features are concerned, by noting the length between two gauge-marks on the test-bar corresponding to various loads or stresses and plotting the results. This is, however, unsatisfactory, since the more minute and, in many ways, the most interesting features of the curve can only be obtained by a continuous curve and not by the plotting of intermittent points. For this purpose various forms of autographic apparatus have been devised, but those formerly in use have all proved unsatisfactory, so that for the great majority of tensile tests as carried out at the present time no stress-strain diagram is taken, but merely the yield-point, the maximum stress and the total extension are determined. The recently-devised optical apparatus of Dalby (4), however, overcomes the disadvantages hitherto attaching to autographic apparatus for this purpose, and makes it possible to obtain extremely accurate and detailed diagrams with very little trouble, and even on tests carried out at exceptionally rapid rates. We have already referred to it as a means of measuring the stresses applied to a test-bar without the use of a lever or hydraulic measuring chamber, but the manner in which the autographic stress-strain diagrams are obtained is worthy of brief mention.

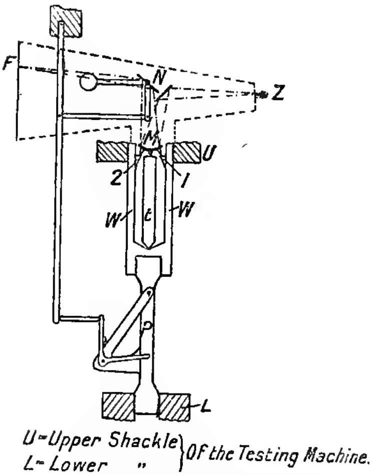

FIG. 86.—Diagram of the Dalby Apparatus.

As already indicated, in the Dalby apparatus the stress is transmitted to the test-bar through a "weigh-bar," whose elastic extension measures the amount of the stress. This weigh-bar takes the form of a cylindrical rod of nickel steel whose core has been bored out so as to form a thick-walled tube. This tube is shown as WW in the diagram of the apparatus given in Fig. 86. To the lower end of the weigh-bar, W, is attached the test-piece, P. Inside the tube, W, is placed a vertical distance-piece, *t*. If now W is stretched through a short distance, there will be a small relative movement of the upper end of the piece, *t*, and of the small projections (1 and 2) connected to the upper end of W. A small mirror is mounted on three points in such a way that the slight relative movement of *t* and 1, 2 causes the small mirror to tilt, thus forming a sensitive "optical lever," by means of which the minute extensions of W are sufficiently magnified. A beam of light from the lamp Z is reflected down on to the mirror of this optical lever and up again from it to another mirror, N, and thence to the ground-glass screen or the photographic plate at F. Now matters are so arranged that the movements of the little mirror at the upper end of *t* serve to move the beam and the resulting spot of light on the ground glass or the plate in a horizontal direction, thus providing the horizontal ordinates of the final diagram, which represent the extensions of the weigh-bar, *i.e.*, the stress applied to the test-bar. By an ingenious system of linkage the stretch of the test-piece is caused to rotate the second mirror, N, in a sense at right angles to that of the mirror M at the top of *t*. Movements of this mirror, N, which, therefore, correspond to changes of length of the test-bar, are thus translated into vertical movements of the spot of light on the screen or the plate, so that the vertical ordinates of the resulting diagram, which is traced by the spot as a test proceeds, represent the extension of the test-piece. A stress-strain diagram is thus obtained from which the loads and extensions at all stages of the test can be read off with great accuracy by the use of a calibration plate, which is laid over the plate obtained at each test. With this apparatus the entire operation of making a test and taking the diagram resolves itself into setting up the apparatus and then putting the hydraulic ram into steady action, care being taken to see that no load is put on which could damage the weigh-bar by loading it above its own elastic limit. If the weigh-bar is reasonably well proportioned to the size of test-piece to be employed, however, there is no risk of this, since the test-piece will break at a load which is perfectly safe for the weigh-bar.

An example of an actual diagram obtained with the Dalby apparatus on a specimen of mild steel of a satisfactory kind is shown in Fig. 87. The various stages of the test can be readily recognised. There is first the very nearly vertical line representing the elastic range, in which the extensions of the test-piece are too slight to be well shown on such a diagram. Then there is the well-marked drop at the yield-point, followed by a range of nearly constant load, with minor irregularities. Then we have the steady upward sweep to the maximum load, and the drop at the end as local contraction sets in.

The diagram chosen for this example corresponds exactly with the behaviour of a tensile test-piece which was described previously in some detail. But this typical mode of behaviour is by no means universal. It is normal in iron and its alloys, although some of the special alloy steels do not show the same features. In the majority of non-ferrous alloys a totally different type of diagram is obtained, for which the behaviour of brass is typical. This is illustrated in another diagram from the Dalby apparatus in Fig. 88. Here, even during the first stage of the test, there is a visible curvature of the line, thus indicating that the material does not really behave elastically, *i.e.*, does not show true proportionality between stress and strain even at low loads. The slightly curved line, however, breaks away fairly sharply at something that corresponds to the yield-point, but there is no drop, nor is there any period of extension under constant load ; the quasi-elastic range merges direct

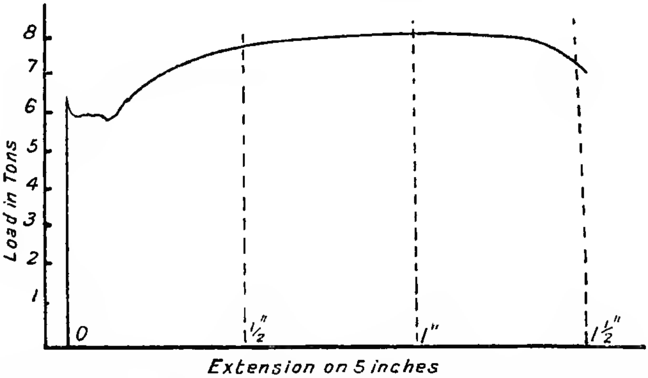

FIG. 87.—Stress-Strain curve of Mild Steel, showing Yield-Point.

into the large upward sweep. This wide divergence in behaviour under the tensile test must necessarily possess a deep physical significance, but these differences and their causes have not yet been sufficiently studied. When these features have received the explanation which is no doubt attainable by the methods of Physical Metallurgy, the full value of the tensile test will be realised. At the present time there is too great a tendency to consider little beyond breaking stress and either elongation or reduction of area. Even the significance of the yield-point, and its variations in various conditions of the same material, is only slowly gaining recognition. In the chapter dealing with the internal mechanism of plastic strain in metals, and in that dealing with the relation of microstructure to mechanical properties, these questions will again be considered. Here we have been principally concerned with the methods of tensile testing and the general nature of the data which those tests could afford.

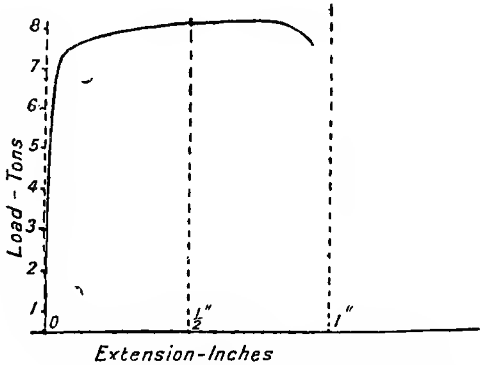

FIG. 88.—Stress-Strain Curve of Rolled Brass, showing Gradual Yielding.

Another form of static test which is closely akin to the tensile test is that by compression ; it is not, however, by any means so simple or satisfactory a test, owing to the fact that, except in very short test-pieces, pure compression stresses cannot be realised without the intervention of bending. As soon as a test-piece, particularly of a ductile material, intended for compression testing exceeds a length equal to five times its diameter, it behaves as a short column and fails by bending, the precise shape which it assumes depending entirely upon the manner in which it has been attached to or placed between the compression plates of the testing machine. On shorter specimens measurements of changes of length cannot readily be made, and the frictional effects of the ends of the test-piece also play a disturbing part. Consequently the compression test is rarely, if ever, used in the commercial testing of ductile material, such as steel, but such tests are frequently applied to non-ductile metals, such as cast-iron. Accurate determinations of the elastic limit in compression have, however, been made, among others, by Bauschinger (8) and by Muir (9), and their results are of great importance in connection with some of the problems discussed in Chapter XI.

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CHAPTER X

THE MECHANICAL TESTING OF METALS—*continued.*

In the preceding chapter we have dealt briefly with the simplest forms of mechanical tests—viz., tension and compression, and the indications which they afford. We have now to consider certain other types of test, confining our attention, in the first place, to those in which stresses are slowly applied. These are sometimes known as "statical" tests in contradistinction to those in which loads are rapidly applied, the latter being termed "dynamic" tests.

The testing of metals in torsion is not very widely practised, probably for the reason that the structural and mechanical applications of metals in which serious torsional stresses arise are not very numerous. Recently, however, the use of numerous small shafts under comparatively heavy loads in automobile construction has drawn fresh attention to the subject, and some work has been done, notably by Larrard (^{1}). This neglect of torsion tests is another example of the tendency of the testing engineer to adopt or to confine himself to those tests which appear to him to apply stresses "similar to those under which the metal has to work." The misleading nature of this apparent similarity has already been indicated. Indeed, from the point of view of determining a definite physical property or constant of a material, the torsion test is probably equal, or even superior to, any of the other more frequently employed tests. This arises from the fact that in a properly designed torsion test, at all events up to the point where plastic flow becomes large, only pure shearing stresses arise. It is true that when a specimen of circular cross-section is subjected to torsion, only the outer fibres are subjected to the maximum stress, the intensity of the stress diminishing uniformly to the centre of the bar. This is, of course, a disadvantage, since it confines the more important portions of the test to a mere skin of material lying on the outside of the test-piece. This can only be remedied by using hollow test-pieces which have been bored out so as to leave only a moderately thin cylinder to be subjected to torsion. In such a test-piece the material left in the cylinder is subjected to a very nearly uniform shearing stress, and valuable results can be obtained. The preparation of such test-pieces is, however, somewhat expensive and slow, while in some materials it is impossible. In any case the thickness of cylinder wall must not be reduced too much, as the action of the cutting tools, as we have seen in Chapter II., leaves behind a layer of material whose physical properties have been seriously altered by deformation ; if the cylinder is made unduly thin, these altered layers will affect the behaviour of the material.

The method of making a torsion test is very simple ; the cylindrical test-piece—hollow or solid—is provided with enlarged ends, which are either made square or, if circular, are provided with substantial keyways. By means of these ends the test-piece is fixed in the two " jaws " of the machine ; one of these jaws is capable of rotation by the aid of suitable gearing, and through this end the twisting moment is applied. The tendency of the other end to rotate is resisted, usually by means of a lever, and the twisting moment of the test-piece is counterpoised and measured, either by means of a long lever and jockey-weight, or by the aid of an hydraulic measuring device similar to that described in connection with tensile testing. In fact, a great many tensile testing machines are fitted with arrangements for making torsion tests, the same measuring apparatus being used for both.

By means of such a machine the relation between twisting moment and angle of twist of the test-piece can be determined for a series of values, or a diagram showing the connection of the two can be drawn by a suitable autographic apparatus. The value of the twisting moment can, of course, be readily converted into shearing stress in tons per square inch. Such a diagram then becomes a simple stress-strain diagram corresponding to the stress-strain diagrams obtained in tensional testing, but we are here measuring the behaviour under pure shear, and what we determine are the "elastic limit," the yield stress and the ultimate or breaking stress in shear, while the strain is measured in terms of angle of twist. In very general terms it is found that for most materials there is a rough agreement between the behaviour under tension and under torsion, a material exhibiting great extension or reduction of area in tension showing a large angle of twist under torsion. On the other hand the values, in tons per square inch, found for the elastic limit, yield-point and ultimate stress by the two methods do not usually coincide. Bearing in mind that, although shear does enter into the tension stresses, there is a fundamental difference in the nature of the applied stresses in the two kinds of test, this divergence of results is not surprising.

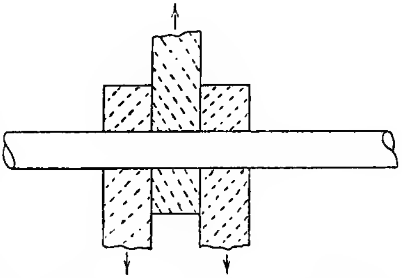

FIG. 89.—Diagram of Shearing Test.

Other methods of testing materials under purely shearing stresses suggest themselves. Thus a test-bar might be passed through three adjacent rings, the two outer ones attached to the lower and the middle one to the upper shackle of a tensile testing machine. When a load is applied to such an arrangement—shown in section in the diagram of Fig. 89—the central ring tends to rise, while the two others remain in their former position. A shearing stress is thus set up in the two cross-sections of the bar (as shewn in the diagram). It is quite possible to obtain results with an arrangement of this kind, but there are serious difficulties. A great deal depends in such a test on the accurate alignment of the three rings, the closeness with which they are held against each other when the load is applied, and the truth and sharpness of their edges. Further, although under moderate stresses such an arrangement results in an approximately pure shear in the material, when plastic flow begins the conditions become vague and complicated—there is a great deal of local crushing of the material, accompanied by lateral flow, particularly in highly ductile metals, and the final result does not possess as precisely definite a meaning as could be wished. It is also difficult to obtain measurements of plastic yielding in such a test.

Somewhat similar in principle, but more manageable in practice, is the "punching test." In this test a flat plate of the metal under examination is placed over a die having a circular hole with sharp edges. On top of the plate is placed a plunger or punch, which also has sharp edges, and which fits accurately into the hole of the die below the plate. The die and plunger are aligned in some convenient manner and then placed between the jaws of a press, such as those of an ordinary testing machine arranged for compression testing, or a special press with suitable measuring arrangements can be employed. As pressure is applied the plunger sinks into the metal, and after a certain depth of indentation has been reached the resistance of the metal diminishes suddenly and a disc of the same diameter as the hole is forced out. In this case somewhat delicate appliances are required if the relation between stress and deformation is to be measured or recorded. The test has to overcome the further difficulties that the results will be materially influenced by the exact fit and condition of the edges of the plunger and die, while small errors of alignment would also be serious. None the less such a test has frequently proved useful, and would appear to be well worthy of further development.

All the static tests so far described labour under the disadvantage, from the purely practical point of view, that if fairly large pieces of metal are to be tested relatively very large forces must be employed, thus requiring the use of heavy and costly machines or the use of unsatisfactorily minute test-pieces. This, of course, arises from the fact that the load employed simply applies a stress which is equal to the total load divided by the cross-sectional area of the test-piece. This difficulty can be avoided by employing a form of test in which the maximum working stresses are large compared with the applied load. Typical of this method are the bending tests, in which the test-piece is used in the form of a beam or cantilever, and the load is applied in such a way as to produce bending moments. This method allows strong and heavy test-pieces to be broken by the application of relatively small forces, but beyond this few advantages can be claimed for it. In the first place the stresses set up in the test-piece are far from being simple in kind, and the results, therefore, do not correspond directly to any single well-defined physical property of the material. Further, the conditions of the experiment are always complicated by severe local stresses which come into play at the points where the load is applied to the beam. A further disadvantage of the method is that the maximum stresses, which only occur in the extreme fibres of the section of the beam, depend, as regards their intensity, upon the exact dimensions of the beam to a very marked extent, so that small errors of measurement or irregularities of form have a much larger effect on accuracy than is the case with simple tension or torsion tests.

The bending test, whose defects have just been emphasised, finds a certain sphere of utility in cases where it is applied in an extreme form, not for the purpose of measuring any particular form of "strength," but for the object of ascertaining whether a given sample of metal possesses a certain minimum degree of ductility. In this form of test a bar or strip of the material is so placed in the testing machine, or in some form of hydraulic or power press, as to become severely bent. Sometimes such bending is carried out in such a way that the material under test is folded over against a steel bar of circular section, so that the bend formed in the test-piece has a certain definite radius. In other cases a more severe test of ductility is made by folding down the two sides of the bent test-bar until they touch one another without the interposition of a radius piece. Such a close bend places the material at the edges of the bend itself under very severe conditions of deformation, and it is a process which only the most ductile materials can undergo without showing signs of cracking. This "cold bending" test has the advantage of being very readily performed without the aid of special machinery, and is consequently much employed as a workshop or works test. Care must be taken, however, in comparing different materials by this test to see that the strips or bars employed in all cases are of the same thickness, since even small variations in thickness make a considerable difference to the severity of this test—a thin bar bending double with much less strain on its outer fibres than a thick one. In any case this test in its ordinary form is a purely qualitative one—no numerical values for "ductility" are obtainable by its means. A somewhat more quantitative form can be given to such a test by using test-bars or strips of such a thickness that they will not bend close without breaking or cracking. In that case, always using bars of the same thickness, it is possible to place materials in a rough order of ductility by determining the angles of flexure at which they break or crack. This test is obviously not comparable with the quantitative tests or measurements which we have so far discussed, but it possesses a definite utility in serving to detect the grosser cases of certain types of brittleness.

We have next to consider a form of test which has attained a very considerable degree of importance, chiefly owing to the ease with which it can be applied, the small amount of material required for its execution, and the comparative regularity and consistency of the results which it yields. This is the test for "hardness" by the method first systematised by Brinell (2), which consists in making upon a flat surface of the material an indentation by means of a small steel ball applied under a known pressure. The size of the indentation produced is taken as a measure of the "hardness" of the material.

In considering this test we are first of all faced with the difficulty of defining "hardness." Perhaps the best form of definition of this property of matter is to describe it as "the power of resisting the local displacement of portions of its substance." But it is at once evident that this "power" is by no means a simple and definite property of the material which will reproduce itself in all circumstances. Thus the displacement of a portion of the substance of a material may occur by plastic flow—the material may be indented at one point while its level is raised at other points; in other circumstances or in other materials the displacement may occur by direct fracture—as in the scratching of a brittle material. Or, again, either of these forms of local displacement may be brought about by the application of a steadily increasing force or by a rapidly applied force, *i.e.*, by a shock or a blow. It is by no means certain that the power of resisting all these various forms of displacement will be identical or even proportional to one another, so that the material which displays the highest "scratch hardness" is not necessarily the hardest under an indentation test. It would seem, therefore, that "hardness" is a somewhat vague term covering a range of properties not necessarily closely connected with one another. Where "hardness" is referred to, therefore, the manner in which it is measured should always be specified.

Among the various methods which have been proposed for the measurement of hardness, it seems probable that the Brinell ball-test, measuring indentation hardness, is probably that one which most nearly approaches our fundamental ideal of constituting a measure of a single definite property. In this case the test probably measures a group of properties of a fairly simple type. That this is the case may be inferred from the fact that tests made with balls of different diameter can be rendered fairly comparable by employing a reasonably simple formula, viz., that of Benedicks (3) :—

$$\text{Hardness number} = \frac{L}{A} \times \sqrt[5]{\rho},$$

in which L = load in kilogrammes,
A = superficial area of the concave surface of the indentation,
and ρ = radius of the ball.

It is also a significant fact that in a series of alloys of similar type the Brinell hardness number is found to be with considerable accuracy proportional to the ultimate stress determined by tensile tests. In view of the great difference in the manner in which the material is treated in these two forms of test, this proportionality is somewhat remarkable. It is found to apply particularly well in the case of carbon steel of all grades. On the other hand, it has been clearly shown, notably by Saniter (4), that the ball-hardness number is not a safe guide to the power of a material to resist abrasion, such as that to which the rails and tyres on a railway are subjected.

The ball test may be carried out in a very simple manner; all that is required is a good steel ball, of the kind used in ordinary good quality ball-bearings, some means of holding this ball, usually a block of steel into which the ball is recessed so that only one hemisphere projects, and some means of pressing this ball on to the surface of the test-piece with a known load. The dimensions of ball frequently employed are ten and five millimetres diameter respectively, loaded with either 1,000 or 5,000 kilogrammes, *i.e.*, one or five metric tons. Any other sizes of ball or weight of load may be employed, provided that all results are reduced to a standard by means of some such formula as that of Benedicks. It is, of course, still better to make all comparison tests with the same diameter of ball and weight of load. When the indentation has been made, it becomes necessary to measure it. This may be done by measuring either the depth of the impression or its diameter at the surface; from either of these measurements the quantity required for the formula—*i.e.*, the actual area of the surface of the impression—can be readily calculated if a true spherical form is assumed for the indentation. Such a form is never strictly maintained by the indentations, and in cast metals having a fairly coarse structure the form of the impression may be visibly irregular, but the mean diameter and the area of the corresponding spherical indentation is calculated for the purpose of obtaining the hardness number. The diameter of the indentation at the surface is readily measured by means of a micrometer microscope, but the process is somewhat laborious, as a number of diameters have to be measured for each impression in order to arrive at a fair mean value. In order to avoid this trouble, special instruments have been devised for the purpose of obtaining the hardness number by direct readings on a scale, or at most by simple calculations from such readings. The machine designed by Martens is a good example of this type of apparatus. Its appearance is shown in Fig. 90, Plate XIX.; it consists of a special form of hydraulic measuring box, which constitutes the base of the apparatus. Connected

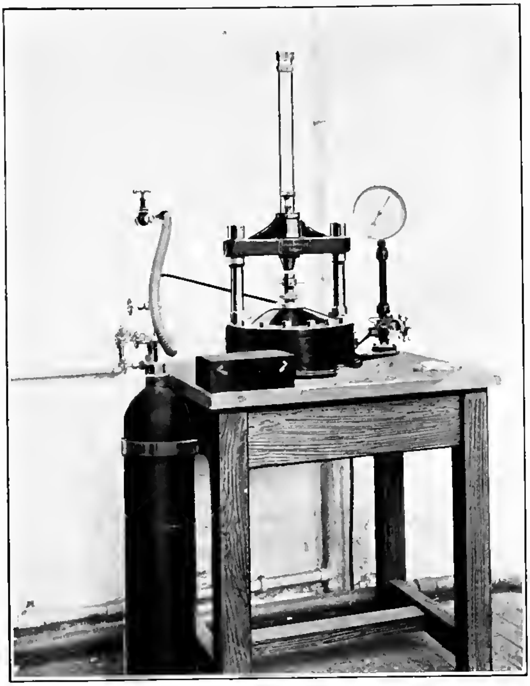

FIG. 90.

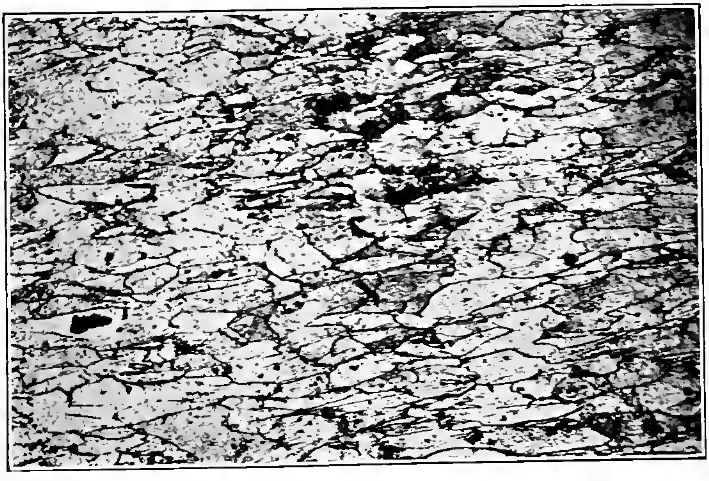

FIG. 96.

[To face p. 220.

to the movable diaphragm of this hydraulic box is a small ram or plunger, which moves upwards through a short distance when water-pressure is permitted to act within the box. On this little ram is placed the test-piece, a ball-and-socket joint being interposed in order to allow the upper surface of the test-piece to assume the horizontal position required. The ball, which in this machine is usually five millimetres in diameter, is held in a steel block attached to the bridge which spans the apparatus. Through this steel block, however, three steel pins or "feelers" project. In their position of rest these project just far enough to be level with the lowest point of the ball. When, therefore, the small ram is set so as to bring the upper surface of the test-piece just into contact with the ball, the three feelers will also just touch the surface of the test-piece. These three feelers communicate with a small piston which works in a small reservoir of mercury. If the piston is pushed up by a movement of one or several of the feelers, it displaces a small amount of mercury, and this mercury is thereby pushed up into a fine capillary tube which runs up the central column of the instrument. The height of the mercury in this tube, indicating the position of the feelers, can be read off on the scale of the instrument. If now a known pressure is applied and measured by means of the delicate manometer attached to the hydraulic chamber, the ball is forced into the test-piece, and the upward movement of the test-piece is communicated to the three "feelers," which are driven upwards from their zero position. The mercury rises in the scale to a corresponding extent. This rise, however, so long as the water-pressure is acting, measures not only the actual depth of the indentation, but the total elastic deformation or "spring" of the whole machine. When a reading is to be taken, therefore, the water is allowed to run slowly out of the pressure chamber and the mercury is watched. For a time it runs down steadily, as the release of pressure allows the machine to recover from its elastic strain. Then a point is reached where the mercury remains stationary for a short time, and this reading gives the true depth of the indentation; after a short period of rest the mercury runs down rapidly, following the descent of the ram as the test-piece is lowered out of contact with the ball.

Several other types of apparatus have been devised for accomplishing much the same object, and particularly one (of Swedish make, by the Aktiebolaget Alpha) is very satisfactory and is widely used. It differs from the Martens type in that the load is applied by weights and not by water-pressure. This latter machine is also intended for the execution of a somewhat different form of the test, in which a conical point of hardened steel is used in place of Brinell's ball for the purpose of producing the impression. Since it appears to be possible to prepare these cones with a sufficient degree of accuracy to secure consistent results, and there are some advantages in calculating the result from the conical indentation, this method—originated by Ludwik (5), of Vienna—is finding considerable support.

Various instruments for determining the " scratch hardness " of metals have been constructed, but these appear to be of interest rather from the mineralogical than from the metallurgical standpoint. The Turner (6) " sclerometer " is an example of an instrument intended for measurements of this kind, while Martens has also designed an appliance for this purpose.

Of more importance from the present point of view is a small " hardness " testing instrument known as the Shore " scleroscope " (7). In this appliance a small steel weight or " hammer" is dropped upon the surface under test ; the little weight is kept to a true course by falling down a glass tube in which it moves with little friction. The lower end of the weight is provided with a sharp point ; at first the point was made of hardened steel, but more recently a diamond point has been adopted. The " hardness " on the scale of this instrument is measured by reading off the height of rebound which is obtained. If the falling weight made no indentation on the surface, the height of rebound would be a measure of the elastic properties of both the weight and of the material under test ; actually however, the weight always indents the surface, and thus does a small amount of work on the material under test. This amount of energy is, of course, abstracted from the kinetic energy of the falling weight, and the height of rebound is reduced to a corresponding extent. This reduction, however, should not be regarded as being deducted from the height from which the weight was originally dropped, but from the height to which it would have rebounded if no indentation had been made, *i.e.*, if the weight had possessed a fairly large flat or slightly rounded end instead of a sharp point. The actual height of rebound is thus a function of the elastic properties (known as the "coefficient of restitution"), the frictional resistances and the work done in displacing a very small amount of the metal under test. It will thus be seen that the "scleroscope" measures a very complex function of different properties, into which one particular form of "hardness" merely enters as one factor. This hardness, moreover, is not the same property as the Brinell hardness, since in the scleroscope the indentation is made under a sudden impact and not under static pressure. Nevertheless, the two sets of determination show a considerable amount of agreement, although there are many cases where the scleroscope gives entirely erratic results. These arise particularly if it is attempted to apply it to small or thin specimens of metal, or if care is not taken to let the falling weight strike the test-surface a perfectly normal blow. The general criticism of the "scleroscope" just given is strongly confirmed by the circumstance that individual instruments are by no means interchangeable, and that, although they place materials in roughly the same general order of "hardness," they do not give strictly comparable readings. The uses of the instrument are, therefore, principally confined to comparative testing, and particularly to exploring the whole surface of a specimen of metal with a view to detecting variations of "hardness" in different parts.

We now turn to a brief consideration of that class of mechanical test known as "dynamic," in which the test-pieces are exposed to the actions of forces which vary more or less rapidly with time. The need for some test of this kind probably arose, in the first place, from the fact that materials which had given perfectly satisfactory results under the ordinary tensile test had yet failed or behaved unsatisfactorily in service; more frequently still the reverse order is followed and materials which have failed in service are found on subsequent testing to show nothing abnormal under ordinary static tests. The conviction has thus arisen—and it is probably quite justified—that "strength" as measured by a tensile test is not the only property involved in the power of a metal to resist destruction under service conditions, and that the power of resisting a steady load is not necessarily identical with, or even proportional to the power of resisting shocks or alternating loads.

The fundamental discovery in this field is due to the work of Bauschinger ([8]) and of Wöhler ([9]), who worked out methods of of testing metals under alternating stresses. Wöhler discovered the phenomenon now generally known as "fatigue" in metals, by showing that loads which were not sufficient to produce more than a moderate amount of permanent "set" or extension in a piece of metal if applied and allowed to remain in continuous action for an indefinite period, were yet sufficient to produce fracture if applied in an alternating manner, *i.e.*, if the stress were applied and removed at frequent intervals, or—more markedly still—if the stress were alternately applied in opposite directions, *i.e.*, a tension alternating with a compression. This subject has been very fully worked out since Wöhler's and Bauschinger's original work, and although the results obtained and the conclusions arrived at will be dealt with as fully as our space permits, it is not possible to follow the history of the subject. For the moment we are primarily concerned with the methods of applying alternating and other "dynamic" stresses in the form of tests or experiments, and with the nature of the data obtainable by such means. To a very large extent the inner mechanism of the processes involved is now well understood, but the explanations of the phenomena which metallographic research has revealed cannot well be dealt with until the general effects of strain on the microstructure of metals has been discussed. This is done in Chapter XI.

