

LF1217.5 I5,1966

LIB. BOOKS

PHYSICAL METALLURGY:
PAST, PRESENT AND FUTURE

*Inaugural Lecture of the
Professor of Physical Metallurgy
delivered at the College
on 22 February, 1966*

by

PROFESSOR J. BURKE
B.Eng., Ph.D.(Liverpool)



UNIVERSITY COLLEGE OF SWANSEA



Classmark: LF1217.5 I5 1966

Accession no: 66/1268

Location: Archives

SWANSEA UNIVERSITY COLLEGE
LIBRARY

1002423755



PHYSICAL METALLURGY:
PAST, PRESENT AND FUTURE

*Inaugural Lecture of the
Professor of Physical Metallurgy
delivered at the College
on 22 February, 1966*

by

PROFESSOR J. BURKE
B.Eng., Ph.D.(Liverpool)

Synopsis

Physical metallurgy is concerned with the relationship between the properties of metals and alloys and their structure and also with the way in which the structure depends upon the composition and the previous treatment given to the material. The development of the science from its beginnings in the middle of the last century has been closely linked with the exploitation of experimental techniques capable of revealing information about structure. This development is traced by showing how our present understanding of the hardening of steel by quenching has evolved over this period. This phenomenon has been recognized and put to practical use for at least two thousand years but it is only within the last five years that we have got a reasonable explanation for it.



PHYSICAL METALLURGY: PAST, PRESENT AND FUTURE

CONTEMPORARY university courses of study in science and technology seldom devote much attention to the historical development of the subject. The reasons for this attitude are (a) pressure on curriculum time by other more important topics (b) the feeling that reference to discarded theories and obsolete experiments is more likely to confuse the inexperienced mind than produce enlightenment and (c) the urge to ensure that the young student has his mind set on future developments rather than past accomplishments. Nevertheless it is occasionally helpful in trying to obtain a perspective view of present day knowledge to examine how it was built up over the years. It appeared appropriate to use this lecture to trace the evolution of physical metallurgy in the hope that it would be of interest and value to both the metallurgists and the non-scientists in the audience. In order to provide a focal point I am going to discuss the development in terms of one specific phenomenon, namely the quenching and tempering of steel. This process has been known and put to practical use for at least two thousand years. Furthermore the principles involved are sufficiently general that the progress achieved in understanding it is a very good indication of the progress made throughout physical metallurgy as a whole.

The Scope of Physical Metallurgy

Before embarking on a discussion of this type it is desirable to define physical metallurgy so that the position of the quench-hardening of steel in relation to the whole subject may be appreciated. The parental subject of metallurgy is concerned with all aspects of the science and technology of metals and alloys. For convenience this may be sub-divided into three over-lapping branches: (a) chemical metallurgy, which is concerned mainly, but not entirely, with the extraction of metals from their ores, refining and with aspects of behaviour involving chemical

reactions such as corrosion and oxidation; it has little to do with chemical analysis of ores and alloys, (b) engineering metallurgy, which is concerned with the problems of producing metals having particular properties in the forms required by the user, and (c) physical metallurgy, which is concerned with elucidating the basic principles governing the structure and properties of metals and alloys and the application of these principles to the design of new materials and/or treatments of existing materials to create improved properties. In this context are included all properties relevant to the ultimate use of the material and this includes all mechanical properties and physical properties such as magnetic and electrical properties. The name of physical metallurgy was first proposed for this branch of metallurgy by Rosenhain in the title of a book published in 1914.

The question is often raised of the difference between physical metallurgy and metal physics. In recent years many important contributions to physical metallurgy have been made by men who originally were physicists and the distinction between the two subjects has become increasingly blurred. Nevertheless I think there is a difference and basically the difference is one of outlook. Pure physics is concerned with identifying the basic laws of nature governing the behaviour of materials and bodies. To a physicist the practical significance of the results of an experimental or theoretical study is of little consequence and thus the only criterion in choosing a system for study is that it should enable the desired phenomenon to be investigated. The physical metallurgist, whether engaged in research or practical development work, should be essentially an applied scientist whose major concern should be the ultimate practical value of his work.

The Evolution of Physical Metallurgy

Since the subject is concerned with correlating properties with structure it is primarily, but not exclusively, an experimental science. Methods of measuring most of the

important physical and mechanical properties of metals had been devised by the middle of the nineteenth century but no really satisfactory method of observing structure existed. Prior to this, structural observations had been restricted to the appearance of fractured surfaces and to the examination of the solidification patterns revealed on the surface of cast metals as a result of shrinkage. The evolution of the science was thus geared to the discovery and exploitation of techniques capable of yielding information concerning structure. The first of these occurred in 1863 when H. C. Sorby developed the technique in which the structure is revealed by etching a carefully polished surface and then studied under a microscope. This was the birth of physical metallurgy. It required another two score years for a sufficiently coherent, ordered body of information and principles to emerge for the new discipline to be recognisable.