The form of alternating stress test adopted by Wöhler was that of a bending test, and, although necessarily attended with all the difficulties and disadvantages already mentioned in relation to static bending, this form of experimental arrangement still holds its own as one of the most satisfactory and consistent ways of making a test of this sort. The apparatus is extremely simple in principle; a cylindrical bar or rod of the material is held at one end in the jaw of the testing machine, which in this case may be simply the chuck of a heavy lathe or some similar arrangement by means of which the test-bar may be rotated about its own longitudinal axis at a steady rate—speeds up to 1,000 revolutions per minute are employed. The free end of the test-rod is then loaded in some simple manner with a known weight or pull; this may be applied either in the form of a dead weight or by means of a suitable spring. In any one position the test-bar is thus made to act as a cantilever, the upper side of the bar being placed under tensional stress while the lower side is in compression. The arrangement will be quite readily understood from the diagram of Fig. 91. When the bar is revolved, each side in turn becomes first the "upper" and then the "lower" side, so that any given portion of the bar is exposed to alternate tension and compression once in every revolution. It is true that the maximum stress is only experienced by the outer layers of the material of the bar, but this limitation is inherent in all bending tests, as has already been indicated. The principal difficulty in carrying out tests of this kind—generally known as "Wöhler" tests—lies in securing the absence of vibration from the test-bar and the weight or spring by which it is loaded. If vibration occurs, the working stresses in the test-bar may become very much larger than those calculated from the bending-moment of the applied load, and the results of the tests thus become valueless. In the latest machines designed for this purpose, however, vibration has been very largely eliminated, and they accordingly yield very fairly

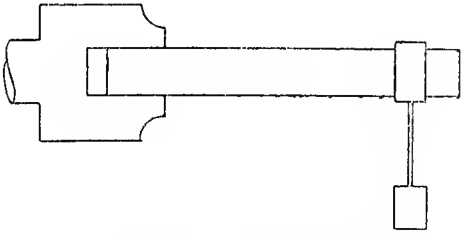

FIG. 91.—Diagram of the Wöhler Test.

consistent results. Some reference is required, however, to the way in which such results should be interpreted.

An apparently simple way of testing the relative value of various materials as regards their power of resisting "fatigue" stresses—*i.e.*, alternating stresses—would seem to be that of exposing test-bars of equal size to the same bending-moment and the same rate of rotation and then simply to compare the number of revolutions required to bring about fracture. For reasons which will be better elucidated when the internal mechanism of failure under fatigue comes to be discussed, such a method yields results which, even for purposes of comparison, may be quite misleading. It does not in the least follow that because at one particular stress one material will break only after 400,000 revolutions, while another fails after 150,000, that the first is really superior to the second in power of resisting fatigue. The number of reversals of stress required to bring about failure, once the process of break-down has begun, is a measure rather of the rate at which the material fails than of the stress required to initiate failure. For practical purposes, however, as well as from the scientific point of view, the fact which it is desired to ascertain is the intensity of stress which the material will resist indefinitely—the so-called "safe range of stress." Once this range is exceeded, failure will result, and the rate at which it occurs is of minor importance—in a rotating shaft in actual service, for instance, a power of enduring even many millions of reversals before failure would be of little more value than the power of enduring a few hundred thousand reversals only; failure would occur in both cases, and the advantage of a slightly longer life would be small. If, however, the true safe range is once determined, then shafts and other parts can be so designed as to remain well within this range, and failure from fatigue will thereby be entirely excluded. At first sight it would seem difficult to determine the true safe range in any simple manner, but research has shown that this determination is really a fairly simple matter. It is only necessary to carry out a Wöhler or similar alternating stress test under at least three, but preferably four, different intensities of loading, so chosen that under the heaviest loading the test-bar breaks after a few thousand reversals, the subsequent loadings being diminished in such a way that under the last—and lightest—loading the bar either does not break at all or only does so after several million reversals. The results thus obtained are then plotted with the number of reversals endured as abscissae and the intensity of the stress as ordinate. It is found that the points so plotted lie on a curve of parabolic form which tends to become parallel to the axis as the intensity of the stress diminishes. The horizontal asymptote of this parabola is

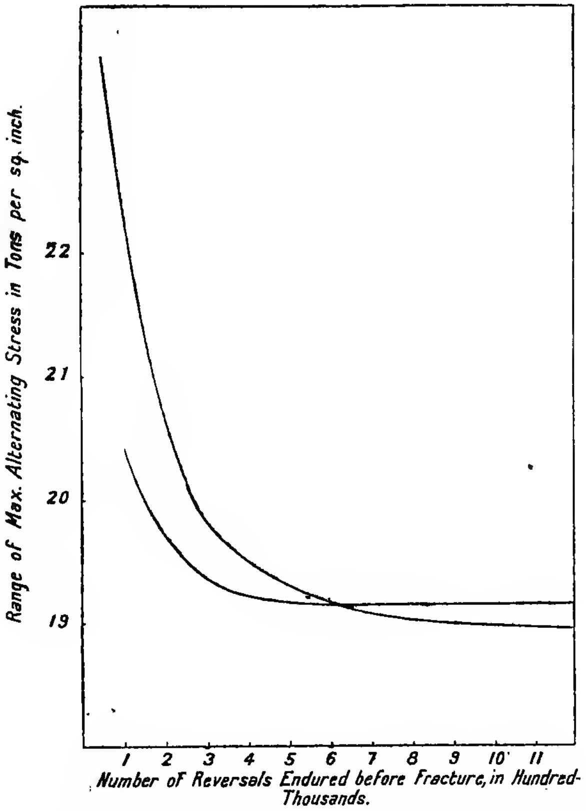

FIG. 92.—Alternating Stress Test Curves for two Materials.

the limit of the safe range of stress to which the material may be exposed indefinitely under reversal, without risk of failure through fatigue. In Fig. 92 are shown the plotted curves for two materials having different limits of safety in this respect ; it will be seen that the two parabolic curves cross one another, so that, if compared by their behaviour under a somewhat severe loading, the worse material would actually appear to have the better endurance. The necessity for carrying out such alternating stress tests in the manner indicated above, by determining the parabolic curve of resistance and the safe "range," must, therefore, be strongly emphasised. Comparisons by tests made under a single intensity of loading are very likely to be misleading and should be entirely avoided.

The objections which apply to the Wöhler method, involving the use of cantilever or beam under bending stresses, have long been recognised, and special machines have been devised, notably by Osborne-Reynolds (^{10}) and by Stanton (^{11}), with the object of applying direct reversals of stress, *i.e.*, reversals of simple tension and compression to test-pieces of metal. The principle adopted in one type of such machines is illustrated diagrammatically in Fig. 93. A revolving crank, C, and connecting-rod, R, operate the reciprocal movement of a cross-head, H, in guides. The cross-head, H, is made fairly light, but attached to it and moving with it is a mass, M, whose magnitude can be adjusted. This mass, M, moves in the same guides as the cross-head, H, but is connected to that cross-head by means of the test-bar, B. The action of this apparatus on the test-bar is of a very simple kind. When the crank is near the top of its stroke, the cross-head and mass, M, are in the mid-position and are moving outwards or inwards at the maximum velocity. As the crank revolves further, the

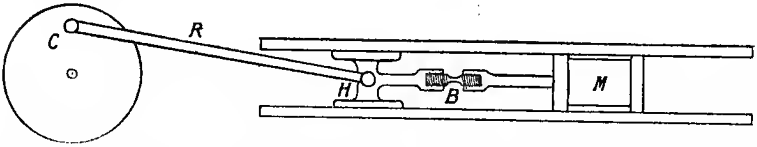

FIG. 93.—Diagram of Testing Machine for Reversals of Direct Stress.

outward speed of the cross-head diminishes and the change of velocity is transmitted to the moving mass, M, through the test-piece. The effort to arrest the motion of M and to reverse it in a given time involves a definite maximum tensile stress in the test-piece, and this maximum tensile stress can be calculated with considerable accuracy. When, on the other hand, the mass, M, is moving inwards, *i.e.*, towards the crank C, and that end of the stroke is approached, the motion of M has again to be reversed by the action of forces transmitted through the test-piece, and it will readily be seen that in this case the stress in the test-piece will be a compression. Owing to the effect of the connecting-rod it is not easy to secure exact equality between the maximum tensile and the maximum compressive stress thus alternately applied to the test-piece, but in the latest machines of this type the ratio between the two is 0·96. In the actual machine, a number of units such as that indicated in the diagram are arranged on a single crank-shaft, as, in order to avoid excessive vibration, it is necessary to balance the various moving masses.

Alternating stress tests made in this machine—again yielding a series of figures from which the parabolic curve can be plotted as from the Wöhler tests—have the great advantage that the material under test is exposed to simple homogeneous stresses and not to mere maximum fibre stresses. The tests are, therefore, at once more searching and also more likely to give a fair idea of the average behaviour of the material. On the other hand, the machines are costly and complicated, there are many parts moving at high speeds, and the whole apparatus is liable to get out of order. Further, continued comparison appears to show that if the Wöhler test, on rotating cantilever specimens, is carried out under the best conditions there is little difference between its results and those of the direct alternating stress machine.

In this connection it is interesting to point out that in the Wöhler rotating cantilever test it is possible so to arrange matters that the test becomes one of alternating[1] shear instead of alternating compression and tension. In a cantilever loaded at one end there is a total shearing stress at every section equal to the load divided by the cross-sectional area. If the cantilever is long, the load required to produce a given fibre stress at the "fixed" end is small, and the shearing stress correspondingly small also. If, however, a heavy load is applied quite near the fixed end, then the resulting bending moment, and the corresponding compressions and tensions are small, while the shearing stresses are heavy. In this way the Wöhler test can be converted into an alternating shearing test, but results of such tests are not yet available for discussion. Alternating torsion, also, is a form of test which does not appear to have been worked out, although from the simplicity of the stresses involved it should offer promising results. Up to the present, however, although the test has been suggested, the author is not aware that a machine for the purpose has yet been designed.

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[1] Strictly speaking, the shearing stresses developed in a cantilever rotating under a load so arranged as to produce pure shear do not

The obvious disadvantage of the alternating stress tests just described is the circumstance that they occupy a somewhat long time. Even if the machines are run at high speeds, as, for instance, at 1,000 revolutions per minute, a test-piece requiring a million reversals for failure would occupy the machine for 1,000 minutes, or sixteen hours forty minutes, and at times specimens require runs of three or four times that duration. To obtain a reliable result, as has been emphasised above, at least three, and preferably four, test-pieces must be broken. In the hope of avoiding this loss of time a number of tests, intended to be "alternating stress" tests, have been devised from time to time with the object of bringing about fracture under alternating treatment after a comparatively few reversals. Now whether these be done

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"alternate" between maximum values in opposite directions, passing through a zero value. The actual shearing stress on the cross-section of the test-bar is constant in amount, the sole result of the rotation being to rotate the direction of the shear in regard to the material, so that for a given element of the cross-section it is only the shear in any given direction that is truly alternating, but there is a shearing stress acting at the maximum value in some direction at each instant—this direction only becomes vertical, for instance, twice in each revolution.

slowly by hand, as, for instance, in the Sankey ([12]) machine, or rapidly by a machine, as in the "Arnold" ([13]) test, the result is the same—they are merely very much exaggerated Wöhler tests lying very close to the one end of the parabolic curve to which we have repeatedly referred. Even if the tests themselves give reliable and intelligible results, they do not afford a valid measure of the real power of enduring alternating or vibratory stresses, and two materials may easily be classed in one order when compared at a single arbitrary point of the curve, which would be placed in the opposite order if the complete curve had been traced. These tests are striking examples of attempts to shorten the time factor while "imitating practical conditions," and of the consequent errors resulting from the departure from the condition of similarity. From this point of view, therefore, these tests cannot be regarded as satisfactory, but this conclusion need not imply that either of these tests, or others of a similar type, may not possess a certain range of special utility for particular purposes. Thus the Sankey machine has the advantage that it can be worked by hand and can, therefore, be used where more elaborate appliances are not accessible, and it undoubtedly affords a means of comparing various batches of material which are intended to be of identical quality. For such comparisons of very similar materials, whose curves of resistance would be very similar to one another, the Arnold test would also prove useful. This machine, in which a bar of the material is forcibly bent backwards and forwards through a distance equal to one-eighth of its length, has also the special feature that alternate bending is accompanied by a good deal of shock and vibration. Neither the stresses applied to the metal, however, nor the amount of shock or impact involved, are known or measured, so that the test becomes one of mere bending through a comparatively large angle and counting the number of times that a specimen will stand this violent treatment. The stresses actually applied must vary enormously according to the stiffness of the material, so that inter-comparison of widely different metals by this method yields results which it is difficult to interpret.

The test which has just been briefly discussed is of a somewhat intermediate type between the true "alternate stress" tests in which the material is exposed to gradually increasing and decreasing stresses, even though the number of reversals per minute is as high as 1,000, and the other class in which the stress is definitely applied as a blow. The adoption of these "impact" tests is based on the view that the physical properties which are involved in resistance to static or slowly applied forces are fundamentally different from those involved in resistance to sudden blows or shocks. The study of the whole subject has not yet gone far enough to make it possible to decide definitely whether this is really the case or not. The feeling that such a difference exists has undoubtedly arisen from the circumstance that materials whose tensile test results—taken in the ordinary commercial way—were excellent, yet failed in service under the action of continual shock or vibration. To some extent these apparent discrepancies may be explained partly by the fact that the tensile properties had only been very superficially studied, and partly also by the circumstance that the mechanism of failure by "fatigue" is even yet not as fully realised as it should be by those who have to test and handle large quantities of metal. In consequence of this lack of appreciation they are apt to be surprised at results in service which are really quite consistent with good test figures. In the author's own experience of the investigation of a very large number of cases of materials which have failed in service, cases are very rare—if they occur at all—in which impact tests have revealed a weakness which could not be traced in an exhaustive tensile test. None the less, there is one good ground for believing that resistance to impact may be different in nature from resistance to static stresses; this lies in the circumstance that the nature of the fracture produced by impact is, in most cases, widely different from that produced by tension or torsion. How far this difference is incidental or really fundamental has yet to be proved. Meanwhile, if there is any possibility that impact tests may reveal properties of metals not otherwise ascertainable, the active pursuit of these tests is fully justified, and even negative results will be well worth establishing.

The simplest of the impact tests is the "single blow" test, such as that of Charpy (14). The majority of such tests which have been hitherto carried out, however, suffer from the fact that their conditions are not sufficiently simple. In order to obtain fractures with a machine of moderate dimensions relatively to the test-piece used, Charpy, Izod (15) and others have adopted a test-piece which is broken by bending, and, in addition, their test-pieces are notched in such a way as to localise the fracture. In spite of these efforts, in the Izod machine, the test-pieces are frequently simply bent over and not completely broken. The importance of this point will be realised when it is pointed out that these tests aim at determining the "specific work of rupture" in foot-tons or kilogramme-metres. The manner in which this is done in the Izod impact tester is shown in the diagram, Fig. 94. The notched test-piece, T, is held in a substantial vice attached to the base of the machine. A heavy pendulum, P, fitted with a suitable striking edge in line with its own centre of gravity, is allowed to drop, by means of a trigger, from a definite height. It strikes the test-piece, either breaking it off or bending it out of the way, and then swings on past the zero. The height to which it would swing if no obstacle had intervened is, of course, readily determined, and with this is compared the height actually reached, which is indicated by means of an idle pointer on a dial which is pushed up by the moving pendulum. The scale is read off in foot-pounds of work absorbed by the fracture, but the figures found for a series of test-pieces from the same bars of steel vary widely and erratically, so that the machine can only be employed

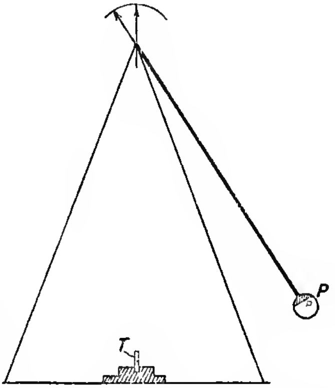

FIG. 94.—Diagram of Izod's Single-Blow Impact Testing Machine.

to detect somewhat wide variations in the "work of rupture."

The Charpy machine is decidedly superior in certain important respects; in it also the blow is struck by a heavy pendulum, and the work absorbed is measured by the reduction of the upward swing of the pendulum after the fracture has been made. In this machine, however, the test-piece is a short beam, and not a cantilever. It can consequently be allowed to rest simply on two massive supports, and no recourse need be had to mechanically "fixing" one end of the test-piece. In view of the violence of the blow struck in these machines, such fixing must always be open to doubt, as any power absorbed by the slightest "give" or movement in the fixing would be abstracted from the pendulum and placed to the credit of the test-piece. But, even apart from the questionable use of the notch, the Charpy machine possesses certain defects. The blow of the pendulum is not solely employed in breaking the test-piece at the notch. Some distortion takes place in the test-piece as a whole, and there is a visible indentation at the points of support and where the pendulum itself strikes the metal under test. Researches directed to investigating whether results obtained with machines of the Charpy type were independent of the exact dimensions of machine or of test-piece have shown that the law of similarity does not hold generally for these tests ([16]). From that point of view they must, therefore, be regarded as unsatisfactory—it follows that they must measure, not a single definite, more or less isolated property of the material, but a complex function of several properties and conditions whose relative action is not yet understood.

In order to overcome these difficulties met with in the Charpy type of bending single-blow impact tester, efforts have recently been directed to the development of the direct tension single-blow impact test. For this purpose, particularly if test-pieces without a notch are to be employed, relatively very large and heavy machines are needed, but the results already attained promise to justify the adoption of such a test very thoroughly. In this case the law of similarity appears to hold, and the data of such tests may be confidently expected to yield extremely valuable information. The machines themselves are very like those of the Charpy type—*i.e.*, the blow is struck by a heavy pendulum falling from a known angle, and the power absorbed by the test-piece is measured in terms of the retardation of the pendulum. The supports for holding the test-piece and the striking face of the pendulum are so arranged that, by means of heavy yokes, the test-piece is broken in direct tension. An additional and valuable modification consists in attaching the test-piece, not to a "fixed" support, but to a heavy "anvil" pendulum. This is set in motion by the blow, but the amount of this motion is measured and the power absorbed thereby deducted from that with which the test-piece is credited.

The application of other simple stresses by impact has not as yet been attempted, although from the fundamental principle of isolating individual properties in our specific tests it would seem that certain other impact tests should offer an interesting field for inquiry. Pure compression could not well be applied owing to the same order of difficulties which arise in static compression tests ; there would be the further difficulty of measuring the amount of work absorbed by a compression test-piece, since fracture could not be produced in anything but brittle materials. On the other hand, the possibilities of shear and torsion impact tests are well worth consideration. In the case of shear, the difficulty of estimating the amount of energy absorbed in any local crushing which might occur would undoubtedly affect the results, but in the case of torsion no special difficulties present themselves. An apparatus could readily be devised in which a massive fly-wheel revolving at known speed is suddenly fastened to the enlarged end of a torsional test-piece by means of some suitable form of clutch—a magnetic clutch, for instance, would answer the purpose. The torsional test-piece would be broken and the speed of rotation of the fly-wheel diminished by an amount which could be readily measured, thus affording a measure of the power absorbed by the fracture of the test-piece.

We now turn to the last class of impact tests—a class to some extent intermediate between the fatigue or alternating stress tests and the single-blow impact tests. These are the repeated-blow impact tests. In these the conditions in so far resemble those of the alternating stress tests that repeated application of the load is required to bring about fracture, and in most cases the blows are so arranged as to throw a given portion of the test-bar alternately into tension and compression. The test-pieces are, therefore, placed under alternating impact stresses. In the machine devised by Stanton ([17]), a tup or hammer of known weight is allowed to fall upon the test-bar from a known height; by a system of linkage and cams, the test-bar is rotated through 180° while the tup is being raised, so that when the tup falls again it strikes the side of the bar opposite to that which it struck at the previous blow. The test-bar itself is a cylindrical rod provided with a **V** groove or notch at the point where the blows of the tup strike it. The blows thus tend to bend the bar and, after a sufficient number of blows, a crack is developed at the bottom of the notch, and this rapidly spreads through the material until fracture occurs.

In many ways this test shares the characteristics of the Wöhler test, and probably the only correct method of interpreting its indications would be to determine the curve connecting the energy of the blow with the number of blows endured, and thus finding the maximum safe blow for a given material and cross-section. Comparison of materials, unless of extremely similar type, on the basis of the number of blows of a given intensity required to produce fracture, is very arbitrary and likely to be misleading. Single tests of this kind do not imitate any practical conditions, nor do they determine any definite physical constant of the material, so that their value is confined to direct inter-comparison of materials which must, in their essential properties, be comparable if the test is to be fairly applicable to them.

Reference has been made to the fact that in a number of tests, particularly of the dynamic kind, "notched" test bars are employed. The object of employing notched bars is principally to secure that fracture shall occur in a definite place and in a definite manner; the notch has, however, several serious disadvantages. In the first place, at the bottom of a sharp notch there is a very marked intensification of stress, as has recently been shown in a very beautiful manner by the optical method of Coker (18)—and, indeed, this fact has long been recognised. The grooves employed in notched-bar testing are not intended to be sharp and are generally specified to possess a standard radius at the bottom. The standard dimension and shape at the bottom of a deep saw-cut or **V** notch, however, is not at all easily attained or adhered to, and a small irregularity may cause an entirely disproportionate error in the result. A still more serious disadvantage of the notched bar is the circumstance that it confines the test to one cross-section or, in some cases, even to a single line of the material. Now in such a case the test may fail in its object of ascertaining a physical property of the metal in several ways. In the first place, if the structure of the metal varies on a somewhat large scale—and variations of this kind are met with in commercial materials—there may be sections away from the notch which are materially weaker than the particular section at which the notch has localised the fracture. Further, the result of the whole test will necessarily depend upon the stress at which fracture begins in the extreme fibre lying at the base of the notch. Now many materials are made up of two constituents of widely different strength and ductility, while in many others there are alternating bands of relatively pure and impure material—such as the " phosphorus banding " of steel to be described below. If it so happens that the notch ends in a favourable layer, the test-piece will give a much higher value than it would do if the notch had been carried perhaps a tenth of a millimetre further into the metal. In view of these considerations it is not surprising to find that all notched-bar tests are apt to vary somewhat capriciously ; on the other hand, the practical convenience of the notched bar for many forms of test is so considerable that its use is likely to persist in spite of these disadvantages.

An interesting comparison of the relative meaning of various kinds of mechanical tests becomes available in cases where a whole series of alloys, all similar in type, but covering a very wide range of mechanical properties, have been systematically

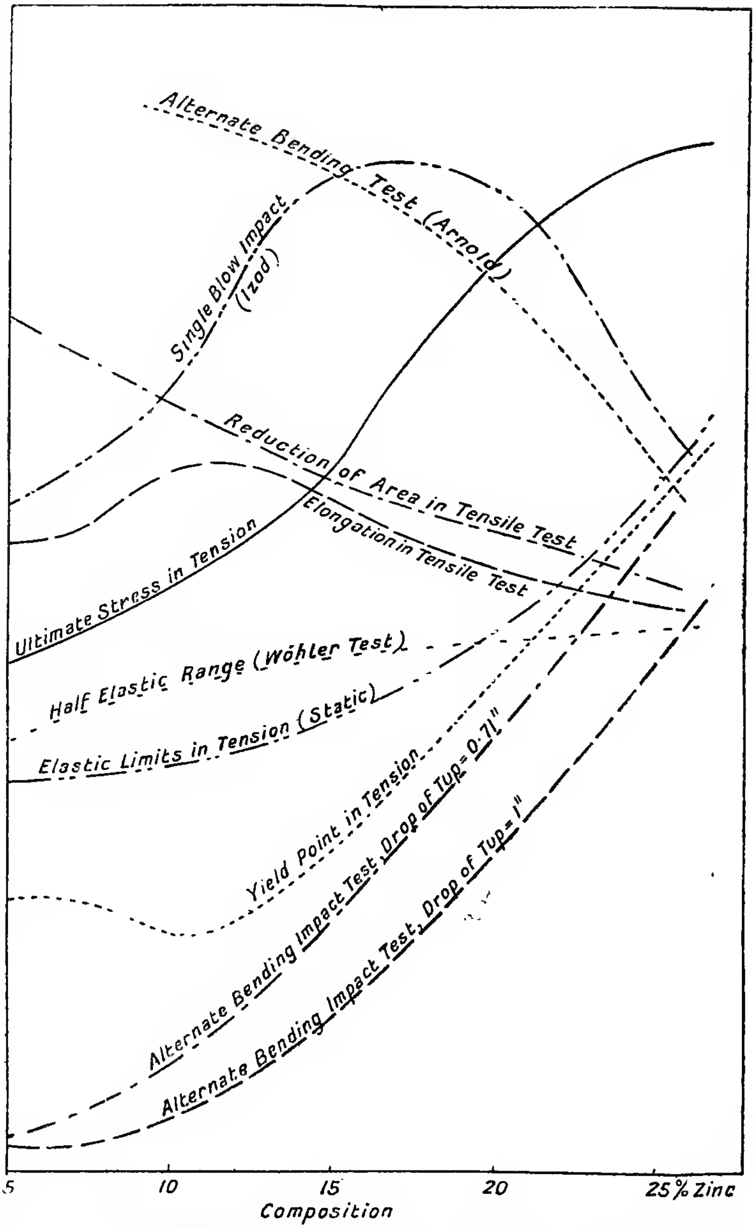

FIG. 95.—Diagram showing Comparative Results of various Tests applied to a series of Alloys. (Zinc-Aluminium.)

subjected to a great variety of tests. An example of this kind is offered by the investigation of the alloys of aluminium and zinc contained in the Tenth Report to the Alloys Research Committee of the Institution of Mechanical Engineers by the author and S. L. Archbutt. The results of the various tests, referred wherever possible to material of strictly comparable kinds, are shown in Fig. 95, which is a graphical summary of the results of all the tests applied. The ordinates of the various curves there shown differ, of course, from one curve to another, so that no comparison of absolute values can be made; the curves are all plotted to the same scale of chemical composition of the alloys, *i.e.*, percentage contents of zinc, so that the shapes of the curves are strictly comparable. It will be seen at once that the curves of alternate bending impact, static elastic limit and ultimate stress all rise steadily with increasing zinc content; the yield-point curve shows a curious dip before it takes the upward course, and this is balanced—and confirmed—by the corresponding hump on the curve of elongation in the tensile tests. The alternating stress curve—*i.e.*, the curve of half the elastic range—also rises steadily, although slowly, with increasing zinc content. The ductility curves, on the other hand—*i.e.*, "reduction of area" and, after a preliminary "hump," the elongation curve also—fall markedly with rising zinc content. It is interesting to note that the curve representing the Arnold alternate bending test practically follows the ductility curves, also falling steadily towards the right. The most remarkable curve, however, is that of the single-blow impact tests (Izod), which rises to a definite maximum and then falls, thus indicating that this test takes account of the combination of strength with ductility. These curves are shown here as an illustration of the manner in which it is desirable that the various methods of test should be systematically correlated in order to enable us to form a correct judgment of their relative values and modes of interpretation.

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CHAPTER XI

THE EFFECT OF STRAIN ON THE STRUCTURE OF METALS

HAVING in the last two chapters reviewed in general terms the methods of measuring the resistance of metals to various forms of stress, we have now to consider the relationship which exists between the mechanical properties of metals and their internal structure and constitution. We will best approach this subject by seeing how the internal structure of a metal is affected when the metal is subjected to strain—*i.e.*, when its shape or dimensions are altered as a result of the application of stress. We shall follow the same plan as in earlier chapters of this book and begin by considering the simplest variety of metal from the structural point of view, viz., a simple pure metal, and by considering its behaviour under a simple kind of stress, viz., tension.

The obvious way of attacking this question is by the examination, under the microscope, of specimens cut from a previously strained piece of a pure metal, such as a broken tensile test-piece. If this is done for any simple metal, such as the purest obtainable iron, the structure is seen to be very markedly changed from what it was before straining. An example is shown in Fig. 96, Plate XIX., which represents strained Swedish iron. The irregular but approximately equi-axed polyhedral crystals of the original material are found to be replaced by elongated grains exhibiting considerable lengthening in the direction of tension. This altered structure could be accounted for by simply supposing each of the original crystals of the metal to have become elongated in much the same manner as the whole bar has become lengthened during the test. But then the question arises, what are these elongated grains—are they still crystals? The answer is that they exhibit all the essential features upon which the conclusion is based that the grains of the unstrained metal are true crystals; there is the uniformity of etching, indicated by the boundaries developed on etching, and the oriented lustre which indicates uniform crystalline orientation throughout each of these elongated areas. Etching-figures can also be obtained which lead to the same conclusion. It would seem, then, that the crystals of a simple ductile metal, when that metal undergoes plastic or permanent extension, are themselves elongated while yet retaining the essential character of crystals. How can a crystal become elongated while yet remaining essentially a crystal? The fundamental difficulty implied in this question lies in the somewhat natural association of the term "crystal" with hard and brittle materials, such as salt or sugar or rock crystal; this association is, however, purely accidental and due solely to the fact that the crystals most commonly and readily observed are those of brittle substances.

The manner in which the constituent crystals of a simple metal undergo extension is conveniently observed by preparing a small test-piece, best, perhaps, in the form of a strip of sheet metal, and polishing and etching one of the flat sides of this piece. Under the microscope it then exhibits the familiar polyhedral structure. By means of a special little straining machine, actuated by a screw, such a thin strip of metal can be readily subjected to plastic extension while its surface is kept under constant observation (1). What is observed in these circumstances is as follows: so long as the metal remains in the elastic stage, or rather until the yield-point is reached, there is no visible change in the appearance of the surface; elastic extension produces no visible effects under the microscope. As soon, however, as the yield-point is reached and plastic or permanent deformation occurs, definite changes are seen to take place on the surface observed under the microscope. Across the previously plain white faces of the crystals fine black lines appear, at first in isolated groups, but in steadily increasing numbers until the surfaces of the crystals are cross-hatched with fine black lines. In iron or very mild steel these lines appear to be curved, irregular and branched, but in such metals as lead, tin, silver, gold, etc., the lines are very straight and regular. The appearance of these lines is illustrated in

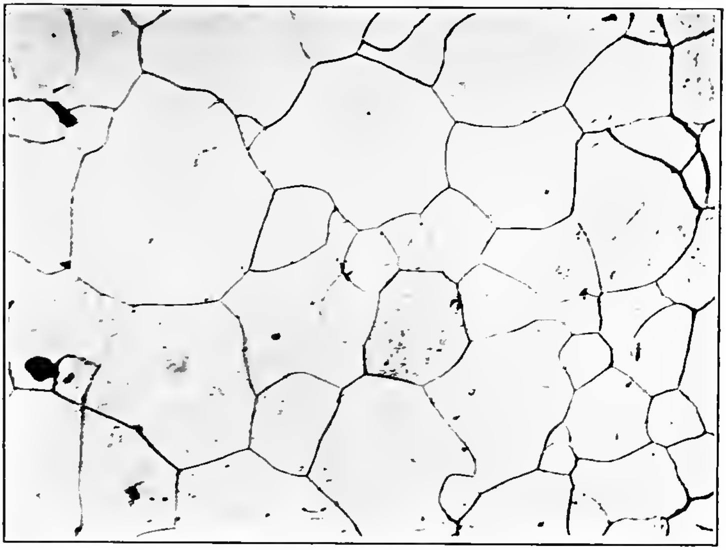

Fig. 97.

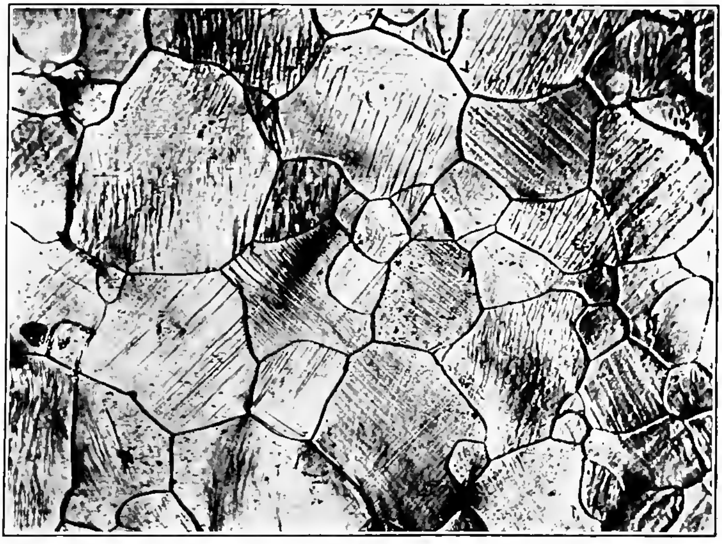

Fig. 98.

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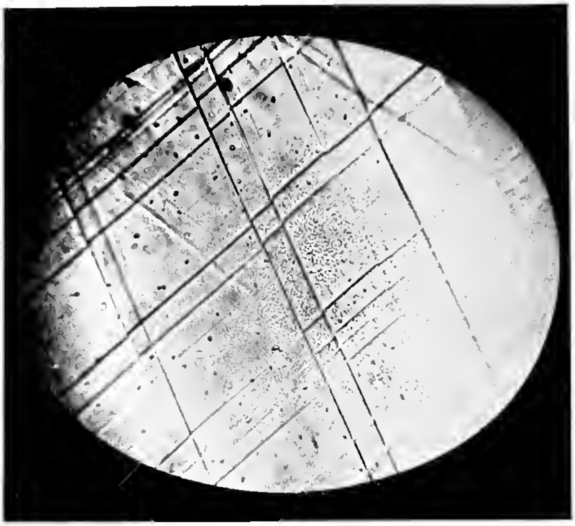


FIG. 100.

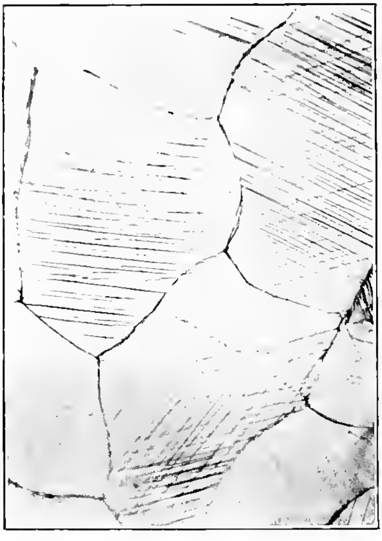


FIG. 99.

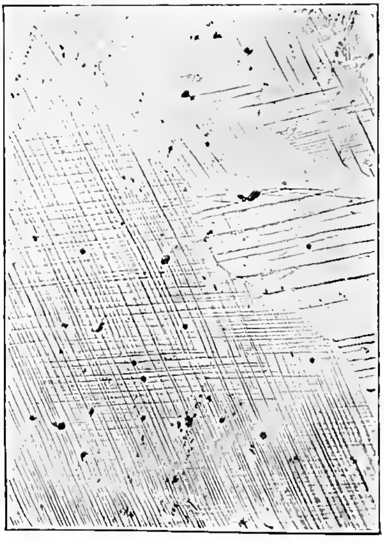
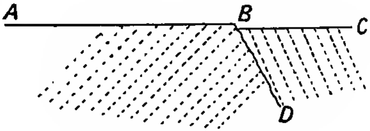


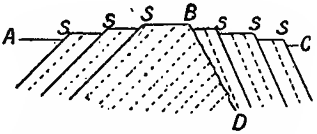
FIG. 101.

[*To face p.* 243.

Figs. 97 to 101. Figs. 97 and 98, Plate XX., show the same field of view, in iron, before the commencement of straining and after a considerable amount of plastic strain has taken place. Figs. 99 and 100, Plate XXI., show the black lines in lead (at 150 and 1,000 diameters respectively), and Fig. 101, Plate XXI., in nickel steel. If the process of straining is carried further, the number and apparent width of the black lines increases until they form a very close network, which becomes confused. As fracture is approached this confusion leads to a general roughening of the surface, which prevents sharp focussing with the microscope, but, even close to a tensile fracture, the lines can be seen in very large numbers crossing one another in various directions.



A. Before Straining.



B. After Straining.

FIG. 102.—Diagram of the Formation of Slip Bands.

The true nature of these lines is now well understood, and is summed up in the name "slip bands" which is given to them. Their origin lies in the fact that when a crystal of a ductile metal is forcibly altered in shape, it adapts itself to the new configuration imposed upon it by a process of sliding or slip which occurs on certain of its crystallographic planes. The manner in which this occurs is well illustrated by the behaviour of a pack of cards, or of a pile of books, when the pile is distorted—the shape of each individual card or book remains unchanged but the shape of the pile is changed by the sliding of the individual cards or books over one another. The process may be made clearer by the diagram of Fig. 102, which is intended to indicate in a very approximate manner the condition of a cross-section of two adjacent crystals before and after plastic straining. The upper sketch represents the unstrained crystals, whose smooth upper (polished) surface is indicated by the line ABC—the step at B is the slight difference of level between adjacent crystals formed as the result of etching; the boundary between the crystals is represented by the full line BD, while the potential planes of gliding or slip, differently oriented in each crystal, are indicated by the dotted lines. After straining, slip has taken place on some of these slip-planes, and minute steps have consequently been formed in the surface at the points marked *s*, *s*, *s* in the lower figure—these steps will, of course, slope in different directions in different crystals. Seen from above, by normal illumination, these short, steep, sloping surfaces will appear simply as narrow black lines. The reason for this appearance is at once explained by reference to the sketch of the paths of rays of light coming from a microscope objective on to such a stepped surface, as shown in Fig. 103. The vertical rays which strike the flat surfaces between the crystals are reflected back directly into the objective, and these surfaces consequently appear bright; those rays, however, which strike the sloping surface of the step—the "slip band"—will be reflected away from the microscope, and the steps will, therefore, send no light into the objective, and will appear black in the field of view.

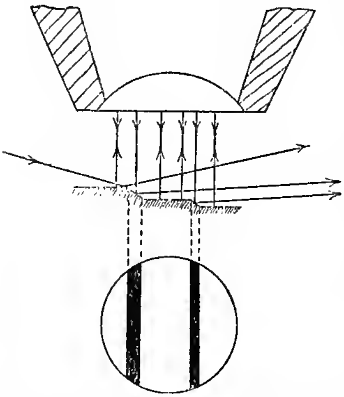


FIG. 103.—Diagram illustrating the Optical behaviour of Slip Bands.

The optical characteristics just described afford a very striking demonstration of the fact that "slip bands" really are of the nature of steps, as indicated in the diagram of Fig. 103. While rays of light falling normally on these bands are reflected outwards, conversely, rays falling obliquely on to such sloping surfaces will, if the angle of incidence be properly adjusted, be reflected into the lens of the microscope; at the same time, oblique rays falling on the smooth flat areas between the steps will pass outside the microscope objective. When, therefore, a crystal on whose surface slip-bands have been developed is

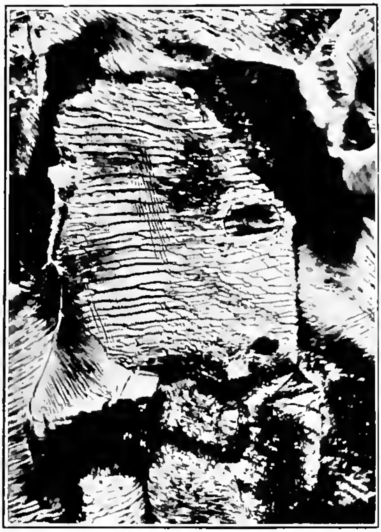


FIG. 104.

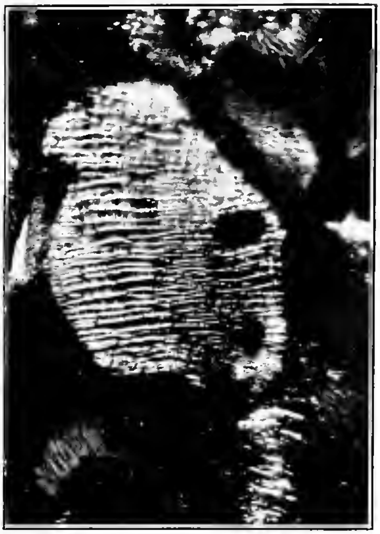


FIG. 105.

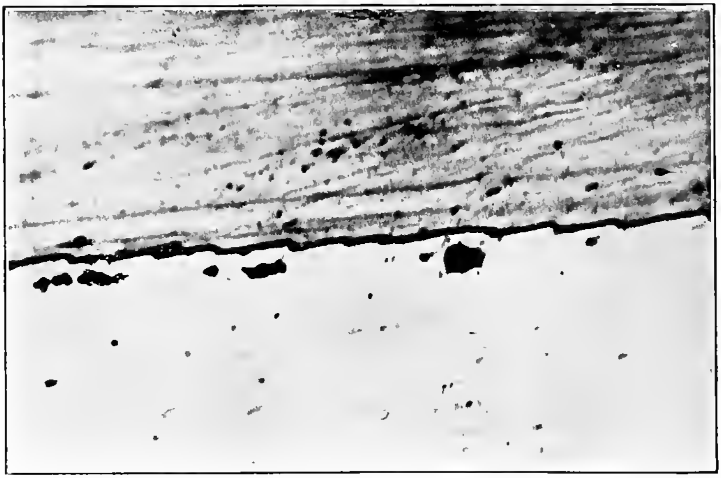


FIG. 106.

[*To face p.* 245.

illuminated by a beam of oblique light at a suitable angle, the slip-bands should appear as bright lines on a dark background. This is actually the case, as is illustrated in Figs. 104 and 105, Plate XXII., which show the same field of view as seen by normal and oblique lighting.

Still more conclusive, if possible, than this optical evidence is the demonstration of the nature of slip-bands which has been obtained by the author by means of actual cross-sections of a surface on which slip-bands had been developed. The difficulty in obtaining such a cross-section lay not alone in the minuteness of the surface features looked for, but also in the fact that, when a specimen is cut and polished, the edges of the surface are always more or less damaged and rounded off. Sharp images at high magnifications, therefore, could not be obtained by simply cutting a previously polished and strained specimen through at right angles to the original surface and then polishing the cross-section thus obtained. The author overcame this difficulty by first coating the surface on which slip-bands had been formed with a thick layer of electro-deposited copper. When subsequently a section was cut through the compound mass—in this case of iron and copper—the boundary on this section, between copper and iron, gave the exact outline of the section of the original surface. When observed at a high magnification, such a section shows the slip-bands as true, though minute, steps. The appearance, under a magnification of 1,200 diameters, is shown in Fig. 106, Plate XXII., and it will be seen at once how the outline there seen corresponds with the outline of the lower figure in Fig. 102. It is of interest to note that the approximate depth of the minute slip-band steps seen in Fig. 106 is $\frac{1}{50000}$ of an inch, which is about the length of a wave of sodium (yellow) light (3).

If we realise the true nature of this phenomenon of deformation by slip, we see at once that it throws a flood of light on the behaviour of metals under stresses sufficient to bring about plastic strain. If such plastic strain occurs solely by slip, then the truly crystalline nature of the metal should remain unaltered by the straining process. We have already seen that strained, *i.e.*, elongated crystals, still exhibit the essential characteristics of crystals, so that, broadly speaking, this generalisation is correct. But there are a whole series of other phenomena connected with the process of plastic strain which would be extremely difficult to explain satisfactorily on any theory which required the structure of metal to remain perfectly crystalline, even when very severely strained. The circumstance that a metal is hardened by strain, in the sense of having a much higher yield-point and limit of elasticity, and even a higher breaking stress, is one of these facts. These circumstances have led the author to adopt a view put forward in the first place by Beilby (^{2}), to the effect that while plastic deformation—and although we have merely discussed its occurrence in connection with tensile strain, its nature and mechanism is the same whatever the system of forces which have brought it about—takes place by slip on the gliding planes of metallic crystals, yet that the act of slipping is accompanied by something further. Just as the rubbing action of polishing produces on metal surfaces a thin layer of altered, amorphous material, so we may well expect that the sliding over one another of adjacent slip surfaces will produce a local disturbance of molecular arrangement. If the slip is slight, then it probably happens that this derangement is also slight and temporary and that the disturbed molecules are still able to rearrange themselves pretty much in their original system. In such a case the crystalline orientation is not at all disturbed. If, on the other hand, the slip has been more pronounced, the resulting local disturbance will also be more far-reaching, a greater number of molecules will be disturbed, and they will no longer be able to re-arrange themselves in the old crystalline system. A more or less thin layer of amorphous metal will thus be formed on each surface of slip. At first—for a short time—these layers will probably possess a certain degree of mobility, like the surface film which adjusts itself under surface tension. During this period these layers would act as a sort of lubricant, facilitating further slip on the same gliding planes. After a time, however, when the disturbed molecules have had time to "set" in the amorphous condition, we should have on each plane where slip has taken place a layer of hard, non-plastic, amorphous metal. These would effectually prevent further slip on that particular set of gliding planes, and the crystals would be limited, in accommodating themselves to further plastic strains, to slip on other surfaces which had not been "used" in the previous straining. But all the surfaces of *easiest* slip will have been used at the first straining, so that to effect plastic deformation the second time more force would be required. Not only this, but the hard and brittle amorphous films on the surfaces of previous slip would also act as a stiffening skeleton for the whole crystal and thus offer additional resistance to the commencement of fresh slip. This conception, therefore, affords a rational and simple explanation of the apparent hardening of metal by plastic deformation. The essence of the whole conception lies in this—that plastic deformation can only occur on the slip-planes of a true crystal, so that plasticity is, in metals, a property bound up with crystalline structure. As amorphous layers are formed, the capacity of the crystals to yield by slip is diminished, and ultimately, when a certain not very large proportion of the metal has been converted into the amorphous condition, the metal has been rendered incapable of further plastic deformation—it has been rendered hard and brittle. As this stage is reached when the metal still consists largely of portions of crystals embedded in amorphous layers, it is obviously impossible to convert the whole of the metal into the amorphous condition, because the straining process whereby this conversion can be brought about is rendered impossible by the skeleton of hard amorphous matter already present.

There is one difficulty about the explanation of the hardening of metal by plastic strain, as given by the conceptions explained above, which requires brief mention. This lies in the fact that the hardening produced by plastic strain is, in certain cases at all events, uni-directional. For instance, a piece of steel which has been "hardened," *i.e.*, has attained a raised yield-point and apparently raised elastic limit, as the result of tensile overstrain, is not really hardened in every way, for, if it is tested in compression, it is found that for stresses of that kind the apparent elastic limit has been lowered, so that the total range of elasticity, from the limit in compression to the limit in tension, has not been materially altered. It is difficult to see how the formation of hard amorphous layers on surfaces of slip can account for a softening of the metal in relation to compression while producing hardening as against tension. It may be, of course, that there is something directional about the manner in which the crystalline arrangement is broken up on the slip surfaces, so that a configuration results which allows of slip in one direction but not in the other. A more probable explanation has, however, been put forward by Humfrey (^{4}), who suggests that amorphous layers present or formed in the crystal boundaries act in such a way that, when distorted by plastic strain, they serve to assist the action of any forces tending to restore the metal to its original shape, but lend added resistance to further change of shape in the same direction as previous strain. This explanation will, however, be better understood when the general question of the structures at crystal boundaries has been discussed.

The conception of an amorphous and temporarily mobile layer formed on all surfaces of internal slip affords an interesting explanation of phenomena connected with over-strain, more particularly observable in iron and steel. These are the phenomena of semi-plasticity, which occur immediately after a tensile test-piece has been exposed to a stress beyond the yield-point. If the load is removed from such a test-piece and small loads are gradually applied to it, extensometer observations at once show that the material is in a peculiar condition. Even under slight loads the proportionality between load and extension is no longer observed ; the test-piece shows a certain gradual creep, the extension slowly increasing with time. If the small load is removed, the metal does not at once return to its original length, but a small more or less permanent "set" is left behind, although this may diminish gradually as the result of backward creeping. The somewhat complex phenomena may be summed up by saying that the material has for the time lost the truly elastic character which it normally exhibits under such small loads, and behaves as if it were in a semi-plastic condition. If left to itself, the original perfect elasticity is recovered after a time which varies from a few hours to several days, according to the nature of the material, while exposure to a temperature of 100° C. for twenty minutes is sufficient to bring about complete " recovery " (5). Such phenomena could only be explained with great difficulty if purely crystalline slip were alone concerned in plastic deformation. The conception of amorphous layers possessing temporary mobility, however, affords a simple explanation. So long as the amorphous layers formed on the slip surfaces retain their temporary mobility, the metal may well be expected to behave in a semi-plastic manner, since the amorphous layers on the slip surfaces would behave like films of viscous fluid, slowly moving under the applied stresses, thus giving the slight permanent " set " and the gradual creeping observed. In the course of time, or more rapidly in consequence of slight warming, these layers become rigid in the permanently hard, amorphous condition, and the phenomena of semi-plasticity accordingly disappear.

Having freely availed ourselves of the conception of " amorphous " metal, it may be well to state precisely what is understood, in this connection, by the term " amorphous." In accordance with Beilby's views, and their recent development by the author and his collaborators (6), the amorphous condition is one in which the crystalline arrangement of the molecules is completely broken up, so that the molecules remain in a state of irregular arrangement similar to that which is supposed to exist in the liquid state. In fact, the " amorphous phase " is regarded as being—from the point of view of the phase doctrine—identical with the liquid phase. Now extremely under-cooled liquids are well known in such substances as glass, vitreous silica, etc., and they are hard, brittle bodies devoid of plasticity and of crystalline structure. Amorphous metal is, therefore, to be regarded as being identical in nature with the liquid metal if that could be cooled down to the ordinary temperature without undergoing crystallisation. It is admitted that such extreme under-cooling of metals has never been actually accomplished, and objections to the whole concept of amorphous metal have been based on that ground.

These cannot be discussed here, but they have been fully dealt with by the author elsewhere (7). At the present moment it may well be claimed that the theory of an amorphous phase in metals, produced as the result of mechanical disruption of the crystalline arrangement of the molecules, holds the field as the best working hypothesis available. There are admittedly outstanding difficulties, but these the author regards as being inevitable in a theory whose wide generalisations cover a field which has as yet been but partially explored (8).

The general effect of slowly-applied or "static" plastic deformation, which has just been discussed, may now be summarised as follows: the metal in the cast or the annealed state is an aggregate of crystals; when the metal undergoes plastic deformation the crystals are deformed in the same general sense as the mass of metal. This change of shape of the crystals is accomplished by a process of slip or gliding by which layers of the crystal slide over one another along certain gliding planes. Such slip occurs on a great multitude of planes in each direction and, as a rule, it must occur on at least three sets of planes, but it may occur on a greater number. This slip is accompanied by a certain disturbance of the crystalline arrangement of the molecules on or near the surfaces of slip. If the deformation has been slight, the disturbed molecules may be able to rearrange themselves in accordance with the crystalline system by which they are surrounded, and the completely crystalline character of the metal will then be unaffected by the deformation. When the deformation is severe, and if it is intensely localised, as when a single crystal is bent upon itself, the molecular disturbances at the slip surfaces become larger, and permanent layers of amorphous metal are formed on each surface where slip has occurred. Ultimately the metal, as the result of extreme deformation, becomes a mass of crystal fragments embedded in relatively thick layers of amorphous metal. This change is accompanied by an increase in the hardness of the metal and—in the majority of metals—by a measurable decrease of density.

Reference must be made here to another process which is

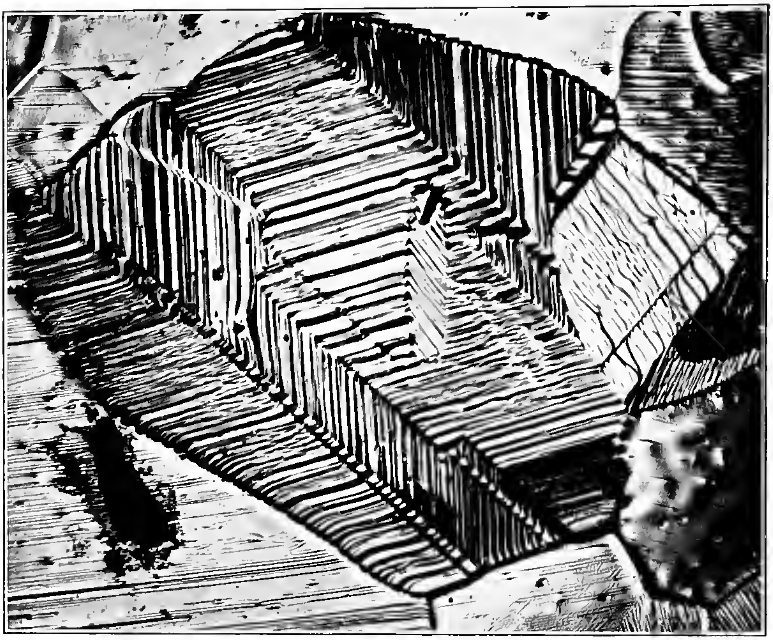


Fig. 107.

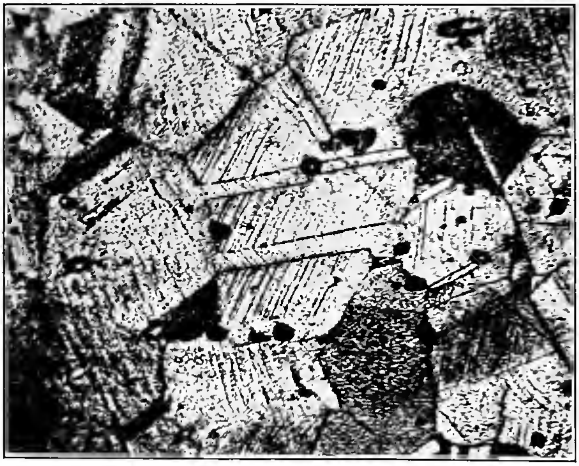


Fig. 108.

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known to occur in the plastic deformation of crystals and which occurs in metals, although it is doubtful whether it is the direct result of strain or only arises during a subsequent annealing process. This is the formation of " twin " lamellæ, or " twinning," as it is generally called. The mutual relationship of twinned crystals is best described by saying that in their internal arrangement and symmetry they are mirror images of one another; we can conceive of the twinned portion being generated from the normal structure by a simple swinging round of all the crystal elements through a definite angle, which is, however, intimately connected with the natural angles of the crystal. In the mineral calcite this swinging round can be brought about by mechanical means, such as the forcible insertion of a knife blade into the edge of the crystal at a suitable point. In metals the presence of twin lamellæ makes itself evident in the etched micro-sections of many metals, such as copper, brass, silver. An example of their appearance, with its typical rectilinear and parallel banding, has already been given in Fig. 55, Plate XI.; another very beautiful example, taken from pure silver, is shown in Fig. 107, Plate XXIII.). The existence of twinned regions is also revealed by the shape assumed by slip-bands in passing through such twinned lamellæ; this is illustrated in Fig. 108, Plate XXIII., which relates to strained copper. The view has been widely held ([9]) that twinning in metals occurs directly as a purely mechanical action under the influence of strain; recent experiments have, however, shown that in the majority of metals, if not in all, twinned crystals are never found in the cast material, if it has never been strained in any way, and that the application of strain to such cast metal does not at once produce twinning; even the very slight amount of strain involved in gently polishing the surface of a piece of pure cast silver is sufficient to produce most vigorous twinning when next the metal is annealed ([10]). This evidence tends to the conclusion that twinned bands are not formed during straining, but that they are a form which the crystals of many metals assume very readily during the re-crystallisation which occurs on annealing after straining. It is interesting to note that typical twinning is not seen in α iron, but that γ iron exhibits twinning in a marked degree.

We have now to consider the mechanism of fracture, first when it results from the application of a steady load and then in relation to the phenomena of "fatigue" described in connection with alternating stress testing in the previous chapter. It will be seen at once that the mechanism of fracture will be different according as it is brought about by a gradually applied load, by shock, or by alternating stresses. Taking steadily-applied tension as our example, we find that the crystals become increasingly elongated with increasing extension, slip occurring to an increasing extent on more and more numerous gliding planes. On these planes, too, amorphous layers are formed, but the amorphous material is still in its temporarily mobile condition. Ultimately the process of slip reaches a limit, and the surfaces part and the test-piece breaks. When a fracture thus produced is examined, it exhibits a typical "fibrous" appearance, but the fibres, in a pure metal, are merely the drawn-out ends of the elongated crystals, and can be recognised as such under the microscope. This can be readily done if the fracture is embedded in electro-deposited metal, such as copper, and a longitudinal section is then cut. Such a section, showing the broken ends of the elongated crystals, is given in Fig. 109, Plate XXV.

When shock acts upon a pure metal, the result is somewhat different. Although a certain amount of deformation by slip takes place, that is essentially a process requiring time, and shock fracture does not allow such time. Consequently, instead of undergoing deformation by slip on the gliding planes of the crystals, the metal undergoes fracture along their cleavage planes. The process of fracture under steady load and under shock have this in common, that in both cases fracture results across the body of the crystal—the individual crystals are not torn apart from one another along their boundaries. This is a typical feature of the fracture of all "sound" materials; where inter-crystalline fracture occurs it is a certain sign of some abnormality in the composition or condition of the metal. Yet the mode of fracture under shock results in an appearance so different from that under steady load that the suggestion has been made that metallic crystals may exhibit either a " ductile " or a " brittle " behaviour. Both are, however, merely manifestations, under differing conditions, of their essentially crystalline constitution.

The explanation of the process of failure by " fatigue," *i.e.*, under the repeated alternations of a stress which would not cause fracture if steadily applied, is also furnished by the conceptions described above as to the behaviour of a crystalline aggregate under strain. A stress which is to cause ultimate failure after repeated alternations must be large enough to produce a small amount of local yielding in the metal. This may be so small in amount as to be unobservable, even with a delicate extensometer, and in that case the stress would be regarded as lying within the apparent or " primitive " elastic limit, but the microscopic examination of polished test-pieces under load has shown that the formation of slip-bands in isolated crystals here and there in the metal may and does occur for stresses of this kind. Some crystals, by their shape and the orientation of their gliding planes are unfavourably situated to resist the particular system of stresses which has been applied, and a slight local slip takes place. If the load remains in steady action, nothing further occurs. If, however, the stress is reversed—*i.e.*, if the metal is being subjected to alternating stress—then this slight amount of slip will also be reversed, particularly as the slip surfaces will still be covered with the temporarily mobile layer of amorphous metal. Such reversal will be repeated with each reversal of the applied stress, and at each successive slip the layer of amorphous material will be increased. After a time, however, by virtue of its temporary mobility, this film of quasi-liquid metal will be squeezed out between the gliding surfaces, and the site of the initial minute slips will develop into a fine crack. As this process continues, that particular crystal soon begins to lose its strength, and additional stress is thereby thrown upon its immediate neighbours, which undergo slip and gradual disintegration in the same way. Ultimately, the crack or flaw thus originated works its way across the entire section of the metal, and failure of the piece results. If the action has been fairly rapid, *i.e.*, if the stress was high enough to produce somewhat rapid disintegration by repeated reversals of slip, the resulting fracture exhibits the crystal faces upon which slip has taken place as a number of bright facets resembling those produced in a " brittle " shock fracture, and it is this appearance which has led to the mistaken idea that alternating stresses cause metal to " become crystalline." Actually, as we have seen, the metal is crystalline from the beginning, never really " fibrous," and the " fibrous " or " crystalline " appearance of the fractures depends on the mechanism of fracture, and not on any change in the crystalline structure of the metal.

The explanation of fatigue fracture which has just been given, although it has been deduced from the general character of plastic deformation by slip, was first given by Ewing and Humfrey (^{11}), as the result of direct experimental observations in which they watched the formation of slip-bands in certain crystals, and their gradual growth into cracks on the polished and etched surfaces of pieces of Swedish iron submitted to the Wöhler test. One set of photo-micrographs obtained by them in this way is reproduced in Figs. 110 to 113 inclusive, Plate XXI.

The manner in which fracture under comparatively low alternating stresses takes place affords an insight into the true meaning of the parabolic curve obtained by the Wöhler or other fatigue test. With the higher stresses, fairly rapid failure results, because slight slip takes place in a considerable number of crystals, and this slip is also greater in amount than it would be under lighter stresses—the exact relation between the two is, however, dependent upon certain properties of the crystals with which we are not well acquainted. On the other hand, when the stress has been reduced to such a value that no local slipping occurs anywhere in the metal, then an indefinite number of reversals produces no effect on the metal—*i.e.*, the test yields a point on the horizontal part of the parabolic curve. The limiting stress at which slip ceases to occur within the metal is thus the " safe range " for alternating stresses, and its physical meaning is simply that it is the " true "

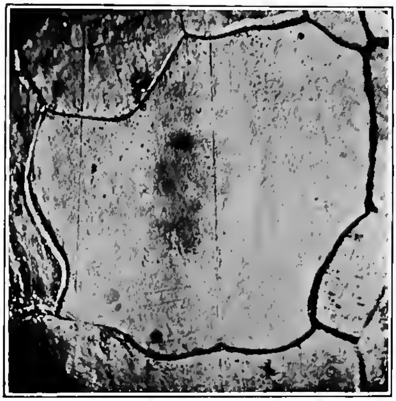

FIG. 110.