The other major milestones, each of which presaged periods of intense development, were (a) Osmond's use of Le Chatelier's thermocouple to detect the critical temperatures in steel, which was the start of thermal analysis, (b) the development of the use of X-Rays to study the structure of crystals by W. H. and W. L. Bragg in 1912, and (c) the development of the electron microscope in the early 1950's.

In subsequent sections the contribution of these various techniques to our understanding of quench hardening of steel will be outlined.

The Development of Iron and Steel Metallurgy

The first ferrous material made by man was a kind of wrought iron made by heating ore and fluxes in a charcoal fire. It contained very little carbon, probably less than 0.1%, but many other impurities together with appreciable quantities of non-metallic slag dispersed throughout as a result of forging into the desired shape. The 'modern' process for making wrought iron—the puddling process—

was invented in 1760. The product of this process was the most important constructional material for bridges and railways until the late nineteenth century when it was replaced by mild steel.

The blast furnace was introduced in Germany in the 14th century, the product being a liquid—pig iron—containing perhaps 4% C and various other impurities. Cast iron is remelted pig iron.

Steels are alloys of iron containing up to about 1.5% carbon as the essential alloying element. The first steels were made by heating iron in a charcoal fire causing carbon to diffuse into the iron. The ancients either by accident or experiment found that the properties of the 'steel' were sensitive to the way in which the part was cooled. By 200 B.C. both Greeks and Romans knew, and put to practical use, the fact that quenching steel into water from a red heat produced a substantial increase in hardness compared to the same metal slowly cooled. Unfortunately, in the as-quenched condition the parts—swords, implements etc.—were brittle and liable to fail if subjected to a sharp impact, but it was found that the brittleness could be obviated by tempering.

Modern steels are made by remelting pig iron and oxidising out the carbon and other impurities, subsequently adjusting the composition by appropriate additions. There are many hundred different steels used in engineering, many of which contain several other elements besides carbon which each serves some purpose. However, in many cases it is permissible to regard carbon as the essential alloying element and neglect the remainder.

Early work on the nature of steel

The cause of the difference between iron and steel and the reason why the latter hardened when quenched from high temperature occupied a prominent place in the philosophical discussions of the seventeenth and eighteenth

centuries. To place these in perspective it must be remembered that methods of chemical analysis did not become available until much later.

Early in the seventeenth century philosophers began to express the view that matter was composed of particles which could associate with each other in varying degrees of complexity and some tried to explain the hardening of steel in these terms. One view held was that heat opened up the pores of the iron by allowing ingress of the atoms of fire, while quenching caused water particles to penetrate into these pores making the metal hard. Tempering was supposed to evaporate the water and cause softening. An alternative suggestion was that heat put the particles into motion, allowing them to approach nearer together where the rapid cooling caused them to become immobile without allowing time for them to move back to their original position.

Other philosophers of this period, no doubt influenced by the shapes of crystals grown from liquids, thought in terms of the shapes of particles. Hard bodies were those in which the faces of the corpuscles were flat and tightly stuck together across many faces; soft bodies were those in which only a few of the faces of the particles were joined. Heating iron was supposed to introduce some slippery fluid which permitted the parts to re-arrange themselves into the hard configuration which was then retained on quenching.

One of the earliest attempts to examine the structure of steel was made by Robert Hooke in about 1663. He used the recently invented microscope to examine the surface of a razor blade. He made some wry comments that all that could be seen was a mass of scratches. He thought that steel was a substance made from iron by means of vitrification of proportions of certain parts. Heat melts the vitrified substance, opening the pores of the iron. Quenching was supposed to retain this open arrangement causing the steel to be hard and brittle. Tempering drove out the substance

to the surface thereby producing the well-known temper colours.

One of the first methods used to deduce information concerning structure was the examination of fractured surfaces. This technique probably was suggested by the use of the grain of wood as an indication of its quality. Reaumer (1722) early in the eighteenth century made some remarkable studies of metal fracture and recognised that metals are composed of grains and also that within the grains there is an aggregation of smaller parts and beneath that still another. The hardening of steel was accounted for by the diffusion in and between the clusters of 'sulphur and salts' drawn out of the molecules by the heat. Quenching retains these sulphurs and salts, whereas slow cooling permits them to diffuse out. If we substitute carbon for sulphur and salts the theory is remarkably close to the present day view.

Reaumer also made some interesting observations on the effect of temperature on grain size and noted that the temperature had to exceed some value before any significant change occurred.

In the late eighteenth and early nineteenth century, chemical analysis showed that the essential difference between iron and steel is the presence of carbon in the latter. Later, by dissolving irons and steel in acids and analysing the residue it was shown that slowly cooled steel contained an iron carbide (eventually identified as Fe_3C) whereas no carbide was present after quenching.