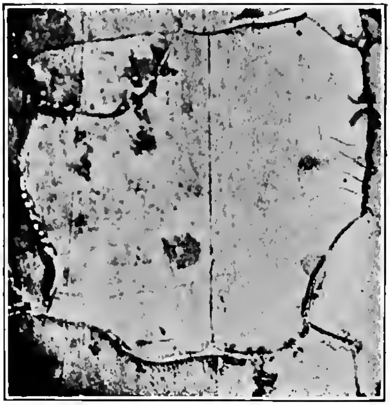

FIG. 111.

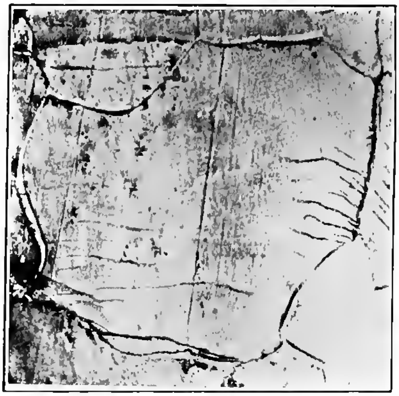

FIG. 112.

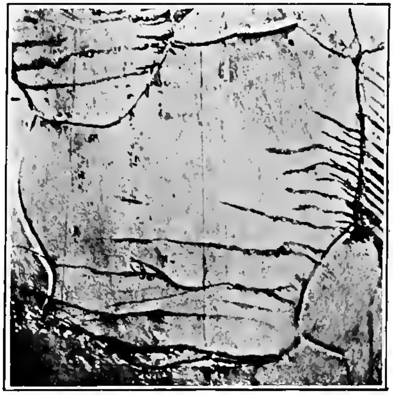

FIG. 113.

[*To face p.* 254.

elastic limit, since nothing but purely elastic deformation is produced thereby. Actually, the alternating stress test is probably the most sensitive method of determining this true elastic limit, and it has the advantage that it is unaffected by the particular condition of cold work in which the metal may find itself, as the application of alternating stresses rapidly restores the elastic limits in both tension and compression to their " true " or normal positions.

While it cannot be claimed that all the intricate phenomena connected with the failure of metals under vibratory or alternating stresses have been fully and finally explained, the methods of Physical Metallurgy have so far elucidated the problem, in the manner indicated above, that a clear insight into the mechanism of failure under the simpler forms of alternating stress has been gained. The myth that metals " become crystalline " under the influence of vibration has been finally dissipated by the demonstration of the manner in which the yielding of crystals by slip can lead to failure under alternating loads. Indeed, microscopic study has shown very conclusively that, so far as iron or steel is concerned, no perceptible change of crystalline structure or arrangement ever occurs at the ordinary temperature. Quite recently, Garland ([12]) has shown, by means of micro-sections of specimens of non-ferrous metal and alloys taken from ancient Egyptian tombs, that the meta-stable cored structures of cast solid solutions, as well as the distorted crystals produced by cold work, persist unchanged through periods of thousands of years. The author's examination of some specimens of ancient iron from Adam's Peak, in Ceylon ([13]), and similar studies by Sir Robert Hadfield ([14]), have shown that in pieces of iron probably over 4,000 years old the structure is exactly the same as in iron that has been made yesterday. It is well, therefore, that the modern explanation of " fatigue " phenomena rests on something much more secure than the unfounded supposition that vibration can cause changes of crystalline structure in a metal so far removed from its softening temperature as iron or steel, or even brass or bronze.

In the discussion of the behaviour of metals under strain we have so far confined our attention, not only to pure or "simple" metals, composed of an aggregate of crystals of one kind, but we have dealt only with the behaviour of the material forming the mass or interior of a crystal and not at all with the conditions which exist at the crystal boundaries where adjacent crystals meet. Yet the behaviour of the crystal boundaries is of primary importance to the qualities of the metal. The extent to which this is the case appears in a striking manner from some early experiments of Arnold (15) with an alloy of gold and bismuth. He showed that such an alloy consists of perfectly ductile crystals of pure gold surrounded—for alloys of low bismuth content—with a thin brittle film in which the bismuth is concentrated. The presence of these thin brittle films in the boundaries is sufficient to render the whole mass of metal extremely fragile, so that it can be readily broken up with a hammer. Individual crystals, however, after being thus broken apart can be hammered out into thin sheets. This is a striking case of a condition which is really abnormal, viz., of inter-crystalline brittleness, due in that case to the presence of a deleterious impurity. In all metals and alloys it is now well known that such inter-crystalline brittleness only arises when the crystal boundaries are weakened, either by the presence in them of a weak and brittle constituent, or because the inter-crystalline cohesion has been weakened by the effects of some special treatment to which the material has been subjected. It has been clearly shown that in all normal fractures, both of iron and steel and of other metals and alloys, even including such a brittle metal as bismuth, the path of the fracture, whether produced by static stress, shock, or fatigue, never follows the inter-crystalline boundaries, but always crosses the crystals, sometimes on relatively straight surfaces, as in cleavage fracture produced by shock, sometimes on greatly stepped slip-surfaces, as in a tensile fracture. An illustration of this fact, which observation of numbers of test-pieces has confirmed, is given in Fig. 114, Plate XXV., which is the section of a shock-fracture of a very mild steel, consisting almost entirely of ferrite. This fracture may be contrasted with that shown in Fig. 115, Plate XXV., which is from

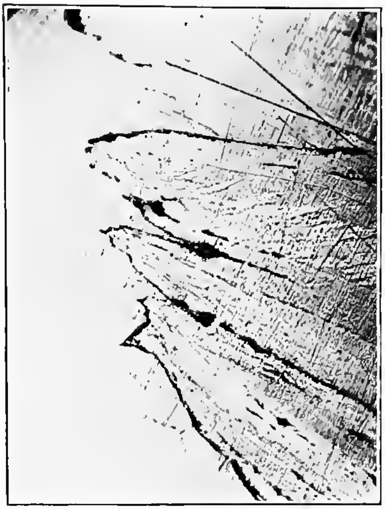

FIG. 109.

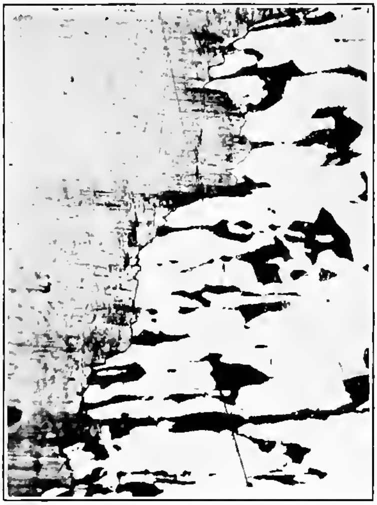

FIG. 117.

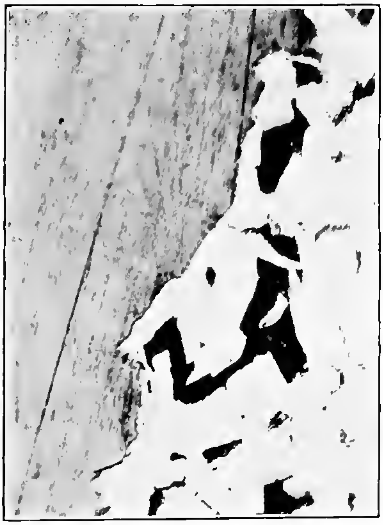

FIG. 114.

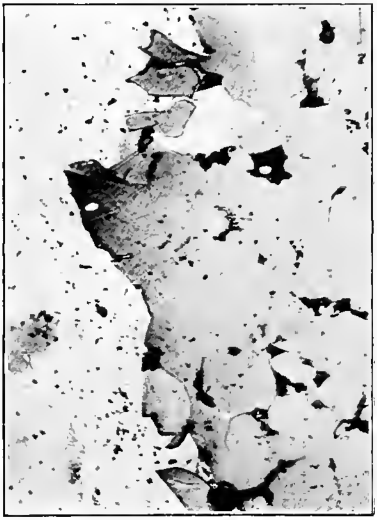

FIG. 115.

[*To face p.* 256.

an abnormal steel in which inter-crystalline brittleness is evident.

If we regard cohesion within the body of a crystal as being due to the attractions between layers of adjacent molecules, we can readily understand the continuity of such cohesion acting throughout the entire mass of any one crystal. The forces which are at work in producing cohesion between adjacent crystals must, however, be of a somewhat different character, for it is obvious that the regular arrangement of molecules in oriented layers cannot be carried on through a crystal boundary, while it appears that the actual cohesion between adjacent crystals is stronger than that between different layers of the same crystal. The view, at one time widely held, that a considerable number of minute cavities exist where adjacent crystals meet in such a way that they do not " fit in " with one another, is obviously contrary to the observed fact that the boundaries are surfaces of extra strength and not of weakness. During the past three years, a view has been independently put forward by a number of workers (^{16}) according to which the interstitial spaces between adjacent crystals are filled up by an amorphous film or layer whose nature is similar to that formed on polished surfaces or on surfaces of slip, but whose origin is entirely different, at any rate so far as cast or annealed metals are concerned. The basis of this view is that where adjacent crystals meet there is a kind of " region between the orientations " where the molecules of the crystallising liquid, or of the re-crystallising solid, are left in a state of approximate balance between the opposing tendencies to arrange themselves according to one or other of the adjacent crystalline orientations. In consequence of this approximate balance of directive forces they remain in the irregular arrangement characteristic of the liquid state, and persist as thin layers of greatly under-cooled liquid, *i.e.*, of amorphous material, which is readily able to accommodate itself to the irregularities of surface of both of the adjacent crystals, and thus, by bridging the gap in the chain of cohesion, acts as an inter-crystalline cement.

This view, although widely supported, is also strongly opposed by those who believe that the tendency to crystallise is so extremely powerful in metals that any considerable undercooling of the kind suggested is impossible ([8]). No satisfactory alternative theory, however, has yet been put forward, and the "amorphous cement theory," at all events holds the field as a satisfactory working hypothesis. How far the picture of what occurs at the crystal boundaries really represents the truth remains for further research to determine. The theory—or hypothesis—as it stands, however, serves to explain a whole series of interesting phenomena. Some of these have only been discovered because the author and his collaborators were led, by the indications of the theory in question, to look for them experimentally. The most interesting of these from the present point of view relates to the behaviour of metals at high temperatures ([6]), and the facts connected with it are well worth careful consideration.

At the ordinary temperature, when a specimen of metal is strained, having previously been polished and etched on a convenient surface, we have seen that the crystal surfaces become covered with slip-bands, as illustrated in Fig. 98, Plate XX. This change of shape of the individual crystals by means of slip cannot, however, go on without some movement at the crystal boundaries. In addition to changing their own shapes, the crystals must move relatively to one another. The strength of the crystal boundaries is found to resist such movement, and the slip-bands are found to be arranged in such a way as to minimise the amount of displacement occurring at the actual boundaries. In other words, the metal takes up the new shape imposed on it, as far as possible, by means of slip within the crystals and with as little disturbance as possible of the inter-crystalline boundaries. That there is some definite movement at the boundaries becomes evident if a polished specimen is strained without being previously etched; the effect of the strain at once causes the crystal boundaries to become visible on the surface.

As the temperature of a metal is raised, it is found that in general its strength—*i.e.*, its resistance to slip and to fracture—becomes rapidly diminished; at the same time, the surface

PLATE XXVI.

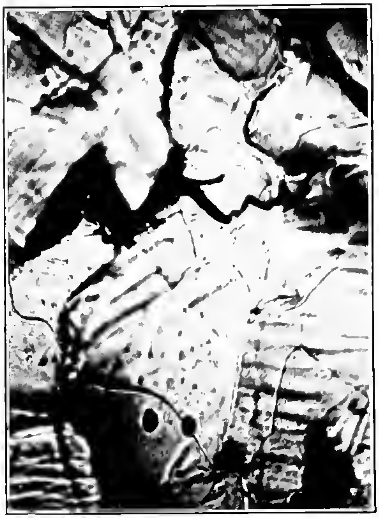

FIG. 116.

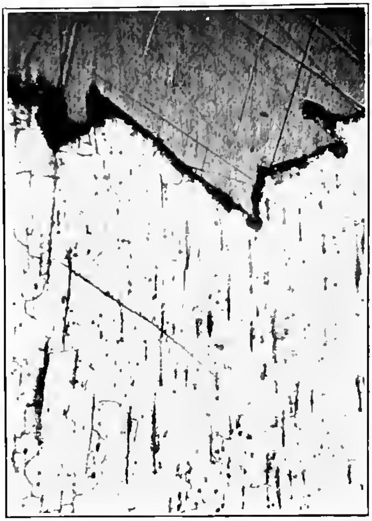

FIG. 118.

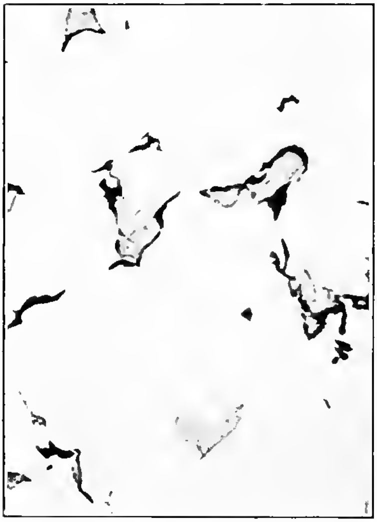

FIG. 119.

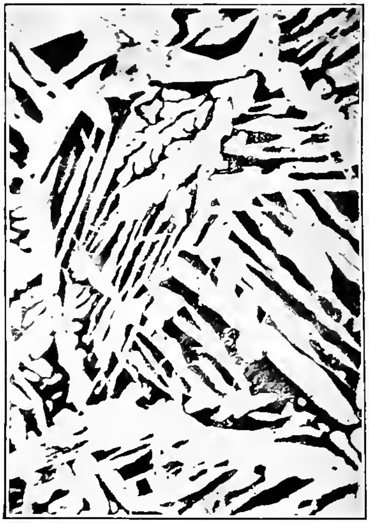

FIG. 120

[*To face p.* 259.

phenomena which are seen on previously polished surfaces also undergo a change. This—according to the amorphous cement theory—is due to the fact that while the resistance to slip, being of the nature of solid friction, is not very much affected by rise of temperature, the resistance of the boundaries—being of the nature of the resistance of a very viscous fluid—rapidly diminishes with rising temperature. While at the ordinary temperature the boundaries are much stronger than the bodies of the crystals, a point is reached. with rising temperature, when this relation is reversed, and the boundaries yield more readily than the mass of the crystal, Specimens strained at such a high temperature—in nearly pure iron this lies in the neighbourhood of 900° C.—show no great development of slip-bands, although signs of their occurrence are still visible, but there are clear signs of much movement at the crystal boundaries. This is illustrated in Fig. 116, Plate XXVI., which shows the previously polished surface of a specimen of very mild steel which has been strained in a high vacuum at a temperature of 1,000° C. That this phenomenon is really due to a viscous yielding of the crystal boundaries is shown by two distinct facts. One of these is that at such temperatures the resistance of the metal is dependent upon the rate of straining according to a law which is that of viscous resistance; the second is that, if a specimen of the same material, heated to the same temperature, is strained by the sudden application of the load, not only is the strength apparently much higher, but the surface phenomena and the fracture revert to the low-temperature type—*i.e.*, there is again a large development of slip-bands and little movement at the boundaries. This—according to our theory—simply means that the rate of deformation has been so great that the fluid, but still highly viscous, cement between the crystals has not had time to flow, and has accordingly behaved like a hard solid, much as does pitch under the action of a blow.

This line of evidence has, however, been pushed considerably further. If the inter-crystalline cement becomes softer as the temperature is raised, at some point not very far below the actual melting-point of the metal, the cement should be practically fluid in the more usual sense of the word—*i.e.*, have only a low degree of viscosity; at the same temperature the crystals themselves should still possess considerable strength, and, consequently, it should be possible to pull the crystals apart, by the aid of a small load, without appreciably deforming them. This leads to the conclusion that at a temperature not far below its melting-point even the most ductile metal should exhibit a very high degree of inter-crystalline brittleness. This somewhat unexpected conclusion has been very completely verified by the author and D. Ewen (6), who produced perfectly brittle fractures of the purest lead, tin, gold and bismuth by means of a slight pull applied to the metals at temperatures ranging from 3° to 10° C. below their melting-points.

This question, with its many interesting points of outstanding difficulty, cannot be further pursued here, particularly as many of the fundamental points are still under active discussion on the part of those interested in the investigation of this subject. On the value of the various arguments employed, the reader—if he is sufficiently interested in the matter—will form his own opinion on reading the various papers referred to in connection with the present chapter. At this point we must pass on to other aspects of our subject.

While we have so far confined our consideration of the behaviour of a crystalline metallic aggregate under strain to the case of a simple metal, consisting entirely of crystals of one kind or phase, a very large number of metallic materials employed in the arts and industries are of duplex constitution, *i.e.*, consist of aggregates of at least two kinds of crystals. We have now to consider how such a duplex aggregate behaves when deformed.

It must first of all be understood that in a duplex, or even in more complex metallic aggregates, all the individual phases or constituents exist as distinct crystals. Where we have two solid solutions, such as the α and β phases in brass, existing side by side, this conclusion is readily established by examining each of the constituents, when each is found to be characteristically crystalline. Where a typical eutectic or eutectoid is present the case is not quite so simple, as we then have an aggregate consisting of simple homogeneous crystals co-existing with grains which are themselves finely laminated and duplex. Yet these eutectic or eutectoid grains have been shown to possess definite crystalline structure of a certain type (17). This type is, however, decidedly less regular in its arrangement than a simple metal crystal, so that the occurrence of slip-bands of the ordinary kind is not frequently observed in eutectics. In fact, if a specimen of a pure eutectic alloy is provided with a polished surface and is then plastically strained, it will be found that the effect on its surface appearance is almost identical with that obtained by etching—the laminated structure is very clearly revealed (1). Close examination has shown that what really happens is that slip occurs along, or very close to, the boundaries of the lamellæ of the two constituents present. When it is borne in mind that these lamellæ are formed by the process of crystallisation, it will be seen that their surfaces must lie on or near to some of the principal crystallographic planes, so that it is not really surprising that slip should occur on these surfaces. When the eutectic structure is somewhat coarse and the applied strain is severe, the formation of ordinary slip-bands can be induced, and these always bear some definite relation to the lamellæ of the eutectic.

Admitting, then, that both constituents of a duplex alloy are essentially crystalline, the duplex metal still differs fundamentally from the simple metal, owing to the fact that, while in the one the various crystals differ from one another so far as resistance to slip is concerned, only on account of their varying orientation, in the duplex metal we have two kinds of crystals which differ fundamentally in their inherent power of resisting slip or of allowing it to take place to any appreciable extent without undergoing fracture. Here we may recall the circumstance that in a large number of duplex alloys one of the constituents either consists of, or contains, a definite intermetallic compound, and that such compounds are characteristically brittle—*i.e.*, incapable of undergoing slip without suffering fracture. Perhaps this may be expressed by saying that in these compounds all the gliding planes are essentially cleavage planes, but the important fact is that, as a consequence, one of the constituents of a duplex alloy is generally hard and brittle.

The condition of a duplex alloy under strain may thus be regarded as very similar to that of a simple metal into whose structure a certain number of hard, brittle grains have been introduced. The influence of such hard interspersed bodies can be readily understood. In the first place, their presence tends to harden and stiffen the whole alloy to an extent quite disproportionate to the quantity of hard material actually present. This is due to the fact that the ductile crystals of the " matrix " metal are supported by the adjacent harder crystals, and in that way the beginning of the slipping process is retarded until the stiffening effect of the hard constituent is overcome by the application of a larger stress. This is equivalent to saying that the duplex material has a higher yield-point and a higher ultimate strength, since the stiffening support of the harder crystals will be continued to the end of the straining process. Further, if the hard constituent is not present in too large a proportion, and if its individual crystals are small and evenly distributed, they in their turn will be supported by the softer material in which they are embedded, and will thus be able to undergo a certain amount of deformation—by slip—without undergoing immediate fracture. That such supporting action is of importance is well known ; thus crystalline limestone, which is ordinarily quite brittle, can be made to undergo considerable flow if it is confined in a tube under great hydrostatic pressure ; similarly bismuth can be extruded under pressure in the form of a wire, although isolated crystals are extremely brittle.

We have, thus, in a duplex alloy a double system whose constituents react upon one another, each supporting the other and aiding it to resist failure in its own particular way. Such a system, however, is necessarily sensitive to the exact arrangement of its parts. Now in an alloy of this kind the arrangement of the two constituents—the size and shape and relative arrangement of their crystals—is dependent upon both mechanical and thermal treatment, so that it is not surprising to find that the physical properties of duplex alloys, more than those of other types of metal, are largely dependent upon the treatment—thermal and mechanical—which they have undergone.

One of the most important and typical of these duplex alloys is, of course, carbon steel, and the influence of the duplex structure is readily studied in this case by the examination of cross-sections of fractures obtained in the manner described above (see p. 245). The path of a tensile fracture is illustrated in Fig. 117, Plate XXV. It will be seen that apparently the fracture passes indifferently through both ferrite (light) and pearlite (dark), in spite of the fact that the tensile strength of a steel consisting entirely of pearlite is some two and a half times that of a pure ferrite material. The reason for this peculiar feature lies in that close inter-relation of the two constituents which has just been discussed. As the yield-point of such a steel is passed, the ferrite, in spite of the support of the pearlite, begins to yield, and the pearlite itself undergoes a small amount of plastic deformation. This process continues until the limit of endurance of the pearlite is reached, when, even with the support of the surrounding ferrite, it can withstand no further stretching. The elongated pearlite crystals then break, leaving the ferrite to stretch further unsupported, finally breaking in its turn ; this final break, however, is bound to occur in such a way that the resulting fracture will run through the fissures already existing in the pearlite. The result is a fracture which appears to run impartially through both constituents. The signs of what has taken place are, however, to be found in the frequency with which the pearlite grains in the neighbourhood of the fracture are found to be fissured, sometimes in several places.

When the same steel is broken in other ways, a different type of fracture results, but in general terms these fractures may be divided into two groups, according as the fracture is or is not preceded by serious plastic deformation. Wherever there is much antecedent deformation the fracture is of the same type as that already described in connection with tension ; on the other hand, if the steel is broken without previous deformation, as by a sudden blow on a notched bar, the fracture appears to occur by the direct cleavage of the weaker and more perfectly crystalline constituent, *i.e.*, the ferrite, and carefully to avoid passing through the pearlite. Thus alternating stress fractures follow the ferrite, as shown by Stanton and Bairstow ; a shock fracture has been shown in Fig. 114, Plate XXV.

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CHAPTER XII

THE THERMAL TREATMENT OF METALS

In the previous chapter the manner in which the structure of a metal behaves under strain has been discussed, and we have seen how, as the result of the process of internal slip accompanied by the formation of amorphous metal in increasing quantities with increasing strain, the original structure of a cast or annealed metal is modified by the application of "cold work," *i.e.*, by changes of shape produced by the application of stresses to the metal in the cold state. The corresponding effects when metal is subjected to "hot work," *i.e.*, when changes of shape are produced in the metal while it is hot, will be discussed in the later portions of the present chapter, but, before we can deal satisfactorily with that branch of our subject, we must first consider the process known as "annealing."

Essentially the annealing process is the converse of the process of straining, since it results in undoing, to a certain extent, the effects produced by the latter. The changes of shape which have been produced by strain are not, of course, undone when the metal is subsequently annealed, but, so far as the internal condition of the metal is concerned, the result of annealing, if properly completed, is to restore the metal to the perfectly crystalline condition which we have learnt to regard as normal, and thus to remove the hardening effects of strain.

The annealing process consists, in all cases, in exposing the metal to a sufficiently high temperature and following this by comparatively slow cooling. In most cases the exposure to a high temperature need not be more than sufficient to allow the whole mass of the metal to attain the same temperature, but if it is desired to obtain an annealing effect at moderately low temperatures, much longer exposure is required. The details in regard to this point vary so much that reference must be made in each case to works dealing with the individual metal in question. Here we can only consider one or two typical cases.

Before considering the properties of any particular metal in regard to annealing, we must first define somewhat more precisely what is meant by such a term as "annealing temperature." When a cold-worked piece of metal, such as a hard-drawn wire or a rolled or hammered sheet, is heated there seems to be no doubt that the first notable effect is that of mechanical softening. Whether we measure this softening by some form of hardness test, such as a ball or cone impression, or by the "scleroscope," or whether we determine the reduction in tensile strength of a wire, it is always found that, for a given period of heating, there is some fairly definite minimum temperature at which softening occurs. If the micro-structure of the strain-hardened material be examined after various intervals of such heating, however, it is usually found that the effects of annealing upon the structure do not become visible for some little time after the first definite softening effect has been produced. This is quite in accordance with the "amorphous" theory, since the first effect of raising the temperature would be to cause the re-crystallisation of the amorphous material present in the metal—so far as such re-crystallisation is possible without a re-arrangement of the whole crystalline structure. If strain has not been too severe, the various layers of the original crystals will still be correctly oriented relatively to one another and, when the intervening amorphous layers are caused to resume the crystalline arrangement, this will result in the practical re-constitution of the original crystals, but these will retain the elongated or otherwise distorted shapes which they assumed under plastic deformation. If the strain has been severe, however, the original orientation of the various layers of a crystal will no longer be preserved, and this reconstitution of the former crystals will only occur to a very small extent, the resulting structure being a mass of extremely minute crystals separated by their boundary films of amorphous metal. In its mechanical properties such a material will differ from the fully re-crystallised material only in certain special directions; as compared with the strength or hardness of the material before annealing had begun, its strength and hardness will be small and practically identical with that of the fully-annealed metal. Even though the amorphous boundary layers are numerous in this state of the material, their total cross-sectional area is still small, and their influence on the hardness or tensile strength is small compared with that which the amorphous layers in the slip-surfaces of the crystals had produced in the strain-hardened metal. It thus arises that the mechanical softening effect of annealing appears to precede the visible effect on the micro-structure. In practice, also, the action is considerably complicated by the fact that the various stages of the annealing process do not occur uniformly throughout any mass of metal.

Somewhat more prolonged heating, after the first mechanical softening effects have been obtained, results in the rapid formation of a large number of minute crystals, which follow the universal tendency of the constituents of a crystalline aggregate to increase in size and to decrease in number. Accordingly some of these crystals grow at the expense of their neighbours. On the hypothesis of an amorphous inter-crystalline cement, this process simply means that the structure of the metal changes in such a manner that the total quantity of amorphous metal—which is essentially in an unstable condition and, therefore, tends to revert to the stable crystalline form—is diminished in consequence of the diminution of the total area of inter-crystalline boundaries in the piece of metal. This tendency to grow is fairly rapid at first, but diminishes with increasing size of crystals; it has been found by Sauveur (1), however, that in mild steel, at all events, there is a "critical deformation," *i.e.*, a certain degree of deformation by cold work, which particularly favours rapid growth of new crystals on annealing, both greater and lesser degrees of distortion resulting in much smaller rates of subsequent crystal growth on re-heating. This is a phenomenon for which it is by no means easy to suggest a satisfactory explanation.

Whatever the theoretical explanation which may ultimately be accepted, there can be no doubt that the process of annealing in most metals occurs in two stages, which sometimes overlap in different parts of the same piece of metal. We have first the simple effect of more or less complete mechanical softening leaving the strained structure apparently unaltered, followed by the process of gradual re-crystallisation by which new crystals of equi-axed shape, and thus possessing boundaries of minimum area, are produced and gradually developed in size. This process of re-crystallisation and of gradual crystal growth is also accompanied by a small change in the physical properties of the metal—there is a further softening effect, accompanied by slight changes in density, thermo-electric power, electric conductivity, etc. One very important point must, however, be borne in mind. If metal is annealed after cold working with the object of fitting it to stand further cold working, it becomes important to allow the second stage of the annealing process to continue for a certain time, so that a crystalline structure of moderate size may be developed. The reason for this necessity lies in the fact that there appears to be a definite limit to the amount of distortion which can be safely applied to a given metal without producing internal fracture. Thus, in wire-drawing, if it is attempted to harden a wire too much by successive cold drawing, a point is reached where the wire begins to "draw hollow,"—*i.e.*, the inner layers of the metal fracture in consequence of excessive distortion. Similarly in cold-rolling, metal may tend to flake and split in consequence of "over work." There is some reason to believe that if a metal is only just softened by slight annealing without permitting the growth of new crystals of moderate size, its power of safely undergoing further distortion is more limited than it would be in a more thoroughly annealed condition. Perhaps the re-arrangement of the amorphous layers within the old crystals is not sufficiently perfect to restore complete ductility, but it is found far safer to allow annealing to proceed far enough to obliterate, as far as possible, the traces of the previous application of "cold work" before fresh deformation is applied. On the other hand, it is equally important to avoid unduly prolonged annealing, with its consequent coarsening of crystal size. Quite apart from the fact that in many metals prolonged heating causes damage owing to oxidation, the coarser crystals do not appear to possess as great a degree of strength and ductility as an aggregate of smaller ones. The difference is not very marked on a tensile test, particularly in the case of a pure metal, but shock tests show a decided difference in favour of the finer structure. In duplex alloys, which depend for their valuable qualities upon the co-operation of two constituents of widely different mechanical properties, the time of annealing is often of vital importance, since it governs the relative arrangement of the constituents ; with this aspect of annealing, however, we shall deal in connection with the subject of " heat treatment " generally.

The annealing process has been studied with great care in several pure metals, notably in lead (Ewing and Rosenhain ([2])), copper (Beilby ([3])), and in gold (Beilby ([3]), Rose ([4])). In regard to duplex alloys, the matter is complicated by the presence of the second constituent, and, for the sake of simplicity, we shall confine our attention to the pure metals just named.

In the case of lead, it has been found that very rapid re-crystallisation occurs at a temperature of 200° C. ; at 100° C. re-crystallisation occurs to a marked extent after an exposure of thirty minutes, while it is found that definite signs of re-crystallisation can be detected after a few months in very severely cold-worked lead, even if stored at the temperature of an ordinary room. Ancient lead, as found on the roofs of old buildings, always exhibits a coarsely crystalline structure, which has, no doubt, grown slowly during many years. As regards the softening effect, the author has recently made some experiments by means of a ball-hardness test, and has found that definite softening of severely strained lead occurs, without the application of artificial heat, after a few weeks, while slight effects may even be observed after a few hours at the ordinary temperature. Some of the other soft metals—*i.e.*, metals with a low melting-point—also undergo annealing at the ordinary temperature. Rose ([7]) states that tin, cadmium and zinc all undergo softening at the ordinary temperature.

In regard to copper, Beilby has shown that exposure to a temperature of 200° C. is sufficient to produce definite effects on the mechanical properties of a hard-drawn wire. Here, of course, the question arises how " annealing temperature " is to be defined. The influence of a given temperature depends upon the time for which it is allowed to act, and the degree of straining or hardening to which the metal had previously been subjected also plays a part in the resulting data. It is therefore necessary to adopt some arbitrary definition of " annealing temperature." Different workers have adopted different standards, suitable to the particular purpose for which the data were required in each case. Probably the best course is to realise that there is no definite and absolute " annealing temperature," although for the purpose of any practical process there is always a definite temperature and duration of heating which gives the best results. Since, however, such a temperature could not be calculated from any arbitrarily defined and experimentally determined " annealing temperature," it scarcely seems worth while to attempt to lay down any general definition or convention on this subject.

The annealing of gold has been very fully studied, more particularly by Beilby and Rose. Beilby finds that an effect on the mechanical properties of a hard-drawn gold wire only makes itself felt when a temperature of 250° C. has been attained. Rose, on the other hand, taking the " temperature of annealing " as the " temperature at which a piece of metal becomes almost completely softened and re-crystallised in half an hour," finds that the very purest gold, not containing more than one part of impurity in 10,000, has an " annealing temperature " as low as 150° C., while the corresponding temperature for gold containing 0·05 per cent of copper is 250° C. This striking influence of slight impurities on the temperature of annealing has also been traced in copper, and no doubt serves to account for the higher temperature found by Beilby.

In the case of wrought iron and steel, there is evidence to show that even a temperature of 100° C. is sufficient to bring about a notable change in freshly over-strained material.

Muir (5) has shown that the elasticity of iron or mild steel which has been temporarily destroyed by straining beyond the yield-point can be rapidly restored by exposure to boiling water. The common practice of exposing a razor to steam immediately after stropping probably also acts by removing the traces of over-strain from the thin edge of the steel which has been over-strained by bending backwards and forwards during stropping. Steel fully hardened by quenching in cold water also appears to be very slightly altered by exposure to 100° C. Strain-hardened iron or steel, however, although some slight and gradual changes of properties become noticeable at temperatures near 300° C., does not undergo any serious or rapid annealing until a temperature of 500° C. is reached, and for all practical purposes this temperature may be regarded as the lowest possible annealing temperature. This fact appears very clearly in the curves published by Goerens (6).

It is perhaps desirable to point out here that the " annealing temperatures," in so far as they have been mentioned in the preceding paragraphs, refer to the minimum temperatures at which certain effects have been obtained. For practical purposes very much higher temperatures are universally adopted ; primarily the reason for this practice lies in the fact that these higher temperatures produce the desired effects of softening and re-crystallisation very much more rapidly and, under proper control, without damaging the metal. The duration of exposure and the temperature attained must be carefully adjusted to each requirement, and it is particularly important to note in this connection that the various metals differ very widely in regard to the rate at which re-crystallisation takes place. Thus aluminium exhibits extreme sluggishness in this respect, so that prolonged exposure to a relatively high annealing temperature is required to bring about complete re-crystallisation. In brass and copper, on the other hand, the rate of crystal growth is relatively rapid, and a few seconds exposure to a temperature of 600° or 700° C. is sufficient to bring about fairly complete annealing in these metals.

We have already referred to the evils associated with excessive annealing, but the matter is of such considerable importance that rather more detailed consideration is required. The effects of prolonged annealing, more especially in the case of those metals which are usually annealed at temperatures above 600° C., are two-fold. In the first place, there are the effects of mere exposure to a high temperature upon the internal structure of the metal, and, in the second place, there are in some cases equally serious effects due to the chemical and physical action of the atmosphere in which the metal is heated. Taking the latter first, we have effects of oxidation, which are particularly felt in iron and steel where removal of carbon and formation of oxide in the surface layers always occurs in industrial annealing, even though efforts are made, by packing the steel in iron boxes filled with lime or other powdered material, to exclude the air as far as possible. In the case of very thin pieces of metal this oxidising action may penetrate far enough to impair the value of the piece entirely. A case of the opposite kind is presented by many varieties of copper, which normally contain a certain proportion of oxygen. If such copper is heated in a reducing atmosphere, or if while hot it is even temporarily exposed to reducing gases, the metal is so seriously injured as to be rendered useless for most practical purposes. This action, known as the " gassing " of copper, arises from the fact that hydrogen is able to diffuse rapidly through red-hot copper; in the interior of the copper this gas meets with small grains of cuprous oxide, and a chemical reaction follows by which the cuprous oxide is reduced to copper while the hydrogen is burnt with the formation of an equivalent quantity of steam, thus :—

$$Cu_2O + H_2 = 2Cu + H_2O.$$

The water vapour produced is, however, unable to diffuse away through the copper, and a small blow-hole or cavity is formed in the place previously occupied by the grain of cuprous oxide. This action often suffices to render the copper extremely weak and porous.

Injury to metal as the result of an annealing process is, however, much more frequently caused by the effect of prolonged exposure to a high temperature upon its internal structure. We may consider first the case of a simple metal—*i.e.*, a pure metal or an alloy of the "simple" solid solution type in which crystals of one kind only are present. In such a material the effect of prolonged annealing upon the resulting structure can only be of one kind, viz., the coarsening of the structure by an increase in the size and a reduction in the number of the crystals which compose the mass. We have already seen that the crystals which constitute a mass of metal exhibit a tendency to increase in size and to diminish in numbers—a change which is usually described as the "growth" of the constituent crystals of a metal. At the ordinary temperature such growth is held in check by the internal resistance which the hard and solid metal offers to any molecular re-arrangement. When the temperature is raised this resistance is diminished, and a stage is reached when the tendency to growth is sufficient to overcome the resistance. If the metal has been strained, the tendency for some re-arrangement to occur is probably much stronger than in the unstrained state, and the temperature at which re-arrangement will begin—what we have previously called, roughly, the "annealing temperature"—is probably lower than that at which crystal growth will occur in an unstrained sample of the same metal. Indeed, there is some doubt whether some degree of strain is not essential to start the process of crystal growth at all; if this is the case, however, only very little of such impetus can be required. The real reason for crystal growth lies in the tendency, which every physical system exhibits, to dissipate any stores of potential energy which it may contain. Now there can be no doubt that the crystal boundaries contain stored energy; whether we regard it, in accordance with the amorphous cement theory, as being identical with the latent heat of fusion, or whether we confine ourselves to the more general statement that the crystal boundaries are the seat of "surface energy" or of "surface tension," we reach the conclusion that the final state of physical equilibrium of a crystalline aggregate—towards which it tends to change gradually whenever the conditions are favourable to change—is that of a single crystal forming the entire mass, with a total absence of inter-crystalline boundaries. We do not often meet with metal in this state—the attainment of this ultimate physical equilibrium is even rarer than the attainment of complete physico-chemical equilibrium in accordance with the requirements of the phase rule. None the less, these final states indicate the directions in which changes are likely to occur on prolonged heating. In the present case the tendency results in the growth and re-arrangement of crystals always in the direction of reducing the area of their inter-surfaces. And this tendency extends not only to aggregates of crystals of one kind, but also to duplex and more complex aggregates, with results—in the case of duplex alloys—which we shall have to consider below.

The question then arises whether the increasing size of crystals produced in a simple metal by prolonged heating is injurious or otherwise so far as the useful properties and, more especially, the mechanical properties of the metal are concerned. There can be little doubt that, within reasonable limits, the mechanical properties of a simple metal are better the smaller the constituent crystals of which it is built up. Under the tensile test, coarseness of structure usually results only in a slightly lowered yield-point, while the ultimate stress and the elongation are little impaired, although the reduction of area at fracture is sometimes markedly less. This, of course, refers to ductile metals and alloys, the mechanical properties of brittle materials being relatively unimportant. On the other hand, under both shock and fatigue tests a coarse structure, even in a simple metal, gives unsatisfactory results. The reason is easily understood, for the crystal boundaries act as a species of strengthening skeleton ; at each boundary a crystal is supported by its neighbours, since a slip-band, for example, must change its direction—often in two planes—where it passes from one crystal to another, and if the stresses at work are such as to favour slipping in one of these directions, they will not be so favourable for slip in the other, so that the weakness of one crystal will be balanced by the strength of another. Where the crystals are large, single surfaces of slip or cleavage extend unbroken through relatively large areas, and fracture—particularly under shock or fatigue—may be brought about under conditions which a finer grained structure would have resisted. The whole state of affairs is somewhat like the effect of a "break of joint" in brickwork or masonry; within an individual crystal we may compare the structure to that of bricks laid without break of joint, but at the boundaries there is not only a complete breaking of joint, but also a change in the direction of the courses.

In connection with the effect of prolonged heating or annealing on the general scale of the crystal structure, a further remarkable feature is sometimes met with. This is a tendency which whole groups of adjacent crystals appear to possess of assuming a similar, although not strictly identical, orientation. Etching reveals boundaries between the members of such a group, but the boundaries only appear after somewhat deep etching, and are then very fine, indicating that the difference of surface level produced by the etching process is very small. On straining or breaking such a piece of metal it is often found that slips or cleavages run with very little change of direction through the whole group, which thus behaves almost like a large single crystal. An example of a cleavage shock fracture in wrought iron which had attained this condition is shown in Fig. 118, Plate XXVI., where straight cleavage edges running almost unbroken through whole groups of crystals are clearly shown. Such cleavages running almost unbroken through a number of crystals have also been described by Stead (7) as occurring in certain mild steel sheets after rolling, although their origin in that case was probably not connected with over-annealing.

While examples of the evil effects of over-annealing are most frequently met with in connection with iron and steel, they occur equally in the case of copper and brass. There is, however, in these metals a feature of the structure which tends to mitigate somewhat the effects of a coarse crystal structure. This is the occurrence of the twinned lamellæ which are so constantly found in metal which has been wrought and annealed. Although essentially of the same crystalline system as the parent crystals, yet the twinned regions do impose a change of direction on planes of slip or of cleavage, so that these do not have such a free and uninterrupted path as in a crystal of similar size free from twinning. The boundaries of twinned regions do not contain any amorphous cement and, if one can judge from their behaviour on annealing, they do not serve for the storage of latent energy, since they do not tend to coalesce on heating, so that their value from the mechanical point of view is not so great as that of true inter-crystal boundaries.

The influence of prolonged heating—*i.e.*, of over-annealing or " over-heating "—on duplex alloys is considerably more marked than in the case of simple metals. The tendency towards alterations of structure, which result in the diminution of inter-crystal surfaces, is quite as strong in the duplex alloy as in the simple metal, so that the mere growth of crystal size, quite apart from the arrangement of the two constituents, takes place exactly as in a simple metal, and with much the same results. The mechanical properties of such duplex alloys, however, usually derive their importance, in the manner already explained in the previous chapter, from the proper juxtaposition and co-operation of two constituents of unequal hardness and ductility. In such an alloy we have, in fact, a ductile and relatively weak constituent supported and " held up " to its work by the interspersed crystals of a harder material, while this harder material is in turn prevented from undergoing brittle fracture by being firmly embedded in the softer constituent. Ideally, these effects would be at their maximum if the two constituents were mixed in the most intimate manner, so that the most desirable structure is one in which each of the two constituents is present in the smallest possible crystals while the two constituents are evenly mingled. When, however, a duplex aggregate is exposed to prolonged heating, there is not only the change in average crystal size to be looked for, but also a more or less rapid segregation of the two constituents. As the crystals of the predominant constituent grow they necessarily push before them the crystals of the second phase, until two or more of these meet and coalesce into a larger crystal. Not only this ; when a duplex structure is formed, whether by solidification from the liquid or by separation from a solid solution, the second—and usually the harder—phase is left occupying the points where the crystal boundaries of the primary phase meet, and frequently thin layers of the hard phase extend some little way along the inter-crystal boundaries, thus forming a network which is closely inter-connected with the crystals of the softer constituent. The tendency to reduce boundary areas which comes into play on heating, however, rapidly alters this arrangement ; the crystals of the harder phase tend to assume rounded or polygonal outlines and to retract any outlying arms, thus very materially lessening the interlocking between the two constituents.

Changes of this kind, with their accompanying deterioration in powers of resistance, particularly to shock, are readily observable in all duplex alloys, including such materials as the brasses containing the α and β phases, certain aluminium-copper alloys, and in many types of bronze. The most important and, in many ways, the most interesting case is that presented by steel. The thermal treatment of steel, however, is governed by several considerations of a somewhat special kind, so that a section of this chapter will be completely devoted to it.

The special features in connection with steel which affect the whole question of heat-treatment are: first, the duplex character of the "hard" constituent, *i.e.*, of pearlite, and, second, the critical points and the corresponding constitutional and structural changes through which steel passes on heating and cooling. In view of these latter, it is desirable to discuss the behaviour of steel under two separate heads, according as the temperatures involved lie below or above the critical range—*i.e.*, the lines EG, GI, HI and ID of the diagram (Fig. 64, p. 161), which represents the constitution of the iron-carbon alloys.

At temperatures considerably below Ar_1, represented on the diagram by the line HIJ, the annealing of steel is slow, but if the temperature of Ar_1 is closely approached—*i.e.*, in the neighbourhood of 700° C.—a material amount of structural change is produced. This is exactly of the general type indicated above, resulting in an increase in the size of the ferrite crystals and a balling up of the pearlite into larger, rounder masses with more sharply defined edges. This is the first stage of the process, but, owing to the peculiar nature of pearlite, the process can go a step further. Pearlite consists of laminæ or granules of cementite embedded in ferrite; this laminated or granulated structure, however, is solely due to the manner in which this constituent separates from its matrix and, as a matter of fact, when *very* slowly cooled, steel shows no laminated pearlite. The laminated or granular structure can also be destroyed if the steel is exposed to prolonged heating at a temperature approaching 700° C., provided that the steel has been *raised* to that temperature without first passing through the critical point. This last condition simply means that the steel must be exposed to prolonged heating while in the pearlite condition. If this is done, the laminæ or granules of cementite gradually retract and " ball up " into larger granules, while the ferrite with which they were formerly interlarded becomes incorporated with the adjacent primary ferrite crystals. The resulting structure consists of ferrite with some cementite scattered among it, either in isolated rounded lumps or in the form of layers or films in the crystal boundaries. An example of the latter structure is shown in Fig. 119, Plate XXVI., taken from a steel boiler-plate which cracked in use. Both these structures are extremely undesirable. The cementite, when present as isolated balls or lumps, is of very little use to the steel, which then possesses merely the properties of pure ferrite having a coarse structure—these, of course, being far from equal to those of a mild steel having a correct structure. Where the cementite lies in filaments in the crystal boundaries it is apt to play the part of a mere weak and brittle cement, much as the bismuth did in Arnold's experiment with gold (see p. 256).

When in the condition of pearlite or Sorbite, where cementite is intimately associated with layers of ductile ferrite, the inherent brittleness of cementite is largely neutralised, and the hardness of the duplex constituent—pearlite—is well adjusted to stiffen and support the ferrite matrix of a mild steel. Cementite by itself, however, is not only excessively hard and brittle as compared with ferrite, but it is also too small in quantity and bulk to serve as an efficient stiffener. Its presence in the isolated state thus becomes a source of weakness rather than of strength. The behaviour, both under test and in service, of steels having this "free cementite" structure is now well recognised to be most unsatisfactory. Fortunately the prolonged heating of steel to a temperature near 700° C. is not often likely to occur, and, if steel has accidentally been treated in that way, its normal structure can be restored by the use of the method of "heat refining" to be described below.

It should be added that in the case of very mild steel, containing only very small amounts of carbon (0·10 per cent. and less) the influence of Ar_1 and Ac_1 is small, and the effect of pearlite or cementite on their strength is also less important. Consequently, up to the temperature of the line EG, of the diagram Fig. 64, these steels behave very much like simple metals and undergo gradual coarsening when heated for a prolonged period. As Sauveur has shown, when the steel has been exposed to one particular degree of strain, the subsequent growth of its crystals at these temperatures is exceptionally rapid. On the other hand, the very pure electrolytic iron recently studied by Stead and Carpenter ([8]) does not appear to undergo any marked crystal growth within this range of temperature. These curious facts serve to show that our understanding of the causes at work in crystal growth is by no means complete.

We have now to consider the structural changes which result when steel is heated above the temperature of Ac_3 (*i.e.*, above the line EGI of Fig. 64). We shall confine ourselves to steels containing less than 0·90 per cent. of carbon, *i.e.*, to the hypo-eutectoid steels. In their condition before heating these steels will generally be in the condition of ferrite *plus* pearlite, although the normal arrangement of these constituents may be seriously distorted as the result of cold work or strain. On heating such steel above the temperature of Ac_3 which, according to the carbon content will vary from 900° C. to 720° C. approximately, the ferrite at once undergoes the allotropic change to the condition of γ iron, and, since cementite is soluble in γ iron, the cementite present in the lamellæ of pearlite at once begins to diffuse into the γ iron. At first this diffusion results in the amalgamation of the ferrite and cementite lamellæ or granules of the pearlite itself, but this stage is usually accomplished during the process of heating-up, since the ferrite in contact with cementite undergoes the allotropic change to γ iron at much lower temperatures—*i.e.*, as soon as the steel has been raised above Ac_1. After a time, whose exact length is not accurately known, since it necessarily varies according to the scale of the initial ferrite-cementite structure and also in accordance with the effects upon the rate of diffusion which are undoubtedly exerted by some of the common impurities of steel, the diffusion process is completed, and the steel will consist of an aggregate of homogeneous crystals of the γ iron solid solution.

The transformation of the ferrite from the α to the γ state, however, quite apart from the influence of adjacent carbon in lowering the transformation temperature, does not occur suddenly or uniformly throughout the mass even of a single ferrite crystal. What really takes place is the growth of crystals of the new phase—γ iron—at the expense of the ferrite or ferrite *plus* cementite. Now the growth of such new crystals commences at a considerable number of points, and, as a rule, these points will lie in the boundaries of the existing ferrite crystals, principally because these boundaries are likely to contain particles of cementite or of pearlite here and there whose presence facilitates the beginning of the transformation. The result is, however, of vital importance, for it follows that while the new γ iron structure has some relation to the previously existing ferrite, this relation is not one of numerical equality—*i.e.*, there will, as a rule, be a number of new crystals of γ iron in place of each pre-existing ferrite crystal—and, if the latter have been large, then the corresponding crystals are likely to be fairly numerous. At all events, the new γ crystals will, when first formed at a temperature just above Ac_3, be more numerous and smaller than the pre-existing ferrite.

Like any other variety of crystals existing in a metal at a relatively high temperature, these newly-formed crystals, if maintained at a temperature above that of Ar_3, will begin to grow, and the growth will be more rapid the higher the temperature. If therefore, steel of this kind is kept at temperatures above the critical range for any considerable time, or even if for a short time its temperature is raised above 900° C., a coarse structure is rapidly developed in the γ iron solid solution. If the steel is then slowly cooled, the transformation of the γ iron solid solution into the normal ferrite-pearlite structure takes place during the passage through the critical range; the events which took place on heating are now to some extent reversed, and the resulting ferrite and pearlite crystals are somewhat more numerous than the γ iron crystals from which they have been formed. On this reverse transformation, however, a process of rejection takes place, the dissolved iron carbide being pushed out of solution in the γ iron to form the cementite lamellæ of the pearlite. In such a process the presence of nuclei is of vital importance. Such nuclei may possibly exist in the form of traces of undissolved cementite remaining from the original structure, but this is only likely to occur if the steel has not been overheated, since prolonged exposure to a high temperature should result in the complete solution of the cementite. In that case nuclei may be furnished by particles of impurity mechanically enclosed in the steel. It has in fact been shown by Ziegler (9) that such particles can and do act as nuclei and play an important part in determining the structure of a steel. If this is the case, we may meet with instances where a very similar type of structure is formed repeatedly after successive heatings and coolings to temperatures beyond Ac_3. Kroll (10) describes some experiments in which this took place. As a rule, however, the action of such foreign nuclei is not very prominent, and the new structure formed on cooling is directly dependent as to scale and arrangement on the γ iron structure from which it springs.

The processes which have just been outlined are of practical importance in two ways. First, we find that by "overheating" steel, *i.e.*, by exposing it to unduly high temperatures, or for too long a time to any temperature above Ac_3, the growth of a very coarse γ iron structure results, and this, on cooling down, gives rise to a correspondingly coarse ferrite-pearlite structure. Not only this, but the arrangement and forms assumed by the pearlite which is formed from such steel is characteristic; there is a strong tendency for the ferrite to take the form of straight bands with elongated and sharply angular patches of pearlite between them, the ferrite bands frequently crossing one another at angles of 60°. This is a structure very similar to that found in steel ingots as cast, or in steel castings which have been annealed. A typical example is shown in Fig. 120, Plate XXVI. Such a coarse, sharply angular structure is, of course, extremely undesirable; there is a minimum of interlocking between the ferrite and the pearlite, and the straightness of the arrangement facilitates the propagation of slip or cleavage through the crystals. Such structures are, in fact, frequently met with in steel objects which have failed in service. Under test they generally exhibit some degree of weakness as regards shock and alternating stresses, but their tensile strength and elongation are frequently quite satisfactory. The most typical feature, however, is a decided drop in the yield-point as compared with that of the same material in a more normal condition. The use of steel showing this type of structure is, of course, to be strongly deprecated wherever strength and reliability are of importance.

The second practical application of our knowledge of the processes of re-crystallisation which occur when steel is heated and cooled through the critical range lies in the process known as "heat refining." Steel possessing an undesirably coarse structure may have to be dealt with, whether it be found in the form of castings or of overheated material, or as a product of special processes, such as case-hardening, where prolonged exposure to high temperatures is unavoidable. Even ordinary forged or rolled material—particularly if finished too hot—may stand in need of having its structure refined. This can be done by making use of the re-crystallisation processes which occur as described above. By rapidly heating the steel to a temperature just above Ac_3, maintaining it there for a time only just long enough to allow the whole mass of material to attain the temperature, and then cooling as quickly as practicable, the maximum refining effect is obtained. From the description given above, the mechanism of this process can be readily followed ; only in rare cases does the presence of foreign bodies acting as nuclei serve to interfere materially with such a refining operation. While rapid cooling is desirable in order to secure that the pearlite shall be formed as far as possible without any " balling up," actual quenching is neither necessary nor desirable for the purpose of heat-refining itself—the temperature of Ar_3 being decidedly too high for safe quenching of any but small pieces of steel. If there is a case to be hardened, as in case-hardened objects, or if, for other reasons, it is desired to convert the pearlite of the steel into Martensite or Troostite, this is best done by re-heating the steel to a temperature just above Ac_1, cooling down to just above Ar_1, and then quenching.

There is one condition of steel, more or less akin to simple over-heating, which does not permit of restoration to a satisfactory condition by any form of heat treatment. This is what is known as " burnt " steel, and is the result of heating to an excessively high temperature. The explanation of " burning " now usually accepted is that it occurs when the steel is heated to a temperature above that of the *solidus* curve AD of the constitutional diagram, Fig. 64. It is supposed that when incipient fusion occurs in the boundaries of the crystals an opportunity is given for furnace gases, and more especially oxygen, to invade the steel and to oxidise the crystal boundaries, and thus to render the steel permanently weak and brittle. Whether this explanation be correct or not, the microscope shows in burnt steel the presence of foreign matter, probably oxide, at points corresponding to the location of the boundaries of the large iron crystals which existed at the time when the steel was excessively hot. These traces cannot be removed by heat treatment, and, although the general structure may be refined, the brittleness along these old boundaries is never removed and the steel is only fit for re-melting.

In the discussion of heat treatment which has here been given, attention has been confined to pure carbon steels, and, even in regard to these, no attempt has been made to follow the exact details of the genesis of the various features to be met with in the micro-structure of steel as variously treated. Some reference must, however, be made to the thermal treatment which is of vital importance to the newer varieties of steel, in which other elements, such as nickel, chromium manganese, vanadium, titanium. and, finally, tungsten and molybdenum are introduced in notable and, sometimes, in very considerable proportions. It is impossible within the limits of an introductory volume to enter upon the wide field of the metallography of these alloy steels, but it is not too much to say that their practical value is very largely, if not entirely, dependent upon a knowledge of the proper thermal treatment to be applied to them. The use of these alloying elements has given us the power of influencing the position and relative importance of the critical points in low-carbon steels, and, in consequence, we are able to obtain materials which are still in the range of stable existence of γ iron at the ordinary temperature ; others again are in an intermediate or " Martensitic " stage in which they are capable of attaining great hardness, while in others the fundamental properties of the ordinary constituents of carbon steel are so profoundly modified that we are practically dealing with a new material, although microscopically it may still be " ferrite " or " Austenite." The study of the correct thermal treatment of these complex steels is thus obviously a matter of considerable difficulty ; in many cases the true causes at work are not yet understood, and results are obtained on empirical lines—a certain form of heat treatment being found to yield the desired results. The study of these ternary and quaternary alloys by the methods of Physical Metallurgy is being steadily taken up, and in time it may be confidently expected that we shall have as sound and complete a knowledge of their transformations, and a correspondingly certain command over their properties and treatment, as we now enjoy in the case of pure carbon steels.

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CHAPTER XIII

THE MECHANICAL TREATMENT OF METALS, INCLUDING CASTING

IN this chapter, under the heading of "Mechanical Treatment of Metals," we shall deal briefly with those processes which are employed in order to bring metal into the shape or form in which it is required. The majority of these processes are strictly speaking "mechanical," in that they depend upon the direct application of mechanical forces or agents to the metal. For the sake of convenience we propose, however, to include the process of "casting" under this head, for although in that process the mechanical—*i.e.*, the hydrostatic—pressure of molten metal is employed in order to bring the material to the shape of the mould, yet casting is not usually regarded as a "mechanical" process. Castings, in the form of ingots, however, form the starting-point for all rolling and forging processes, and many of the qualities of the ingot are of vital importance to the final result.

While, in general, the primary object of all the processes to be considered here is the production of a definite shape or form, these processes exert a great influence upon the internal structure and mechanical properties of the metals to which they are applied, and it is largely from that point of view that they will be considered here, as bearing upon the correlation of constitution and structure with strength.

In regard to the process of casting, we shall leave on one side the whole art of the foundry in regard to the design and construction of moulds and all matters connected with the furnaces for melting the metals. Although these matters do not lie outside the scope of Physical Metallurgy, their treatment is best relegated to a special treatise dealing with that branch of the subject. Here we are concerned principally with the effects of the casting process upon the constitution, structure and properties of the resulting material.

Two totally different types of "casting" must be distinguished at the outset. In one, which is the essential province of the founder, the casting itself is the final product, and—subject to some thermal treatment, such as subsequent annealing—the properties of the material are those which it receives as it solidifies from fusion. In the second type of "casting" the object which is directly produced from the molten metal is merely a step in a long process; the ingot is to serve as the starting point for the production of rolled, forged, drawn or otherwise wrought material. In consequence of this difference, the methods and aims of the processes employed vary very widely between the two types of "casting." It must be pointed out, however, that in many respects the long and costly processes of "working" metal are rendered necessary by the imperfection of the cast material itself—its internal structure requires thorough refining before it reaches the requisite standard, whether of strength or ductility. Modern practice, always tending to seek economy by reducing the number of manipulations, is constantly seeking to produce by direct casting, products which could formerly be obtained only by more complicated and costly methods. The great growth of the "malleable castings" industry is a striking example of this kind, while recently in Sweden the production of large steel castings has been pushed so far that it was thought possible to produce guns of fairly large calibre by casting direct (^{1}). The production of very satisfactory crank-shafts for marine engines by casting alone is claimed as a commercial success in certain Continental works.

For a given material, the constitution and structure of any casting will depend almost entirely upon the rate of cooling, and principally upon the rate of solidification which the metal has undergone in the mould. In castings of our first type, which are to be used as such, it is obviously important to secure the best possible structure by securing the correct rate of cooling. For the majority of materials the best rate of cooling is simply the most rapid rate that can be employed without producing cracking or warping of the casting. Thus it is almost universally found that metal from the same pot cast in "chill" moulds yields a far finer structure and better mechanical properties than the same material cast in a mould made of sand. A "chill" mould, being made of metal, conducts the heat away rapidly and leads to rapid solidification, while the sand mould is a poor conductor of heat and keeps the metal hot for a long time. Exceptions to this rule occur in metals which undergo one or more critical transformations during cooling, and in such cases it may be necessary to avoid that suppression of such changes which too rapid a rate of cooling might bring about. A typical example of this kind is found in cast-iron, whose structure and constitution varies very markedly according to the rate of cooling. If the iron is cooled rapidly, particularly if it contains little silicon, the formation of graphite during the first stages of solidification is prevented by casting in a chill mould, with the result that the iron when cold consists of cementite and pearlite, or even Martensite-Austenite. This constitutes what is known as "white iron," which, but for the usual impurities, is practically a very hard high-carbon steel. Such chilled iron has its important uses, and in other cases its great hardness is not objectionable, but where the castings have to be cut or machined, this hardness would render them useless.

Even apart from the effects of chill moulds, or of chills locally introduced in order to produce special effects, the rate of cooling or of solidification of a casting can be regulated to a considerable extent by controlling the temperature of the metal at the moment of pouring. A high casting temperature, quite apart from other disadvantages attaching to it, reduces the rate of solidification, because the excess heat of the metal is communicated to the mould before the freezing-point of the metal is reached, so that the thermal capacity of the mould is largely exhausted before solidification begins. The resulting very gradual solidification causes not only a very coarse structure, but allows of the occurrence of serious segregation, the more fusible portions of the alloy tending to rise into that part of the casting which is the last to solidify. It is, therefore, an almost universal rule that casting temperatures should be kept as low as possible, consistent with adequate fluidity of the metal to allow of the proper filling of the mould.

Not only is it desirable to keep down the temperature at which metal is poured into the mould, but any overheating of the molten metal should be avoided, although, if it is allowed to cool down to the proper temperature before pouring, the greater part of the harm is avoided. None the less, there seems to be some ground for thinking that metals which have been thus over-heated tend to develop a coarser structure than would otherwise be the case. There is also a considerable likelihood that the metal will be injuriously affected as regards chemical composition during such over-heating. It must be borne in mind that there is a constant tendency to establish a state of chemical equilibrium between the molten metal and any substances with which it is in contact. When very hot, the chemical actions due to this cause are much intensified, and many metals absorb or reduce some of the constituents of the crucible, stirring or skimming rods, etc., with considerable avidity. The absorption of silicon by aluminium or its alloys, when heated in a crucible containing any form of silicates, is a typical example. The metal is, moreover, in contact, not only with the walls of the crucible or furnace, but also with the furnace atmosphere. The absorption of gases by liquid metal appears to increase with increase of temperature—this departure from the laws which govern the solution of gases in liquids such as water, is probably due to the fact that the metals form loose compounds with such gases as hydrogen and nitrogen. The gases thus absorbed are frequently retained by the metal until crystallisation sets in, when the gases are liberated and render the casting unsound.

While rapid cooling of castings through the freezing range is eminently desirable from many points of view, a limitation is imposed in many cases by the circumstance that contraction stresses will produce fracture or warping if too great a rate of cooling is adopted. These stresses arise if the inner layers of a casting are still fluid while the outer layer has already become solid and rigid. All metals undergo changes of volume at the moment of solidification, and if a fluid core is contained in a solid envelope, severe stresses must be set up as soon as the core begins to solidify and endeavours to change its volume in accordance with its normal behaviour. The outer shell will resist any such change of volume, whether it be expansion or contraction, and severe stresses will be set up, which may easily result in fracture. The manner in which a casting is allowed to cool will also affect its behaviour in this respect; if the relative rates of cooling of thick and of thin portions are equalised, much more rapid rates can be adopted than would otherwise be permissible.

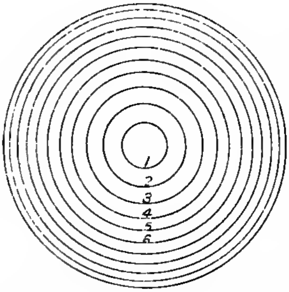

Fig. 121.—Diagram of Isothermals in a Cylindrical Rod while Cooling.

The shape of a casting, quite apart from either the character of the metal or the other circumstances of casting, exerts a considerable influence on the resulting structure, since the shape frequently regulates the manner in which cooling occurs, and thus determines the directions in which the most rapid flow of heat takes place during solidification. Now, it is a universal fact that crystals always grow along the lines of heat flow, the growth taking place in the direction opposite to that of the flow. The reason for this behaviour on the part of the crystals is readily understood when we realise that in a fluid metal whose temperature is at the freezing-point each crystal will continue to grow in all directions until it meets with the growing arms, or "dendrites," from an adjacent crystal. Now consider a mass of cooling metal whose cross-section is circular, represented as the outer circle in the diagram of Fig. 121. In such a mass the centre will be at the highest temperature, and we may draw as isothermal lines—*i.e.*, lines of equal temperature at any moment—the circles 1—2—3—4, Fig. 121, each representing a fall of temperature of—say—5° C. Now take the instant when the outer layer, represented by the outer circle, just reaches the freezing-point. At a number of separate points in this circle, crystal nuclei will spring into being more or less simultaneously, and each will begin to grow outward in all directions. In the direction radially outwards this growth is arrested by the walls of the mould, and parallel to the circumference of the circle the growing arms of adjacent crystals soon meet one another and put a stop to further extension of individual crystals in that direction. Only in the direction radially inwards is there room for unimpeded growth. There the metal is, at any instant, too hot to allow of the formation of fresh nuclei and, as each successive layer cools to the freezing-point, the advancing dendrites of the circle of existing crystals occupy the area.

This process of growth in directions at right-angles to the isothermal surfaces, or contrary to the lines of flow of heat, governs the crystalline arrangement of all castings so far as a fringe around their external boundaries is concerned. The depth of this fringe will depend upon the rate of cooling, since the process, as described above, continues so long as the temperature gradient is steep enough to ensure that the layer which is at any instant at the freezing-point is never thick enough to allow of the formation of any considerable number of fresh crystal nuclei. In castings of moderate thickness this state of affairs usually persists until the whole of the metal is solid, and the casting is seen to consist of crystals growing inwards from the sides. When the casting is thicker, however, a period is reached when the temperature-gradient becomes very slight in the interior of the metal, which is still molten. In these circumstances a large number of independent nuclei spring up in the liquid, and each of these grows in all directions, thus producing a mass of approximately equi-axed crystals. Thick castings, therefore, usually consist of fringes of crystals growing inwards from the outer boundaries of the casting, with a large mass of equi-axed crystals forming the centre or core. An example of this kind, taken from a casting of lead, is shown in Fig. 122, Plate XXVII.

An important feature in the crystalline structure of castings is that which is met with where sharp angles, and, more particularly, re-entrant angles, occur. The arrangement assumed by the crystals in such a case is that illustrated in Fig. 123, Plate XXVII., where we see the two systems of "fringe" crystals meeting at right-angles. Such a structure is known to be weak, and castings frequently crack at such sharp corners. This is often ascribed to the existence at such points, of surfaces where a number of crystal boundaries all lie in one plane. We know, however, that crystal boundaries are not in themselves sources of weakness, but rather the reverse, and the true explanation of weakness at such points must, therefore, be sought elsewhere. Actually, several sets of circumstances conspire to render such re-entrant corners weak. In the first place, if we draw the isothermal surfaces, as sketched in Fig. 124, for such a portion of a casting, we see at once that, close to the corner, the heat conducted into the mould from one of the cooling surfaces which forms one branch of the angle must retard the cooling of the adjacent surface and *vice versâ*; therefore the isothermals must curve inwards towards such a corner. It follows that the metal actually at the corner will, for every successive layer, be the last to solidify. The metal at these points will, therefore, still be liquid when the remainder of the corresponding layers is already solid, and, as these already solid parts tend to contract as they cool, there is an obvious tendency to produce shrinkage cracks at these points where the metal is weakest, because hottest. There is also a tendency for gases and other impurities to be forced into these positions, and thus to assist the other forces in bringing about local injury.

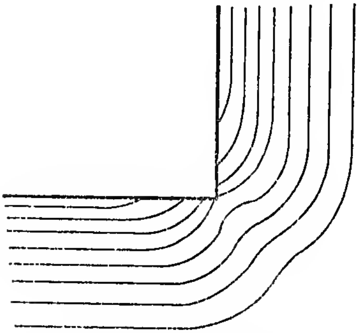

FIG. 124.—Diagram of Isothermals at a Re-entrant Angle in a Cooling Casting.

The simple cases which have been discussed above serve as sufficient examples of the principles which apply to the behaviour of castings during solidification. If we can

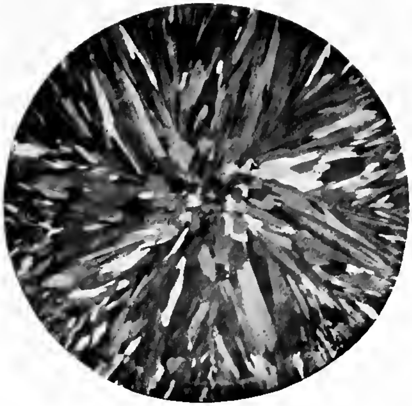

Fig. 122.

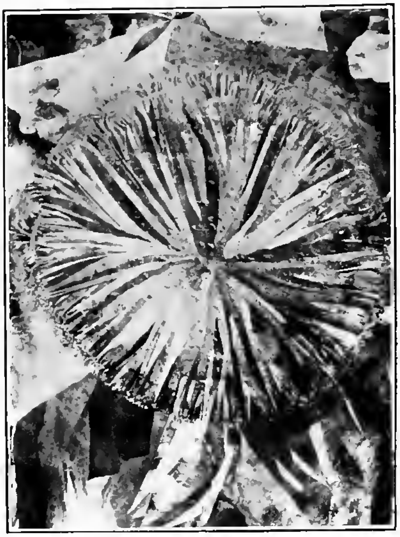

Fig. 125.

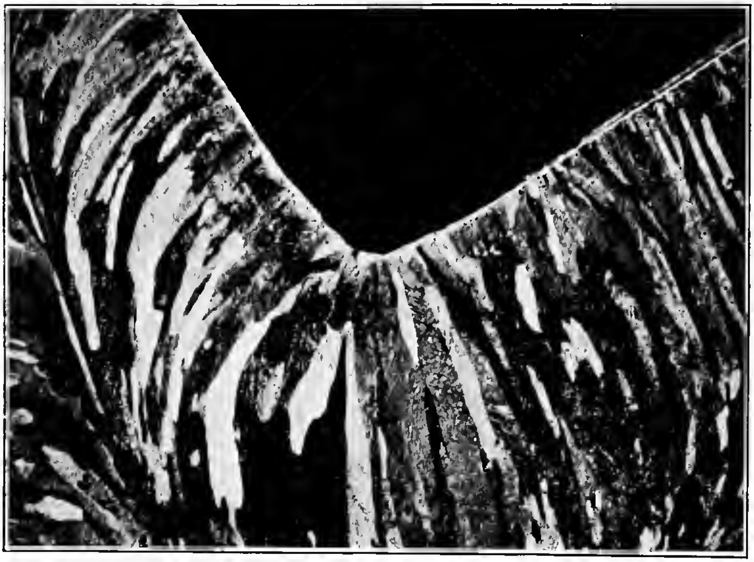

Fig. 123.

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draw the isothermals representing the cooling process—and their general outline can usually be inferred from the shape and conditions of cooling of the casting in each particular case —we know at once the direction in which fringe crystals will grow. The isothermals themselves practically indicate the successive stages of solidification, since the edge of the solidified portion at any moment is necessarily an isothermal—viz., that of the freezing-point. Strictly speaking, the arguments here set forth apply only to the solidification of a pure metal, every portion of which undergoes solidification at one temperature; in practice, however, the majority of alloys behave in a very similar manner. In the case of most solid solutions the freezing-range is short as compared with the temperature gradients met with in solidifying metal. In eutectiferous alloys the comparatively tardy solidification of the eutectic tends to accentuate most of the effects due to unequal cooling and contraction. Incidentally, this method of considering the isothermals of a cooling casting will also enable those interested to work out the effects of special features, such as the insertion of local "chills" in sand moulds or other devices for producing local rapid or slow cooling. It is only necessary to bear in mind that the isothermals are close together where cooling is rapid, and far apart where it is slow, in order to be able to sketch with some accuracy the shape of the isothermals for any given case.

The various points discussed and, in a few instances, illustrated here can be demonstrated in a very simple manner by means of an ordinary piece of good tin-plate having a fairly thick coating of tin. By heating a portion of such a plate over a flame, the tin can be melted, and it will then solidify very much as if it were a section of an ingot; if left to itself crystals of the "fringe" type will grow inwards, giving a structure typical of a small ingot cast in a chill mould. Other types of crystallisation, illustrating the relation between crystal growth and isothermal lines, can be readily produced by local chilling or heating, and the effect on the resulting structure watched. This structure is readily revealed by etching the tin surface with strong hydrochloric acid or some other suitable reagent, the crystals thus revealed being amply large enough to be visible without magnification. An example of the structures produced in this way on tin-plate is given in Fig. 125, Plate XXVII.

The structure and constitution of a casting cannot always be rendered satisfactory, since in large masses of metal the rate of cooling is not under ready control. In the particular case of steel, the structure can be refined by the process of "heat refining" described in the previous chapter, and such treatment has a further advantageous effect in altering the manner in which impurities, notably sulphides and phosphorus, are distributed in steel castings, thin inter-crystalline films becoming coagulated into small and relatively harmless globules. It must be noted, however, that the process of heat refining is almost entirely confined to steel. It is entirely inapplicable to metals or alloys which do not undergo a critical transformation resulting in the crystallisation of a new phase. In the case both of brass and bronzes of certain compositions such critical changes do exist, but their power of producing a refining effect on the structure is smaller than in the corresponding case of steel (2).

In the case of ingots, whose shape is subsequently to be altered by working, the exact character of the internal structure appears to be of less immediate importance than in ordinary castings which are to retain the shape in which they solidified. Yet, even in ingots, for forging or rolling, certain features resulting from the casting and the solidifying process are of great importance. The actual size and arrangement of the crystals, although it does affect the ultimate structure of the wrought material, is of secondary importance, but the mechanical soundness of the ingot is vitally important.

We have already seen that metals, on freezing, are apt to become porous, or to contain cavities of various sizes from two distinct causes, one being the liberation of gases and the other the shrinkage or contraction of the metal. The liberation of gases can be minimised by keeping the temperature of the molten metal as low as possible, but, even then, some gas appears always to be liberated on freezing. On the other hand, the shrinkage of the metal during freezing cannot be prevented, and the only course which can be adopted is either to secure that all the shrinkage shall take effect in one part of the ingot, or in an attached "header" or "riser" from which liquid metal is allowed to run into the mould, thus "feeding" the ingot as it solidifies.

The exact nature of these actions has, perhaps, been most fully studied in steel, partly because the very large ingots which are habitually cast in that metal exhibit these phenomena on a correspondingly large scale. The phenomena occur, however, equally in all alloys. In the case of steel, the question of gases can be largely reduced by allowing the metal to remain in the furnace until it is in perfectly quiet fusion or "dead melted." If this is not done, it implies that the chemical actions of the refining furnace, which lead to the generation of gases, have not been completed, or at least that the gases thus generated have not been allowed time to escape from the metal. It is probable that the action of aluminium in rendering steel "quiet in the mould" consists in stopping these chemical actions; the metallic aluminium reduces any iron oxides still present, and the alumina thus formed is incapable of reacting with the carbon still present in the steel; the generation of carbon monoxide or dioxide is thus at once arrested, and the steel becomes quiet. The aluminium may also exert a purely physical effect in assisting the internal circulation or "feeding" of the ingot; at all events, the net effect is that steel which has been treated in that way forms a perfectly solid ingot so far as small scattered cavities or "blow-holes" are concerned, but, on the other hand, a deep central cavity or "pipe" is formed. When an ingot is subjected to rolling, if it contains numerous small cavities, these are closed up, and at worst appear as fine longitudinal tubes in the finished steel—in many cases the surfaces of such blow-holes are sufficiently clean to become welded together during rolling or forging. In other cases, however, they leave discontinuities in the steel, and these are dangerous in the finished material. On the other hand, the deep central "pipe" of an otherwise solid ingot can never be removed by rolling—nor even covered up—and the steel-maker is reduced to cutting off as scrap the whole of the piped portion of the ingot. The maker of steel ingots is thus placed between two serious difficulties, and many efforts have been made to develop a system whereby ingots could be obtained which, while solid, shall yet be free from any deep pipe. Among these the Whitworth process of "fluid compression," in which the steel is exposed to intense hydraulic pressure during solidification, is well known. Such treatment will undoubtedly close all small shrinkage or gas cavities, and to some extent it also prevents the formation of a pipe as a result of contraction and internal "feeding." It is, however, a very costly process, particularly as regards the plant required. Almost equally costly is the "Harmet" process of ingot compression; in this process the steel is poured into a conical ingot mould whose thinner end is upwards. By means of suitable hydraulic presses, the steel, as it solidifies, is slowly driven upwards into this mould, so that it is slightly "wire-drawn." The result is a compression of the solidified shell of the ingot and a gradual squeezing out of the still liquid core. The resulting ingots are very perfect in every respect, but the cost of the plant and the time occupied make it impossible to use this process except for special work. Recently, Talbot ([3]), has suggested a process in which the compression of the outer solid shell of an ingot, while the interior is still fluid, is accomplished by passing the ingot in this state through the rolls. There is, of course, the obvious risk that the shell may burst and the liquid contents squirted out into the mill. Apart from this, the process appears to be a promising one, although proofs of its practical value on the large scale have yet to be obtained.

Another method for obtaining sound ingots is that described by Hadfield ([4]), in which the upper portion of the ingot-mould is developed into a very small furnace, burning charcoal fuel in a blast of air, thus keeping the top of the ingot very hot and fluid, with the object of providing a "head" of liquid steel from which the interior of the shrinking ingot below may be freely fed.

For the non-ferrous metals such processes have been worked out in a few special cases, but, as a rule, in these industries the ingots are used as they are formed by simple cooling. Owing to the smaller size of the ingots, and the fact that the value of the metal itself is so much higher in comparison with the cost of re-melting it than is the case with steel, the whole question has never attained that degree of importance which it has assumed in the steel industry. A study of the methods of the steel industry in this respect would, however, be of undoubted value to those who have to deal with other metals, and it is unfortunate that the somewhat arbitrary distinction often drawn between "ferrous" and "non-ferrous" metals and their treatment tends to keep the two branches of metallurgy distinctly out of touch with one another in such matters.

Apart from the question of mechanical soundness in an ingot, the casting and solidification processes exert a powerful influence on the character of the final product in regard to the distribution of the constituents and impurities. It may be well to point out here that metallographic examination has fully proved that the changes of form which are imposed upon an ingot by subsequent working are participated in by each small section of the ingot, so that the relative positions of different parts remain as undisturbed as possible in the resulting product—*i.e.*, the metal which formed the core of the ingot forms the core of the finished bar, or rail or forging, and similarly for the skin and intermediate parts. If, therefore, there is a marked difference of composition between different parts of an ingot, there will still be similarly marked differences between the corresponding parts of the finished piece—there is no "mixing" action in the hot or cold working of a metal, except in regard to a certain amount of diffusion, which, however, generally merely affects the minute structural constituents, but not the composition of any considerable regions of metal.

Our insight into the process of solidification is sufficient to explain why and how differences in the chemical composition in different parts of an ingot may arise. The principal factors are that the ingot undergoes solidification in a certain succession, the peripheral and, usually, the lower portions freezing first while the inner and upper portions are still liquid. But solidification occurs in stages or succession, not only in regard to position in the ingot, but also in regard to chemical composition. The materials usually cast in ingots are not pure metals, and, therefore, consist of portions having different freezing-points. Solidification, therefore, begins by the separation of the least fusible constituents—those whose crystals are deposited when the "*liquidus*" of the particular alloy present is first passed. These crystals, as they grow, push before them the more fusible constituents. This separation, however, will be very far from complete, yet a certain definite concentration of the more fusible constituents must and does occur. It follows that the portions of an ingot which solidify first contain an excess of the primary metal, while the last portions to solidify contain a larger proportion of eutectic and other relatively fusible constituents. In this way the phenomenon known as "segregation" is produced. This makes itself very strongly felt in such a complex body as steel, in which relatively fusible impurities are always present; in a comparatively simple metal like brass, on the other hand, where the whole freezing-range is short and fusible impurities are not usually present, segregation is not an important feature. Each material must, however, be considered and examined on its merits in this connection.

The prevention of segregation in alloys where it occurs to a serious extent is always a difficult matter. Rapid cooling, which does not give the materials time to separate appreciably, is one remedy, but this is frequently inapplicable. The surest remedy is the alteration of the composition of the metal in such a way as to lessen the total freezing-range. As a rule this simply amounts to the careful removal of impurities, particularly of those which produce a relatively fusible constituent and thereby increase the total freezing-range of the alloy—since, from this point of view, impurities must be considered as component members of the alloy system in question. In some cases, as, for instance, by the operation of the Harmet press referred to above, it is possible to squeeze out the most fusible and most impure portions of the metal, and in other cases the drastic remedy of severely "cropping" the ingot and thus cutting to waste the most segregated portions of the metal can, and must, be adopted. The difficulty of eliminating segregation and its evils is, however, very considerable, and increases rapidly with increasing size of the masses of metal to be dealt with.

We now pass on to consider some of the mechanical operations by which the ingot is brought into the desired shape or form. These operations may be applied to the metal either while it is hot, and then constitute "hot working," or while it is cold. A mere distinction by temperature, however, is unsatisfactory for this purpose, since a temperature of 400° C. is such as to constitute "hot" working for an aluminium alloy, while it would imply cold working for steel. The real basis for a rational distinction between hot and cold working lies in the effects which the operation produces. We know now that at all temperatures the application of strain—*i.e.*, of forcible changes of shape—results in certain processes within the metal, such as deformation by slip accompanied by more or less movement at the crystal boundaries and a more or less considerable disturbance of the molecular arrangement at all surfaces where displacement has taken place. The vital distinction between hot and cold work, however, lies in the fact that at high temperatures a compensating annealing action is continually taking place, allowing the disturbed molecules to re-assume a crystalline arrangement, and thus constantly tending to re-establish the normal condition of an aggregate of equi-axed crystals in the metal, even while deformation is going on. The rate at which this annealing action takes place will, of course, depend, in a given metal, upon the temperature. At a sufficiently high temperature the rate at which the crystals are re-formed and grow will be as rapid, or even more rapid, than that at which they are disturbed by mechanical deformation. If the working operation is stopped at any instant and the metal is allowed to cool down from such a high temperature, there will be no direct signs of the application of work, *i.e.*, the metal will be completely annealed and will consist of an aggregate of equi-axed crystals. These crystals will be very small compared with those of the original ingot, for example, because the crystals have been deeply disturbed, and those finally present have only been allowed a very short time for their formation and growth, but there will be no signs of distortion and no mechanical hardening effect which could be removed by subsequent annealing.

If now we lower the working temperature, a point will be reached where the rate of annealing is no longer rapid enough to obliterate the effects of progressive deformation or working. If such metal is cooled down, there will be signs of distortion and of strain-hardness. Such metal will be capable of softening by subsequent annealing. In such a case we see the beginnings of "cold work." In the great majority of industrial rolling and forging operations the process of working is continued down to a temperature well below the limit at which this stage is reached, so that all ordinary wrought metals show signs of "cold work" and are more or less strain-hardened. This condition, due to what is known as a "low finishing temperature," is, however, still far removed from the extreme of cold working which is met with in hard-drawn wire or cold-rolled sheets, where very large amounts of deformation have been applied in the cold deliberately with the intention of producing strain-hardening.

The considerations which have just been indicated serve at once as a guide to the nature of forging and rolling operations. At very high temperatures large deformations can be applied without hardening the metal, simply because continuous re-crystallisation undoes the work of straining. On the other hand, this same process of re-crystallisation will set in unchecked the moment that the deforming process is stopped, so that a rapid coarsening of the structure is likely to result, even during the mere gradual cooling of any large mass of metal. For that reason it is generally desirable to continue the working operations until a moderately low temperature is reached. This will result in slight strain-hardening of the metal, but will, at the same time, prevent the growth of coarse crystals. The slight strain-hardening thus introduced is not in any way objectionable, since the apparently raised yield-point or elastic limit which it causes is readily recognised and allowed for when the material is tested—a coarse crystalline structure is a much more serious disadvantage in a material. It should be noticed here, also, that the temperature at which strain-hardening will set in depends upon the rate of deformation to which the metal is subjected. To a given temperature belongs a certain rate of annealing or re-crystallisation; if the amount of deformation applied per second is so large that re-crystallization cannot reorganise the crystal structure before deformation is repeated or continued, then strain-hardening sets in. The influence of the modern rapid methods of rolling and working metal thus generally tend to the introduction of strain-hardening at finishing temperatures which would be amply high enough to leave the metal completely soft if slower methods of working had been employed.

The lower limit of temperature to which ostensible "hot work" can be pushed is thus defined by the amount of strain-hardening which is permissible in a given case. An upper limit also exists. In the first place, the majority of metals cannot be raised above a certain well-defined temperature without "burning" them. We have already referred to this matter in relation to steel, but a similar limitation applies to most metals and alloys—viz., that it is not safe to heat them above the temperature at which the "*solidus*" curve of the constitutional diagram is crossed—and in impure commercial alloys this often lies as much as 100° C. below the temperature of the *solidus* in the pure binary system to which the alloys ostensibly belong. In pure metals the *solidus*, of course, coincides with the *liquidus*, and there is thus no risk of "burning" a really pure metal in the usual sense of the word, although excessive heating will bring about great oxidation—in some metals—and disintegration will follow. Even apart from this, however, all metals become extremely weak and brittle close to their melting-points, so that much lower temperatures should always be adopted for purposes of hot working.

Our existing knowledge of the behaviour of metals under deformation, when applied slowly and quickly respectively, affords some insight into the effect of rapid hot working, as by hammering or rolling, and the slower process of forging in the press. Under the hammer there is a sudden application of stress and, unless the metal is at such a temperature that the viscous resistance at the crystal boundaries is exceptionally low, the deformation will take effect chiefly within the crystals, producing a maximum of slip and a minimum of displacement of the crystals as a whole. With steady, slow deformation as in a press, the reverse is likely to be the case if the metal is in a really soft condition. Rolling occupies a somewhat intermediate position, since the deformation, although rapidly applied, is sometimes applied in very numerous and gently-graded stages. Most industrial rolling processes must, however, be regarded as applying deformation by something much akin to shock. How far the differences in the internal mechanism of deformation affect the resulting structure is not yet known, and it is not a matter upon which we have anything to guide an anticipation. That there are differences between materials forged under a hammer or under a press is well known, but the internal mechanism by which they are set up, once the original deformations have been applied, yet remains to be discovered. The whole subject of the behaviour of metals when deformed at high temperatures has only been taken up quite recently ([5]), so that further important results may well be anticipated from continued research on those lines.

Although we have said above that the annealing action which occurs in hot metals "undoes" the effects of the straining actions of hot working, this is true only with certain limitations, as there are some effects which ordinary annealing does not readily remove. These effects are in reality nothing but internal changes of form, just as the general change of shape is an external change of form. If, for instance, an ingot contains a core of different composition which lies as an ellipsoidal mass in the original ingot, this ellipsoid will be elongated into a rod with slightly tapering ends when the ingot is rolled out into a long bar or rod. Now if this is done at a high temperature, or if the rolled bar is afterwards annealed, although the crystal structure will be restored to that of an equi-axed aggregate, the core of different composition will not be restored to its original position or shape. If now a longitudinal section of such a bar is examined and traces of the elongated rod-like core are found on the section, these traces will be symptoms of the work to which the metal has been subjected. Rightly regarded, however, such a trace of deformation is neither more nor less a trace of working than is the elongated shape of the bar itself.

What we have just said of a single central core or layer of different composition applies necessarily also to a considerable number of distinct layers of different composition, so that ultimately we may expect to find even certain of the micro-constituents arranged in long lines or rods in a piece of metal which has been hot-rolled or forged. In such cases each individual crystal of these constituents is restored to its equi-axed condition by annealing, but ordinary annealing does not, and cannot, undo the longitudinal distribution of the various particles of the different constituents. Such longitudinal distribution must not, in itself, be taken as a sign of "cold work"—the only really sure sign of cold work, *i.e.*, of deformation which can be in a sense "undone" by annealing, is that of elongated individual crystals.

The disposition of the constituents in elongated lines or threads is most frequently met with in duplex alloys, such as mild steel, or in the $\alpha + \beta$ brasses ; in a pure metal there can, of course, be no such disposition of constituents, and the same applies to any simple solid solution. The case of steel is peculiar, since that material, at high temperatures, is a homogeneous solid solution in which two separate constituents do not exist. The hot working of steel is, however, usually continued down to temperatures well below Ar_3, with the result that, during the later part of the operation, the material already has a duplex structure, and the pearlite can and does arrange itself in longitudinal lines, which are not obliterated by ordinary annealing, particularly if the steel is not taken into the γ-iron range. We may thus have, and indeed frequently find, steels in which all traces of cold work have been removed by annealing at moderate temperatures, but in which the pearlite is still arranged in long lines. An example of this kind is seen in Fig. 126, Plate XXVIII., where the etching has been carried far enough to show the outlines of the ferrite crystals whose equi-axed forms indicate the absence of serious strain-hardening.

These longitudinal distributions in rolled materials are not confined to structurally distinct constituents, but may be traced in regard to substances which are present in solid solution, but which were not uniformly disseminated in the original ingot. In the case of steel, phosphorus occurs typically in this way, being present in solid solution in the ferrite of the ingot, but in the form of solid-solution cores, so that the phosphorus content of each crystal increases from its centre to its periphery. When rolled out, these crystal cores assume the form of elongated masses, and, although the ferrite itself undergoes complete re-crystallisation, possibly repeatedly, there is nothing to cause the phosphorus to migrate except the process of diffusion, which is particularly slow in that case. The result is that in the finished material the phosphorus-rich ferrite still remains in long bands or streaks, and these bands pass indifferently through numbers of individual crystals—indeed, an individual crystal may lie partly within and partly outside one of these bands—the growing ferrite crystal has simply used the material it found at hand, whether rich in phosphorus or not. The existence of these bands has been clearly shown by Stead (6), who develops them on the polished surface of steel by the process of heat-tinting. The phosphorus-rich bands do not oxidise at the same rate as the rest of the steel, and the bands appear as regions of different colour. The author and Haughton (7) have recently shown that the same effect may be produced by the electro-chemical deposition of copper from a solution of ferric chloride and hydrochloric acid containing a small amount of copper chloride. This reagent develops the banded structure of steel containing phosphorus in a striking manner, as illustrated in Fig. 127, Plate XXVIII. The striking persistence of these bands, not as a matter of cold working, but as an indication of actual displacement, apart from crystalline structure, is clearly shown by an experiment made by the author. A typically banded steel was subjected to a Brinell ball impression; a section was then cut and polished, and the manner in which the impress of the ball has displaced the bands is clearly seen in Fig. 128, Plate XXVIII. The piece of steel was then very thoroughly annealed, so as to remove all strain-hardness and to allow of complete re-

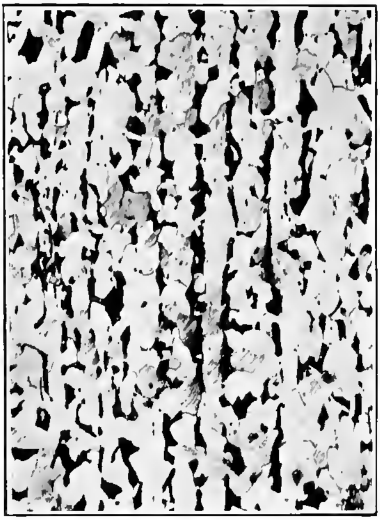

FIG. 126.

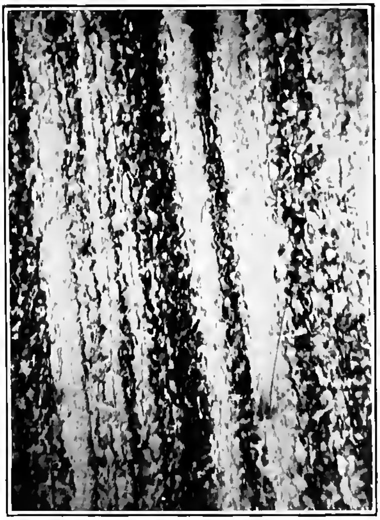

FIG. 127.

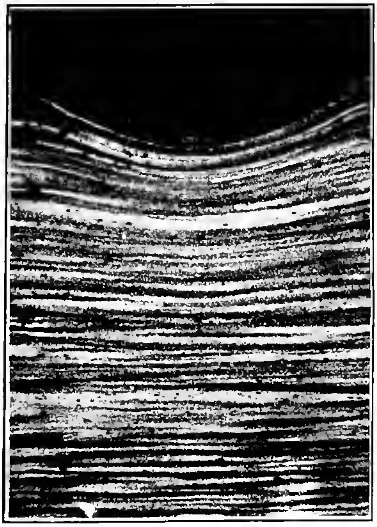

FIG. 128.

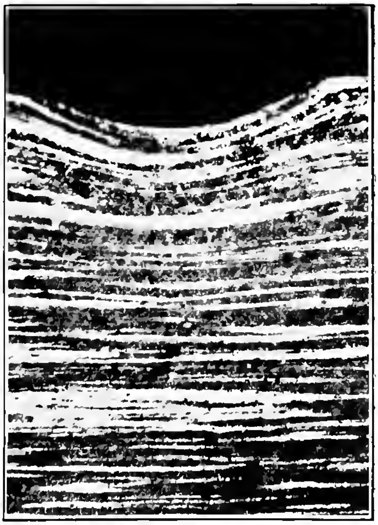

FIG. 129.

[*To face p.* 304.

crystallisation; a second photograph (Fig. 129, Plate XXVIII.) shows the distorted bands still in existence. Such bands can, in fact, only be removed by a sufficiently prolonged heating, allowing diffusion to take place, which would render the distribution of the phosphorus uniform and thus remove the banding completely.

A somewhat striking fact in connection with the hot working of metals, which deserves mention at this point, is the circumstance that while, of course, there are many metals and alloys which do not permit of working, either hot or cold, there are also some which, while readily workable in the cold, are quite brittle when hot, and, therefore, cannot be subjected to hot working.[1] The best-known examples of this kind are the zinc-copper alloys (brasses) which contain less than 30 per cent. of zinc. This fact is the more remarkable since other alloys containing a solid solution of the a type, mainly consisting of copper, are readily worked hot; the aluminium-copper alloys are a good example of this kind. In the zinc-copper series the possibility of hot work again arises as soon as the β solid solution appears in the alloys, in spite of the fact that, in itself. the β body is a much harder material than the a solid solution. This anomalous behaviour of the brasses suggests that there may be a transformation in these alloys occurring at some temperature between that at which they are ductile and that at which they become brittle, which accounts for the change, but there is no thermal evidence for such a change, and no miscroscopic evidence has as yet been obtained. The matter is one, however, which has not been exhaustively investigated, although it is a subject which would well repay careful study. In some cases where alloys which are ductile in the cold prove to be brittle when hot—and such cases are really rare—a transformation is always known to occur which results in the appearance, at high temperatures, of a brittle phase not present at low temperatures. The alloys of nickel, zinc and copper, known as "German silver," also become brittle when hot and are always rolled and drawn in the cold.

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[1] See also p. 145 and footnote.

The general mechanism of cold working has already been considered, both in our general treatment of the plastic deformation of metals in general and in connection with our discussion of the respective meanings of the terms "hot" and "cold" work. But little need be added here. The cold working of the more ductile metals, owing to its convenience and cleanness, and the possibility which it presents of producing finished articles in large numbers by such processes as drawing, stamping, spinning, etc., possesses very great practical importance. Not only is the process employed for the purpose of bringing metals into the desired shape, but the hardening effect of the operation is also relied upon to give to otherwise soft metals the hardness and stiffness requisite for many purposes.

Where the strain-hardness of cold-worked metal is merely required to afford stiffness for small articles, and where—generally—it is not a question of resistance to serious and continued stresses, the utilisation of strain-hardness is perfectly legitimate and rational. In some cases—particularly in the case of cold-drawn wires—the artificially induced strength appears to be more or less permanently reliable, although even there, in the case of wire ropes subjected to repeated bending, fatigue failures occur owing to the circumstance that as regards alternating stresses strain-hardness is of no avail. More serious are those cases where rods of hard-drawn or cold-rolled alloys are employed for such purposes as bolts or in other positions where they are called upon to carry important loads. Practical experience in such cases confirms the conclusions to be drawn from research data, that the extra "strength" due to strain-hardness cannot be safely relied upon for continued resistance, particularly where stresses are alternating or intermittent. The best recent practice shows a strong and highly rational tendency to avoid the use of any material which has been severely cold-worked, unless it has been subsequently annealed in such a way as to remove strain-hardening more or less completely.

The behaviour of various metals and alloys under the action of cold working varies very widely, the amount of plastic deformation which can be safely employed without intermediate annealing depending partly upon the actual ductility of the annealed metal and also upon some other properties which are not yet well understood. It is not always the material which shows the greatest " ductility " under a tensile test, for example, which will " stand " the greatest amount of cold working. The actual size of the crystal structure appears to exert an important influence, extremely small and very large crystals being apparently alike unfavourable to the application of a large amount of cold work.

Excessive cold working makes itself felt in various characteristic ways, according to the shape and nature of the metal object which is being formed. A typical case is that of a rod or wire which is being reduced in diameter and increased in length by " drawing " through a draw-plate. In this process the metal is drawn through a hole, which tapers in the direction of drawing in such a way that the metal is caused to flow as it passes through the hole. In this operation, which is indicated diaggramatically in Fig. 130, the outer skin is not only extended longitudinally, but is at the same time subjected to considerable radial pressure. This pressure serves to " hold up " the outer skin and to enable it to endure a larger amount of deformation than the material could withstand in the absence of such support. When such a rod or wire is too severely treated it follows that fracture takes place in the interior relays, and it usually occurs at the centre where the metal is furthest removed from the supporting effect of the external pressure exerted by the sides of the hole. The result of these internal fractures is that the rod or wire " draws hollow " the internal portions breaking up into short lengths, although the outer skin may remain completely intact, as indicated in the sketch, Fig. 131. Such " over-drawn " or " hollow-drawn " material is, of course, useless and cannot be restored by annealing or by mechanical treatment. Somewhat similar

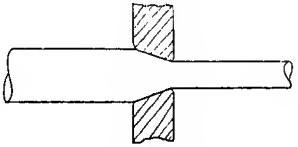

FIG. 130.—Rod passing through a Drawing-die.

although less perfectly defined, effects are also produced when the cold-rolling of sheet metal is pushed too far, the effect in that case generally taking the form of an exfoliation of the sheet, thin layers peeling off or crumbling away. In many cases, however, in the case of sheet metal, cracking at the edges occurs before this stage is reached.

A question which cannot as yet be answered with entire certainty is, whether metals which have been extremely severely strain-hardened as the result of cold work can or do undergo any degree of spontaneous annealing or re-crystallisation in the course of time, even without any elevation of temperature. There can be no doubt that in the case of the softer metals, such as lead, tin, cadmium, etc., spontaneous annealing at the ordinary temperature takes place with considerable rapidity. On the other hand, so far as iron and steel are concerned, the evidence is entirely in the opposite sense; no signs of any spontaneous annealing or re-crystallisation in these metals have ever been observed, and, in view of the fact that definite annealing does not occur in these metals until a temperature of 500° C. is reached, it is hardly to be expected that any notable rate of re-crystallisation or of annealing can exist at the ordinary temperature. In regard to metals and alloys of an intermediate type, the state of affairs is somewhat doubtful. The most important case is that of brass, such as that used for the manufacture of cartridge cases. These, if excessively hardened during the stamping process, and particularly if stored in hot climates, such as that of India, exhibit a tendency to what is known as "season cracking," the brass becoming fissured in a way which suggests that a change of volume, *i.e.*, a contraction, has taken place. This phenomenon is explained by some observers as a result of spontaneous annealing or re-crystallisation taking place slowly in the course of months or even years, and accelerated by the slightly elevated temperature. Such "season cracking" is also met

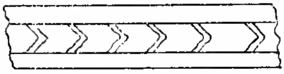

FIG. 131.—Diagram of the Longitudinal Section of Hollow-drawn Rod or Wire.

with in other articles made of cold-worked brass, but very often these are articles which have been placed in positions where a decided rise of temperature has been experienced—as, for instance, in the chains of a gasolier—while similar articles kept in stock in a cool place have remained sound. Cohen (^{8}) accepts the view that spontaneous annealing does occur in extremely strain-hardened brass, and that rapid re-crystallisation can be induced in such metal at the ordinary temperature by "innoculation" with a piece of the same metal in the fully crystalline condition. In some experiments described by that author an etched surface of annealed brass was pressed against the surface of a piece of cold-rolled brass, and local re-crystallisation of the latter resulted at the points of contact. Cohen calls this—somewhat fancifully—the "strain disease" of metals, but his views have not yet attained general acceptance, and the whole matter requires much further investigation. Meanwhile it is well, however, to bear in mind that excessively strain-hardened metals are apt to develop cracks and faults, and that, at best, strain-hardness is not a particularly reliable factor in constructive or other work.

Under the heading of the mechanical treatment of metals, and more especially under that of the "cold working of metals," must be included yet another class of operations which are applied to metals on the most extensive scale, viz., the cutting of metals by means of tools of every description, but usually by what are known as machine tools. The operations of cutting tools have for their purpose the shaping of metal objects, and frequently also the production of a finished surface required for various purposes. In most respects the operations of cutting are matters which concern the engineer who has to deal both with the finished products which are turned out by the machine tools and with these machine tools themselves. The manner in which the tools actually operate on the metal is, however, a question of Physical Metallurgy.

The action of all cutting tools may fairly be described as depending upon the production, over very small areas at a time, of stresses severe enough to produce local failure or breakage—generally by crushing—of the metal which is being worked. In the ordinary type of edge-tool this concentration of stress is brought about by the sharp edge of the tool. This really constitutes a very small area of contact, at any instant, between the tool and the work, and, since the whole pressure of the tool is concentrated on this minute area, the locally-developed stress attains a very high intensity, resulting in local fracture by crushing or shear, or both. That such crushing or shearing action really exists may be demonstrated by preparing a micro-section through the "root" of a cut taken by a machine tool, such as that used in a lathe. This can be done by suddenly withdrawing the tool while in action and then cutting a section through the "root" of the turning which was being removed. A photo-micrograph taken in this way is reproduced in Fig. 132, Plate XXIX., where the deformation of the structure of the steel in the vicinity of the cut can be readily traced.

It is easily understood that the sharper the tool and the lighter the cut, the more completely localised will be the straining effects of the applied stress. If, on the other hand, very heavy "cuts" are taken with heavy tools whose edges are comparatively large in area, very large forces must be applied to the tool and to the work, and a much wider region of disturbed and strained structure will result. Thus, the operations of shearing and punching are really extreme cases of the operative process in all machine-tool cutting, but, owing to the fact that in these operations large masses of metal are removed simultaneously, the applied stresses are not so minutely concentrated, and relatively large regions in the vicinity of the "cut" are seriously strain-hardened. This is the reason why the material in the neighbourhood of punched holes or of sheared edges is always brittle—a circumstance long known to engineers (9). The presence of this strain-hardened material is the more injurious because it exists in the middle of, or at all events closely associated with, the general mass of normal material, while its properties are so materially different that the two cannot act together in resisting stresses, and cracks are liable to be developed in the strain-hardened regions.

In the case of light cuts taken with sharp tools there is little

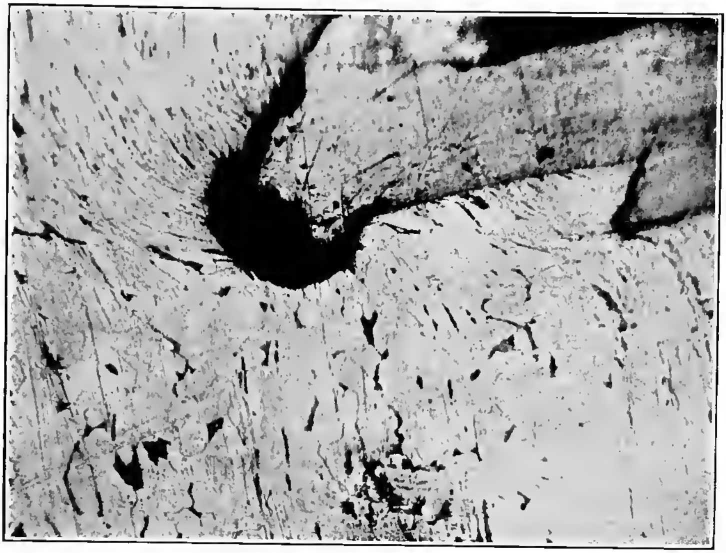

Fig. 132.

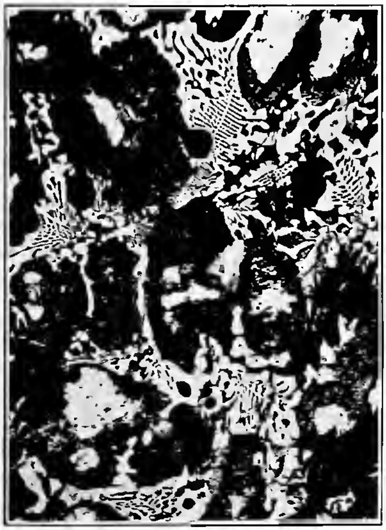

Fig. 133.

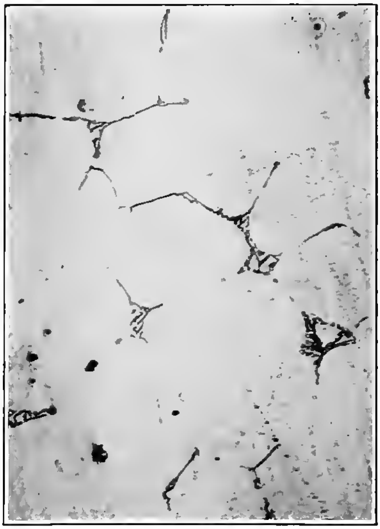

Fig. 134.

[*To face p.* 310.

or no strain-hardening of adjacent layers—or, rather, the strain-hardened layer under the machined surface is extremely thin and its mechanical effects may be neglected. The modern development of high-speed steels, however, has brought about the practice of taking exceedingly heavy cuts at high speeds, and where this is done the thickness of the strain-hardened layer becomes much greater. Whether, even in cases of extreme practice, this layer ever becomes thick enough to be of mechanical importance has yet to be ascertained, but it is well worth noticing that the difference between machining and shearing or punching is one of degree rather than of kind, and that the acceleration of the machining processes tends to make them approximate in their effects to those of shearing and punching. Should the development of high-speed cutting be carried considerably further than is at present the case, this aspect may become a serious one.

The behaviour of various metals and alloys under the action of cutting tools is well known to differ widely ; some materials are easy to machine, a good surface can be produced upon them, and the cutting of screws or other more or less delicate work is readily executed. In other materials, machining is difficult ; smooth surfaces cannot be readily produced, owing to the tendency of the metal to tear up or to clog the tool. "Machinery brass," which usually contains a notable proportion of lead, is an example of an easily machined metal, while pure aluminium and pure copper are both examples of difficult metals. The difference is, in reality, very simply explained by differences in ductility. In an extremely ductile metal the very severe local stresses produced by the edge of the tool are not sufficient at once to cause local fracture by crushing or shear—the soft and ductile metal flows even under this extreme local pressure, and the effect is to clog the tool, which tends to "dig" into the metal or to tear it up in flakes. In order to machine well a metal must possess a certain degree of brittleness, which will allow it to fracture readily and cleanly under the stresses applied by the cutting edge, thus leaving a freely-curling turning to flow away from under the tool. That this explanation is correct may be inferred from the fact that a small addition of an embrittling element immediately improves the machining qualities of an otherwise difficult metal. Ordinary soft brass is rendered slightly brittle, and enormously easier to machine, by the addition of a few per cent. of lead; aluminium is rendered distinctly less ductile by the addition of 15 or 20 per cent. of zinc, but such an addition suffices to convert one of the most difficult metals, from the machining point of view, into one of the best and easiest. Even in the case of mild steel, the normal ductility of the pure, or approximately pure, iron-carbon alloys is too great for easy and rapid machining in automatic machines for the production of screws and bolts, and for that purpose a "special" steel is sometimes employed which is intentionally kept high in phosphorus content; this, by slightly increasing brittleness, greatly improves the behaviour of the steel under the machine tool.

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CHAPTER XIV

DEFECTS AND FAILURES IN METALS AND ALLOYS

In the course of the general survey of the more important aspects of Physical Metallurgy contained in the preceding chapters, frequent opportunities have occurred for referring to injurious results which are liable to follow upon certain forms of treatment, or, rather, of maltreatment of metals. Since the more detailed study of the physics of metals is intended, so far as the practical point of view is concerned, to aid in lessening the liability to defects and failures, this treatment of the subject throughout the present book is obviously justified. On the other hand, there are several important classes of defects whose nature and origin has either not been discussed or has not been dealt with to the extent which their importance justifies, so that a summary of the whole subject from this point of view is required.

Throughout our treatment of the constitution and structure of alloys we have intentionally confined our attention to the pure alloys, and have, for the sake of simplicity, left impurities out of consideration entirely. In practice, however, impurities are of very great importance, since the art of the metallurgist who is concerned with the purification of metals is not sufficiently advanced to afford a commercial supply of really "pure" metals, although the materials at present available are far superior to those which had to be employed some twenty years ago. Curiously enough, it seems that this increase in the purity of metals, employed either as such or in alloys, has not proved an entirely unmixed blessing; in certain industries difficulties have arisen which are commonly ascribed to the "excessive" purity of the modern metal. There may be a sound basis for such a view in some cases, but this simply means that the material formerly employed was really an "alloy," *i.e.*, that the particular impurity present exerted a avourable influence on the resulting metal, and that the purer metal from which this alloying influence is removed has ceased to be equally satisfactory. In such cases the difficulty can generally be overcome by seeking the exact nature of the difference between the modern and the old " pure " metal and making a suitable alloying addition, if that be found necessary.

In general, however, the term " impurity " is employed to denote a chemically " foreign " element which may be present in a metal or an alloy, and which exerts a more or less injurious influence on the resulting material. Such impurities may be either metallic or non-metallic elements present as such, or they may be compounds. The nature of their action depends upon whether they exist in one or other of the three possible states, viz. :—

(*a*) As solid solutions ;
(*b*) As separate constituents crystallising from the metal or alloy ; or
(*c*) As mechanical enclosures or suspensions.

In the case of the two former classes of substances, which are generally other metals or metalloid bodies (such as phosphorus, silicon, etc.), the impurities are in reality additional constituents of the alloys, and their effects are of the same nature as those of the intentionally added elements—they really make the material an alloy of a more complex order, whose constitution and properties require careful investigation. Within the limits in which they occur in practice the effects of such impurities are in most cases well known, and, although there may well be considerable differences of opinion as to the proportions of various impurities which are admissible in materials required for specific purposes, there is general agreement that a definite limit to the allowable proportions should be set. In some instances this is accomplished by the specification of certain mechanical properties in the final material, while in other cases direct chemical analysis is required. There seems to be little doubt that the latter is much the safer course, and in those cases where the imposition of a chemical analysis in a specification has been shirked this is probably due to the influence of manufacturers who find it difficult to maintain the standard of purity which analytical results would demand. Mechanical tests depend upon many factors besides the chemical composition in regard to impurities, and direct determination of every important factor is surely the only sound plan.

To enumerate the various impurities which are ordinarily met with in the whole range of industrial materials would be impossible in this book, so that reference will only be made to a few typical cases. Of impurities which exist in a state of solid solution, in iron and steel, phosphorus and silicon are the most typical examples. The injurious influence of phosphorus on mild steel is well recognised, and specifications demand that the proportions present shall not exceed a limit which is fixed in the case of the most important class of articles, such as axles, tyres, springs, etc., at the low figure of 0·035 per cent., while for steel rails as much as 0·080 per cent., and in some cases even 0·10 per cent., is allowed. It would be difficult to believe that such a small proportion of phosphorus, if uniformly disseminated in a state of solid solution in the ferrite of a mild steel, could produce any seriously injurious effect. Two factors must, however, be borne in mind. In the first place the phosphorus is present, not as free phosphorus, but as iron phosphide, Fe_3P, so that every 0·10 per cent. of phosphorus involves the presence in the steel of 0·48 per cent. of iron phosphide. Further, this iron phosphide is not uniformly disseminated throughout the steel. When the solid solution first crystallises from fusion the typical process of core-formation takes place, and the phosphorus is concentrated in the peripheral parts of the first large crystals which are formed. As has already been pointed out, when such material is rolled or forged, these phosphoric portions are elongated and the phosphorus retains this distribution, thus forming the typical banded structure which has already been illustrated (see Fig. 127, Plate XXVIII.). This condition implies that the phosphorus concentration in certain portions of the steel may be from four up to as much as ten or twelve times as great as that indicated by the average value furnished by analysis, and it is these higher local concentrations which lead to failure under test or in service.

In the non-ferrous metals, impurities which exist in solid solution are not frequently met with, although in copper there is reason to believe that a small proportion of arsenic remains in that condition. Opinions as to the value, or otherwise, of arsenic in copper are very much divided; some English metallurgists claim great advantages for arsenical copper, and require an arsenic content of not less than 0·35 per cent. in such materials as copper for fire-box plates in locomotives, etc. Others in this country, and the majority of foreign metallurgists, regard the presence of arsenic as definitely undesirable and prefer the use of pure copper. It is fairly evident, however, that arsenic in copper cannot be regarded with anything like the suspicion which rightly attaches to phosphorus in steel.

Impurities which separate from solution in the molten alloys and form distinct micrographic constituents are a much more numerous class, particularly in the non-ferrous metals. In iron and steel they are found only in cast-iron, where the iron-phosphide eutectic is an important example of this type of impurity. This constituent is characteristic of practically all varieties of cast-iron, where it is seen generally in the form of a granular eutectic differing slightly in colour from the pearlite with which it is often associated. An example is shown in Fig. 133, Plate XXIX. At times difficulty may be experienced in distinguishing between granular pearlite and the phosphide eutectic; in such cases heat-tinting at once shows the difference very clearly.

In the non-ferrous metals, impurities of this kind are met with in almost every kind of alloy. Typical examples are the compounds of iron and of silicon which occur in this way in even the purest of commercial aluminium. An example of these is shown in Fig. 134, Plate XXIX. In the case of copper, cuprous oxide is soluble in molten copper and forms a well-marked eutectic on freezing. The most injurious forms of impurity are frequently to be found in this class, owing to the tendency which often exists for such separate constituents to assume the form of thin brittle walls or membranes surrounding the crystals of the primary metal or alloy. The case of bismuth and gold has already been mentioned (p. 256), while bismuth or antimony in copper produce a similar effect. Cuprous oxide, on the other hand, does not tend to form membranes, and is consequently harmless if not present in undue proportion—in fact, in ordinary commercial copper the presence of a certain proportion of copper oxide is found essential to the good quality of the metal.

The class of impurities just discussed—*i.e.*, those which dissolve in the molten metal, but separate as micro-constituents on freezing—shade off, owing to the incompleteness of our knowledge, into the remaining class, viz., those which are present in mechanical suspension both in the liquid and the solid state. The so-called " slag enclosures " of steel (sulphides and silicates, principally of manganese) are of this kind, and so are the majority of metallic oxides and other compounds (other than inter-metallic) present in metals. In many cases it is impossible to state definitely at the present time whether these materials possess any real solubility in the molten metals within the range of ordinary working temperatures. Yet the point is of considerable importance, since if these impurities are always present in mechanical suspension, it should be possible to secure their removal by some process of mechanical separation, the simplest of which is that of allowing them to float to the top or settle to the bottom of the molten metal, according to the relative densities of the metals and the impurities. In the case of steel, the separation of " slag enclosures " by this method has been successfully tried, but it entails serious cost, and is, in practice, only effected in the case of steels kept in quiet fusion in an electric furnace.

The mode of origin of the enclosures of steel (1) is of some interest, as it is typical of that of the enclosures in other alloys. Steel as it ordinarily leaves the open-hearth furnace or the converter contains both iron oxide and iron sulphide, either in solution or in suspension. Both these are extremely injurious ingredients, and a reducing agent—ferro-manganese—is generally added to the steel in the final stages in order to remove these substances. The result is the formation of manganese sulphide or, more probably, of a mutual solution of manganese and iron sulphides, and also manganese oxide, which either takes up silica from the slag or the refractory lining, or combines with silicon, which may be present in the steel, to form manganese silicate. If time is allowed, the globules of manganese sulphide and silicate rise to the top and join the slag to which they properly belong, but the finer particles only rise very slowly, and a great number remain entangled in the steel. Opinions still differ considerably as to the effect which these enclosures produce on the mechanical properties of steel, but in the author's experience a large number of cases of failure in service have been directly traceable to the influence of these enclosures. They are particularly harmful in steel which is to be subjected to quenching operations, as hardening-cracks frequently start from the larger enclosures. Typical examples of such enclosures, taken from cases where failure has been traced to their influence, are shown in Figs. 136 and 136, Plate XXX.

The distribution of sulphide enclosures in steel is readily studied by means of a process developed by Baumann (^{2}) from an earlier process of Heyn (^{3}). This is known as "sulphur printing" and simply consists in pressing against a roughly polished surface of the steel in question a sheet of silver bromide paper such as that used for photographic purposes. This paper is previously soaked in a ten per cent. solution of sulphuric acid in water and the steel is thus exposed to the action of the dilute acid held in the damp paper. Under the action of this acid every particle of sulphide which is exposed in the surface of the steel is attacked and minute streams of hydrogen sulphide issue from every such particle. The hydrogen sulphide thus evolved acts upon the silver bromide, producing a dark speck of silver sulphide opposite every particle of sulphide present in the steel surface, and a direct contact print, generally known as a "sulphur print" is thus obtained which clearly indicates the distribution of sulphur in the steel. Since the various impurities of steel generally segregate more or less together, the appearance of a sulphur print serves as a guide to the presence or absence of general segregation in the steel as well as to the distribution of sulphur itself.

In non-ferrous metals the conditions with regard to suspended impurities are somewhat different. Alloys such as brass or

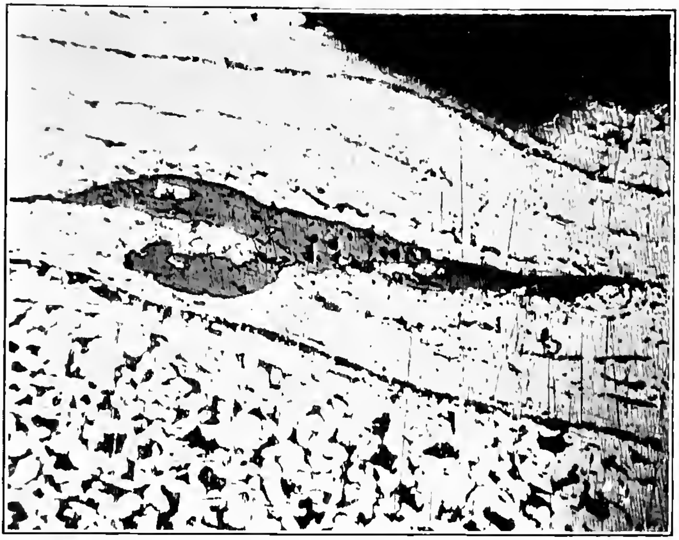

FIG. 135.

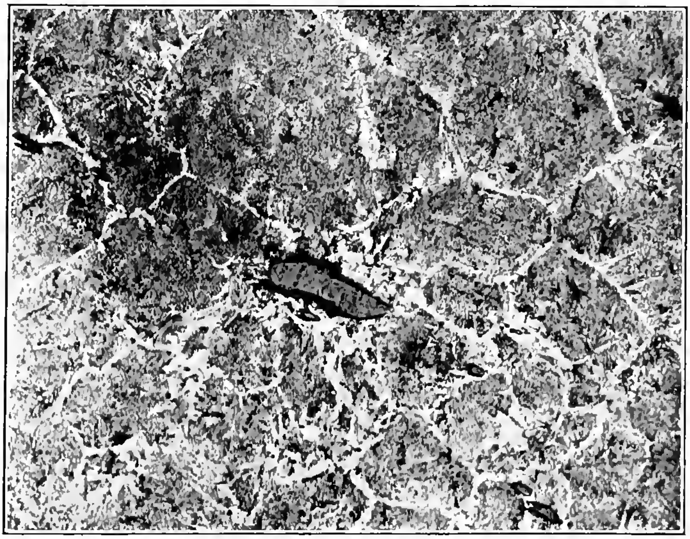

FIG. 136.

[*To face p.* 318.

bronze are not, in modern practice, prepared by any process of direct refining, such as that employed in the case of steel—the production of non-ferrous alloys is analogous rather to the production of high-class steel in crucibles in which pure materials are melted together in the desired proportions, and little or no opportunity for the formation of enclosures on any considerable scale can occur. Slag enclosures comparable to those found in steel are, therefore, unknown in non-ferrrous alloys. The presence of oxides, always in fine particles or crystals, and sometimes in an exceedingly fine state of division, is, however, a common feature of many alloys. The presence of zinc oxide in brass, and of oxide of tin in bronze (^{4}), is known to render these metals " thick," so that they do not run freely when poured into a mould. This is due to the fact that the oxides which are present in a state of very fine division show no tendency to rise to the surface or to flux off with materials derived from the crucible or protective slag. Their removal can, however, be effected by the introduction of some reducing agent whose oxide is fusible, so that it will agglomerate into globules large enough to float to the surface. In regard to alloys of copper this question has already been discussed in Chapter VII., pp. 152, 153.

Finally, before leaving the subject of impurities not dissolved in the alloy, mention must be made of " accidental " impurities which are sometimes found. Thus the writer has in his possession a rod of drawn brass in the centre of which an ordinary three-cornered steel file lies securely embedded. More serious, because more frequent, are the impurities arising from the attempted introduction into an alloy of substances which are either incapable of entering into the metal at all or have not been given long enough time or high enough temperature to pass into solution. Sometimes such " additions " simply fall to the bottom of the crucible and spoil the lower part of the melt, but at other times they become disseminated through the mass and affect it injuriously. Such cases generally occur when attempts are made to introduce into ordinary alloys any of the rarer or more refractory metals. The danger of such an occurrence can, however, be guarded against if the principle is adhered to that in preparing an alloy in its final condition materials of very widely different melting-points should never be directly melted together. In such cases it is most desirable to prepare intermediate " rich " alloys whose melting-points approximate to one another, and, by mixing these according to simple calculations based on the composition of each, to reach the desired final composition.

The defects of metals and alloys so far considered, viz., those arising from the presence of "impurities," form one class of a still wider group which embraces all defects whose nature is that of an error of chemical composition, either local or general. If the general average composition of an alloy is wrong, this can hardly be described as a defect, since we are then in reality dealing with a totally different alloy. Yet such errors of composition are by no means unknown, and, apart from actual errors of mixing, they are apt to occur to a greater or less degree in consequence of actions to which alloys are exposed during manufacture. Thus, during melting, losses of certain metals may occur either by direct volatilisation or by oxidation, or by both. The loss of zinc from brass at every melting is a well-known example, while the elimination of carbon from steel, both during oxidising melting and annealing, is well known.

Much more frequent than serious errors in general average composition, are local differences of composition from one portion of the mass to another, particularly in ingots and in the wrought products derived from them. The origin of these differences has already been considered, particularly in regard to steel, in our discussion of the solidification of an ingot and of castings in general. In non-ferrous alloys segregation may occur in a totally different manner, viz., by the separation of a constituent which appears at a relatively high temperature in the form of isolated crystals or dendrites. These, if either much denser or much lighter than the mother-liquor in which they are formed, show a strong tendency either to sink or to float to the top. The separation of graphite from molten carburised iron in the form of " kish " is a well-known example of the latter kind, which is paralleled in non-ferrous materials by the tendency of the crystals of the antimony-tin compound present in certain white bearing metals to rise to the top when solidification begins. In certain lead alloys, on the other hand, the primary crystallites of lead fall rapidly downwards through the mother-liquor, forming a layer of almost pure lead at the bottom of any slowly-cooled ingot. In some aluminium alloys also, where relatively heavy crystalline compounds of aluminium with the alloying metal are formed, such segregation takes place. In these cases the only method of prevention lies in chilling the molten metal so as to bring about rapid solidification; there is then no time for such gravity-separation to occur.

The sources of defects in metals which have been discussed in the preceding pages may be grouped together as being "congenital," in the sense that they are present in the molten metal before its first solidification and cannot be removed by subsequent treatment—in many cases not even by simple re-melting. The majority of other causes of defects, such as those due to errors in thermal or mechanical treatment, may be grouped together as "acquired," since they are not inherent in the metal. These can always be remedied by re-melting, and in many cases even by less drastic processes.

In the course of the discussion, in the preceding chapters, of some of the principal processes to which metals are subjected we have had frequent occasion to refer to the results which follow on the more important errors of treatment; consequently, any detailed discussion of these causes of defects is hardly required here. In order, however, to afford the reader some rather more systematic insight into the sources of defects in metals, an attempt has been made to tabulate these. This tabulation does not claim to be exhaustive; the field of Physical Metallurgy is so large that it is impossible for any one person to be completely acquainted with the details of all the materials and processes involved, and such an acquaintance would be required in order to draw up a thoroughly exhaustive tabulation of this kind. In some cases, therefore, it may well be found that particular sources of defects which arise in some particular material or process are not indicated in the table or are included in a somewhat vague general group. All the more important causes of defects are, however, at least represented in the table. Where the previous treatment of the subject referred to in any particular section of the table does not appear to be sufficient to explain the nature of the actions referred to, explanatory remarks have been incorporated in the table itself, while in other cases references have been made to actual examples which serve as typical illustrations of the more striking types of defects. In other cases, references to the pages of this book in which the matter has already been dealt with are given. The table may thus serve as a special index to the whole subject of defects in metals in so far as these have been dealt with in the present work.

TABULATION OF THE CAUSES OF DEFECTS AND FAILURES IN METALS.

I.—CHEMICAL COMPOSITION.

Errors in chemical composition may arise either from errors in the original mixture or from actions occurring during melting.

(1) Larger errors in chemical composition may lead to :—
(*a*) Unsuitable mechanical properties. This really amounts to the use of a wrong material for a given purpose.
(*b*) Too low a softening or melting temperature, a defect which only makes itself felt in cases where the metal is exposed to high temperatures or in special circumstances.
(*c*) Undue corrodibility (see pp. 328—333).

(2) Smaller errors of chemical composition may lead to :—
(*d*) The formation of brittle impurities which may be—
  (i.) Suspended or mechanically enclosed (see p. 318).
  (ii.) Structurally formed, sometimes as brittle inter-crystalline envelopes (see p. 256).
(*e*) Variations in critical temperatures leading to subsequent abnormal behaviour under thermal or mechanical treatment. This type of defect applies particularly to the class of "special" or alloy steels.

II.—TREATMENT.

(A) *Casting.*

(*a*) Overheating the molten metal, leading to change of chemical composition either by loss through volatilisation, oxidation or reaction with the containing vessel, etc. Absorption of gases, with subsequent liberation during freezing, may also result.

PLATE XXXI.

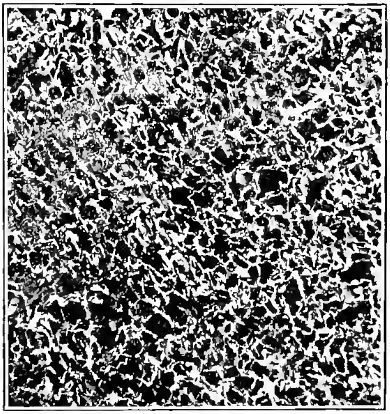

FIG. 137.

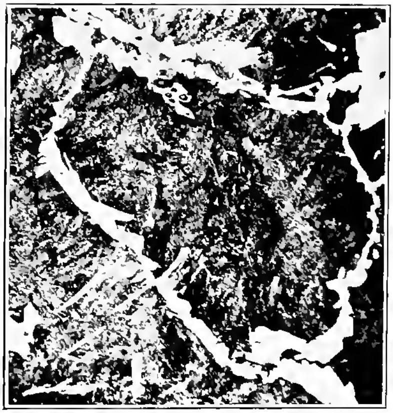

FIG. 138.

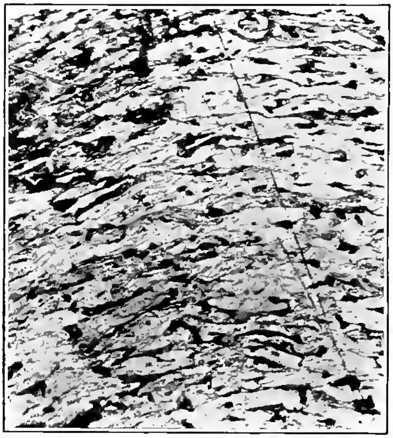

FIG. 139.

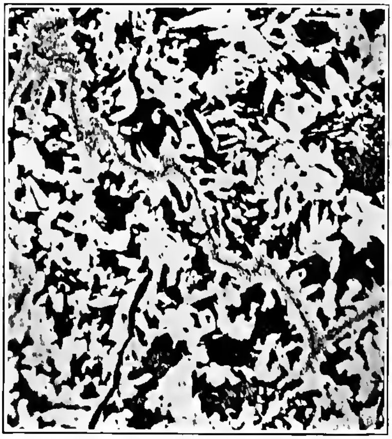

FIG. 140.

[*To face p* 323.

(*b*) Excessively high casting temperature, leading to unduly slow cooling, coarse structure and liability to segregation (see p. 287).

(*c*) Too low a casting temperature, leading to incomplete filling of the mould, " cold shuts " and similar defects.

(*d*) Inadequate cleaning or skimming of the molten metal, leading to the admixture of slag or dross.

(*e*) Admixture of foreign matter from the mould, such as particles of sand, gas bubbles, etc. These defects are due to bad moulds, insufficient drying, inadequate " venting," or to unduly vigorous pouring of the metal resulting in the disintegration of the surface of the mould. The correct design of the pattern to suit the metal employed also plays a part in this connection.

(*f*) Errors in the design of the pattern or the mould leading to " drawing," unsoundness and shrinkage cracks (see p. 292). Here, again, the adaptation of the pattern to the nature and peculiarities of the metal employed plays an important part, since patterns which can be readily cast in one metal sometimes yield unsatisfactory castings with other metals.

(*g*) In ingots the corresponding causes operate to produce piping, blow-holes and segregation (see pp. 295—297).

(B) *Hot Working.*

(Forging, pressing, rolling, hot-stamping, etc.)

(*a*) Commencing at too high a temperature. The metal is then too weak and brittle, and the formation of cracks and fissures results; these are sometimes partially closed or covered over by subsequent operations, but reveal their presence when fracture occurs.

(*b*) Finishing at too low a temperature. This results in more or less severe strain-hardening, which may or may not be objectionable (see pp. 299—301).

(*c*) Excessively rapid deformation or " reduction." This may lead to cracking of the metal.

(*d*) Too gradual an application of work. It is not certain whether this leads to ultimate defects, but in modern industrial practice it is not likely to occur, since the tendency is to accelerate all operations to the utmost limit.

(*e*) Insufficient total amount of " work " or reduction. This is apt to result from a desire to effect economy by the use of an ingot which requires less forging to bring it into the desired final shape. This results in a merely superficial working of the metal, leaving the interior very coarse and weak. A typical case is illustrated in Figs. 137 and 138, Plate XXXI., which show the microstructure of the outer shell and of the interior portions of a large steel shaftwhich failed in service. Had the coarse internal structure been due to over-heating it would have extended to the surface and signs of serious decarburisation (see p. 325 (c), below) would have been found.

(*f*) Defects arising from mechanical causes during hot working, leading to such features as "laps," "rokes," etc., which result from the partial welding up of fissures or of portions of metal which have become accidentally overlapped. These defects should be detected by inspection before the metal is taken into use.

(*g*) Defects due to working into the surface of the metal of scale or other matter left on the surface during rolling or forging. While it is comparatively easy to brush away scale, etc., from the upper surface of metal passing through rolls or under the press, scale may adhere to the under side, which is not in view, and this may become rolled or pressed into the surface.

(C) *Cold Working.*

The operations of cold working may produce defects by being :—

(*a*) Too violent. The use of either too high a speed or of too great an amount of reduction, either at any one pass or by a number of successive passes applied without intermediate annealing, may be grouped together as unduly "violent" cold work. The resulting defects are either cracks on the surface or at the edges in the case of sheet metals, or in the case of rods or wires they take the form of "hollow drawing." Sometimes an alloy is employed for cold working which is really unsuited to the process, such as a brass containing any considerable quantity of lead. If such a material is cold-drawn or rolled only very minute cracks are formed, not visible at the surface, but readily detected in other ways. As a general rule it may be stated that cold working may be continued, without *permanent* damage to the metal, so long as the tensile strength continues to rise.

(*b*) Too slight. This is not only a cause of defect in those cases where the additional stiffness due to strain-hardening is relied upon (see p. 300), but may cause excessive superficial hardening and severe internal stresses.

(*c*) Unequal, portions of the same piece of metal being much more severely treated than others. This leads to a state of severe internal tension, and may lead to the development of "season cracks" (see p. 308), or it may cause the metal to crack on annealing, owing to the unequal rates of re-crystallization in the differently strained portions.

(*d*) Unintentional, inadvertent or accidental cold working. This very frequently occurs in the fitting and erection of engineering objects, such as large boilers, bridges, roofs and other structures. Where things do not fit sufficiently well, they are "set" by forcible means until a fit is obtained. In other cases, minor irregularities of shape or surface are abolished by such processes as "hammer dressing." While such processes are employed, as a rule, in good faith and in complete reliance on the known ductility of the material in question, the result is often a highly dangerous condition of severe local cold-working and consequent strain-hardening. The dangerous nature of such defects arises from the inability of the material at those points to withstand further deformation or working to which it may be subjected, and its inability to co-operate with the ductile material around it. A striking example is illustrated in Fig. 139, Plate XXXI., which represents the structure of a locally severely strain-hardened portion of a steel plate which formed the domed end of a vessel which exploded disastrously under steam pressure. The fracture took place at the point where the severely strain-hardened steel joined the surrounding ductile material. The local strain-hardening in this case was due to an unduly severe "fitting" operation in the workshop. The ill effects of local strain-hardening also occur in connection with such operations as punching and shearing (see p. 310).

(D) *Thermal Treatment.*

Annealing or *Re-heating* may cause defects owing to being carried out—

(*a*) At too high a temperature, leading to—

  (1) "Burning," and
  (2) "Overheating."

An example of "burning" in steel is shown in Fig. 140, Plate XXXI., which represents the structure of a portion of a steel shaft which had been "burnt," the typical enclosure of oxide at the boundaries of large grains or cells being well marked. An overheated structure taken from a steel forging which failed in service is shown in Fig. 120, Plate XXVI.

(*b*) For too prolonged a period, even at a moderate temperature. This treatment tends to cause an aggregation or "balling up" of some of the most important micro-constituents, and especially of eutectoid bodies such as the pearlite of mild steel. A case of failure resulting from such treatment is illustrated in Fig. 115, Plate XXV., which refers to a boiler plate which developed typically inter-crystalline cracks. When etched with sodium picrate, which stains cementite black, this steel is seen to contain little or no pearlite, the cementite having become "balled up" into inter-crystalline masses. These appear as dark filaments in Fig. 119, Plate XXVI.

(*c*) In an injurious atmosphere. Copper is injured by "gassing," *i.e.*, by exposure at high temperatures to a reducing atmosphere (see p. 272). In other metals an oxidising atmosphere is frequently injurious, the oxidation and decarburisation of steel being well known.

Quenching may cause defects if it is carried out—

(*a*) From too high a temperature. This results, in the case of steel, in the development of a coarse martensitic structure with which much brittleness is associated. Too high a quenching temperature also involves considerable risk of cracking and warping.

(*b*) From too low a temperature. In that case the entire operation fails to attain its object, and the metal remains soft or otherwise unaltered.

(*c*) Unequally, so that the rate of cooling is different for different parts of the same object. This generally results in serious warping. Even such large objects as heavy guns are quenched by vertical immersion in a deep oil-bath in order to avoid cooling one side before the other.

(*d*) In an unsuitable bath. The quenching effect depends upon the cooling power of the liquid as well as upon the temperature of quenching, although the most powerfully cooling liquid cannot compensate for too low a quenching temperature. In a liquid, high specific heat, low viscosity and low vapour pressure tend towards great cooling power. Water is therefore particularly powerful, while mercury, in spite of a higher thermal conductivity, is far less effective.

Tempering may lead to defects if carried out—

(*a*) At too high a temperature. The result is to remove the effects of quenching too completely.

(*b*) At too low a temperature, whereby the effects of quenching are insufficiently removed, and the metal (in the case of steel) remains too brittle for its purpose.

(*c*) Unequally. This rarely occurs in small objects, such as tools. Where, however, large masses of steel are subjected to special heat treatment by quenching followed by tempering, the attainment of a uniform condition throughout the mass is of the highest importance, particularly if the object is a gun or an armour plate or a part of a motor-car or aeroplane subjected to severe shocks. Want of uniformity in such cases leads to a concentration of stresses with resulting failure.

The ills to which metals are heir, which have been very briefly discussed and illustrated in connection with the above tabulation, do not by any means constitute a complete list of the causes of failure in metal objects employed in engineering construction, and brief mention of some of the other factors should be made here. The causes of failure, which have been treated above as fully as the introductory character of this work will permit, all reside in the metal itself or in the treatment which it has received during manufacture. At one point only (under II. (C), (*d*)) have we referred to a class of defects due rather to the abuse of the material by the constructor than to the production of the metal itself. There are, however, numerous other cases in which " abuse " of the material may fairly be put down as the cause of failure. The use of a wrong material or insistence on a wrongly-drawn specification may equally be regarded as abuse of the metal; errors of design and of construction come under the same head, and these constitute the most difficult cases which have to be dealt with in the investigation, by the methods of Physical Metallurgy, of cases of failure in practice. The investigator can in such cases only endeavour to exhaust the possibilities with regard to defects in the metal itself, in order to show that the fault must lie elsewhere.

Another class of failure in metals arises from want of permanence of the material under the conditions to which it is exposed. We have already considered such matters as the gradual breakdown of metals under " fatigue " or alternating stresses which exceed the true elastic limits. Another type of gradual disintegrating use is that where the metal is subjected to abrasion. Such objects as the rails and tyres of a railway, the bearings of engines, etc., constitute examples of this class; the conditions of wear existing in such circumstances are, however, fully recognised in engineering practice, and " failure " is only regarded as arising where the rate of wear has been unduly rapid.

Far more serious and difficult in every way is another type of " wear " to which many metals are subjected, viz., the whole class of actions known as " corrosion." This subject is so large that it requires treatment in a separate volume, but a brief reference to it is required here.

Since we find practically all the industrially useful metals in nature in the state of their oxides, or compounds of their oxides or sulphides, it is not surprising to find that there is a strong tendency, which requires to be constantly guarded against, for all metals when in contact with the agents of nature, viz., oxygen, water and carbon dioxide, to revert to their condition of chemically stable equilibrium and, therefore, to undergo one or other of the processes of corrosion, all of which tend to the formation of oxides or of salts. The metallic state, in the conditions which prevail at the surface of the earth, is for the majority of metals a state of chemical meta-stability, and there is room for astonishment that we should be able to defeat the action of the atmosphere to such an extent as to maintain in prolonged existence the great quantities of metal on which modern engineering depends. The general "cause" of corrosion, therefore, is not far to seek, but in regard to its immediate mechanism and the detailed conditions which govern its incidence and rate of progress, a great deal of study has been expended, although definite and finally conclusive results have only rarely been reached.

The possibility of the continued existence of oxidisable metals in the metallic state depends upon that universal property of "inertia" which manifests itself in a reluctance to undergo any change, and more particularly in the reluctance with which the commencement of any change is initiated. In many cases, therefore, the study of the "causes" of corrosion resolves itself into a study of the special conditions which facilitate the commencement of chemical action between the metal and the natural agencies to which it is more or less exposed. In most questions of corrosion two different views may be taken, which are typified by the two schools of thought in regard to the corrosion of iron and steel. One of these schools, headed by Cushman (5) and Walker (6) of America, takes the view that the corrosion of iron and steel is essentially an electrolytic process, the source of the electrolytic action lying in the minute galvanic cells which are formed by the impurities present in the steel. This school, therefore, seeks to render iron and steel more or less incorrodible by making it as pure as possible, and there seems to be some evidence that extremely pure iron possesses very great "inertia" in regard to corrosion. Opposed to this view is the purely chemical theory, according to which iron undergoes direct oxidation in the presence of water, without the necessary intervention of any electrolytic action. In support of this view are the experiments of J. N. Friend (7) and the work of Heyn (8), who have shown that, although the absence of electrolytic cells in a very pure steel does retard the *commencement* of corrosion, it does not affect the rate of corrosion once the process has begun.

Whichever of these rival views should ultimately prove correct, the prospect of producing a cheap form of iron or steel which shall be practically incorrodible is extremely remote. The ancient iron of India and Ceylon is sometimes quoted as an example of practically incorrodible metal, but the permanence of the Delhi column and of the iron chains fastened, thousands of years ago, on the steep pilgrim's paths on Adam's Peak in Ceylon, must be due to some special cause, since samples of this iron, which have come into the author's hands, have rusted freely on the surfaces exposed by cutting them up. The inference is that these irons are not really incorrodible, but were originally covered with a really effective protective coating. Although a definite proof has not been given so far, it seems probable, from the author's observations, that this protective coating was simply a coating of cinder or slag derived from the crude manufacturing process employed (9). In any case it is evident that, even if the purest possible iron really proved to be incorrodible, its use would be limited by its softness and weakness as compared with the better grades of steel.

The principal question of practical importance in regard to the prevention of corrosion in iron and steel thus resolves itself into a question of finding a suitable protective coating which shall effectively protect the metal from corroding actions. Oil paint, as ordinarily made and used, is known to be far from perfectly effective, and not only requires constant renewal, but also allows corrosion to take place beneath it. This is principally due to the fact that there is a certain degree of solubility for moisture in the vehicles of oil paints. Many other protective coatings have been proposed and tried, with varying success, ranging from such substances as bituminous varnishes to coatings of other metals applied in various ways. Of these latter a coating of tin, applied in the molten state, is much used, and is very effective where the coating is perfectly intact. Its expense, however, precludes a very wide extension for engineering purposes. Coatings of zinc—under the name of "galvanised" iron or steel—are much used, and are effective up to a certain point, particularly as the zinc acts as an electrolytic protector for any portions of the steel which may become exposed. In time, however, the zinc coating is entirely corroded away, and then attack upon the exposed iron is rapid. A particularly interesting form of "protective" coating is that formed by a layer of Portland cement or concrete. Steel embedded in this material, which is now so extensively used in ferro-concrete constructions, appears to be perfectly protected from corrosion so long as the concrete retains an alkaline reaction ; any water percolating the concrete finds sufficient free lime to be rendered alkaline, and, therefore, harmless to the steel. In running water, however, the free lime tends to be washed out of the concrete, and it appears probable that ultimately corrosion may set in. A similar action may also occur in the sea—a circumstance which is not without its grave significance in view of the use of ferro-concrete for marine and hydraulic work in many places. It may be hoped that in such places means have been used to render the concrete as nearly watertight as possible in order to minimise the circulation. An extremely serious source of corrosion for all metals is found in stray electric currents which are apt to seek an easy path through the earth by passing into any metallic bodies which may be present. If moisture is present, electrolysis, with rapid destruction of the metal, is set up if the current happens to pass in the unfavourable direction. Such electric currents should be particularly guarded against in the vicinity of ferro-concrete which is liable to be moist. Electrolytic corrosion in ferro-concrete not only results in the destruction of the embedded steel, but, owing to the large bulk of iron oxide which is formed, rapidly disrupts the whole mass.

The corrosion of non-ferrous metals and alloys has been principally studied in regard to brass, although corrosion is, of course, encountered in practically all metals, with the exception of the noble metals (silver, gold, platinum, etc.), and the newly-developed "rare" metals, such as tungsten, which are apparently incorrodible at the ordinary temperature. The corrosion of brass, however, has assumed exceptional importance owing to the large number of brass tubes employed in the construction of condensers for steam engines, more especially for marine purposes. It has been found that in many cases, although not in all, the corrosion of brass takes place by a process which consists in the selective solution and removal of the zinc, leaving the copper behind in the form of a spongy mass containing a considerable proportion of oxide. This process is generally known as "dezincification," and its mechanism has been recently explained (10). The action takes place, in the case of brass exposed to contact with sea water, particularly at temperatures above 40° C., by the formation of a basic chloride of zinc, which adheres to the sides of the brass tubes. On the one side this basic chloride constantly reacts with the sea-water, parting with some of its zinc in a soluble form, either as chloride or sulphate, and, on the other side, constantly renewing its own zinc-content at the expense of the brass. The adherent patches of this basic chloride thus act as a species of catalytic agent. Fortunately it has been found that this action is largely inhibited by the presence in the brass of 1 per cent. of tin or, better still, of 2 per cent. of lead.

The protection of brass and of other copper alloys from corrosion in condenser tubes and other situations where protective coatings are out of the question, by the aid of specially generated electric current, has recently been suggested and adopted with a certain measure of success. The simplest method of applying this principle consists in generating the requisite electric current *in situ*, by attaching to the article to be protected pieces of a more readily attacked metal. The combination of the two metals then acts as a primary cell, in which the "protector" is steadily dissolved while the protected metal remains intact. Thus plates of iron, zinc or aluminium have been attached to brass tubes and have served as efficient protectors where there has been sufficiently good electric contact between the two metals and for a moderate distance from the point of contact. In some cases, as Bengough (10) has shown, the protection is effective over a longer distance, owing to a secondary effect whereby a thin but strongly adherent skin of calcium carbonate is deposited on the surface of the brass, thus protecting it from the sea-water. The principle of electrolytic protection has also been applied in another way, by employing a definite and independent source of current and thus converting the whole apparatus to be protected—boiler, condenser or other apparatus—into an electrolytic cell, in which specially introduced electrodes of some such substance as carbon serve as anodes, while the whole apparatus acts as cathode. This arrangement, if carried out with sufficient attention to the electrical contacts and resistances, gives promise of working very efficiently, although the maintenance of an outside source of electric current is somewhat of an inconvenience. On a ship, however, where electric current is now universally available, this inconvenience is extremely slight as compared with the saving in condenser tubes and the troubles of frequent repairs resulting from perforation of tubes by corrosion.

Finally, reference must be made to the question of the corrosion of aluminium and of its light alloys ; at the present time the use of these materials is still very restricted, but this is due to special causes, one of which is the fear of want of permanence, on the ground both of corrosion by external agencies and of internal disintegration. In regard to corrosion, aluminium itself has long suffered from the excessive zeal of its early friends, who claimed for it practical incorrodibility. This claim probably arose from the fact that brightly-polished aluminium can be exposed to the air for long periods without showing signs of material corrosion, but under the action of sea-water, and particularly in the presence of other metals, aluminium corrodes with decided rapidity. The action of the sea in this respect is largely a mechanical one. Aluminium when exposed to the air rapidly becomes covered with a very thin film, which either consists of oxide or contains a considerable proportion of oxide ; this film serves as a protective coating which, if undisturbed, serves to prevent further corrosion almost indefinitely. When, however, as friction acts on this film it is, after a time, worn away, and, if the friction continues, the fresh formation of a protective film is prevented and corrosion proceeds rapidly.

Pure aluminium, however, owing to its relatively small strength and stiffness, is of little value for structural purposes, and recourse must be had to one of the strong and light alloys which have been produced, as the fruits of Physical Metallurgy researches, in recent years, both in this country and in Germany ([11]). Since these materials rival the strength of steel while only one-third the weight, some considerable importance attaches to their behaviour in regard to corrosion. Those alloys which contain manganese have been found to be rather less liable to rapid corrosion than pure aluminium, but the fact must none the less be faced that, if exposed to the action of sea-water, these materials require protection approximately to the same extent as ordinary iron or steel; for mere exposure to a moist atmosphere, however, the aluminium alloys are far superior to polished steel in regard to their power of maintaining a bright, untarnished surface.

The second factor which still stands in the way of the wider usefulness of aluminium alloys is the prevalent fear that they may not be permanent in their properties, quite apart from corrosion. This belief has no doubt sprung from the behaviour of certain alloys of aluminium with iron, tin, nickel, and some other elements. These exhibit the peculiar property of spontaneous disintegration; a small ingot of such an alloy will, if left to itself, fall into a heap of fine powder in the course of a few hours ([12]). This behaviour, however, is a property of certain definite compounds of aluminium with other metals, and these compounds only exhibit this behaviour when they constitute the whole, or nearly the whole, of the alloy. This only occurs in alloys in which the element other than aluminium is present in comparatively large quantities, so that the whole process is probably unknown in true "light" alloys which consist principally of aluminium. For certain purposes, especially for a process known as "die casting," some alloys containing a large preponderance of another metal, such as zinc or iron, have been used, and the product, which has a white appearance, has been sent out as "aluminium castings." These have shown frequent cases of warping and disintegration, and the unfortunate experiences of those who have had to deal with them have reflected on aluminium alloys as a whole. In order to settle this question as definitely as possible, an investigation on a very large scale has been undertaken at the National Physical Laboratory. Over a thousand different specimens of aluminium alloys, both pure and containing intentionally added impurities, have been prepared in all conditions of treatment, and are being kept under various conditions of storage as regards temperature and moisture. These specimens have been prepared for accurate measurement, both as to dimensions and electrical resistance, and, by periodical observations, are being watched with a view to detecting the slightest signs of change. A preliminary set of castings, which have been watched for over a year, have so far shown no signs whatever of any change, and to this extent the popular belief in the disintegration or warping of certain aluminium alloys is already discredited by the results of accurate investigation. That this is likely to be the case with whole groups of important alloys is indicated by the fact that samples of some of these materials have been tested at the National Physical Laboratory at intervals over a period of eight years without showing any signs of deterioration.

Although the principal interest in this connection attaches to the light alloys of aluminium, some reference must also be made to the very great powers of resisting corrosion and oxidation which are displayed by the alloys of aluminium with copper in which the latter metal preponderates. These aluminium coppers, formerly, but quite erroneously, called "aluminium bronzes" (13), have been tested by prolonged exposure to the sea, first for a period of three years by complete immersion, and then for a similar period "between wind and water." These tests show that the alloy containing approximately 10 per cent. of aluminium is extremely resistant to sea-water corrosion, the test-pieces having lost in weight to a minute extent, which could be detected only by the aid of accurate weighing on a balance, at the end of that period. Alloys of this type can also be exposed to a red heat in an oxidising atmosphere for several days without becoming appreciably tarnished by oxidation. No doubt the formation of a pellicle of aluminium oxide, supported by the great mechanical strength of these alloys, is responsible for this satisfactory behaviour, which places them above any other alloys of copper in these respects. Here, as elsewhere, however, a compensating disadvantage is to be found. The pellicle of aluminium oxide which protects these materials from corrosion or oxidation also protects them from alloying with tin, so that they cannot be readily soldered like other alloys of the brass or bronze type.

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