In the middle of this same century several important observations were made, all pointing to the fact that some structural change occurs in iron during heating. Gore (1869) showed that steel previously heated elongates momentarily at a certain temperature during cooling and Barrett in 1873 noted that when this occurs there is also a sudden temperature rise. Discontinuous changes in electrical properties were also noted. In 1863 Tchernoff published his classic paper in which he demonstrated that steel is not hardened

unless quenched from above some critical temperature which he designated A_1 , thus establishing a nomenclature that persists to this day.

The contribution of microscopical metallography

At the time of Sorby's work, it was known that carbon was essential to the hardening process, that a carbide existed in slowly cooled steels but not in quenched ones and that a critical temperature for hardening existed and it was suspected that some structural change occurred at about red heat.

Sorby mounted thin sections of metal onto a glass slide and produced a flat polished surface by grinding on (a) successively finer emery papers, (b) a soft stone and (c) finishing on a fine abrasive paste. The structure was then revealed by etching in very dilute nitric acid and after washing and drying a second glass slide was mounted onto it, prior to examination under reflected light at magnifications up to 650 times. He showed that each material had a characteristic structure dependent upon composition and treatment and he identified seven distinct constituents including free iron, iron carbide and a 'pearly constituent' which he also showed to be composed of alternating plates of nearly pure iron and carbide.

The technique was later used by Martens in Germany and Osmond in France. By the end of the century the chief features of the metallography of iron and steel had been established and the commonly occurring structures had been assigned names, largely by Howe.

The structure of a steel containing 0.35% carbon is shown in Fig. 1. It consists of grains of ferrite—the light constituent—and pearlite. The pearlite is shown at higher magnification in Fig. 2. As the carbon content increases the proportion of pearlite increases until at 0.9% the structure is completely pearlitic. Further increase of carbon produces

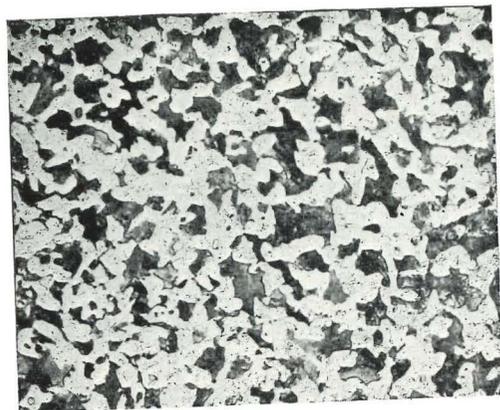


FIG. 1. The structure of an 0.35 % carbon steel etched in a solution of 2 % nitric acid in alcohol. Magnification x 300

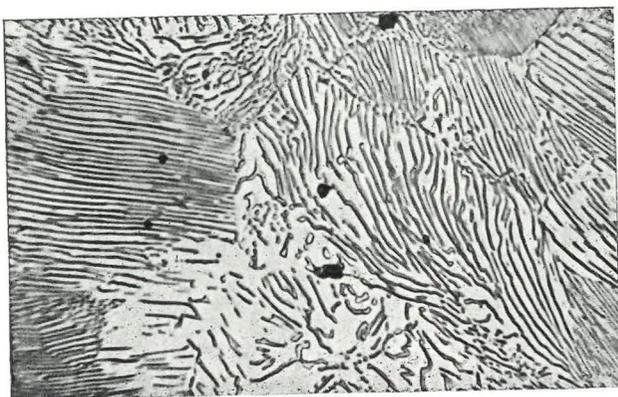


FIG. 2. The structure of pearlite. The steel contains 0.8 % carbon and was etched in a solution of 2 % nitric acid in alcohol. It consists of alternate plates of cementite and pearlite. Magnification 1,500



FIG. 3. The microstructure of a steel containing 1.2 % carbon water quenched from 1,000C. Magnification 750

an intergranular network of carbide around grains of pearlite.

Quenching a steel containing 1.2% carbon produces a structure shown in Fig. 3. which consists of martensite—the acicular constituent—and austenite. The proportion of the latter increases with the carbon content but decreases if the specimen is cooled to below room temperature.

Osmond pioneered the use of the thermocouple to detect structural changes during heating and cooling and laid the foundations of modern thermal analysis. He found three arrests in the heating or cooling rates in iron and one, two or three in steels depending upon the carbon content. All of these he associated with structural changes

and as a result suggested that annealed steel is a mixture of α iron and carbide whilst quenched steel consists of β iron with the carbon in solution. β iron was supposed to be hard and the role of the carbon was to facilitate the retention of β . An alternative theory attributed the hardness to the form of the carbon which could be varied by heat treatment. The β iron theory was eventually disproved by studying the mechanical properties of iron as a function of temperature when it was found that α and β iron had identical properties—Brinell (1905), Rosenhain and Humfrey (1913).

The contribution of X-Ray Analysis

By 1912 it was recognised that the various constituents seen under the microscope were individual crystals. It was also known that the structure of an iron crystal changed at Ac_3 (910°C) and it was thought that a change also occurred at Ac_2 (760°C), the temperature at which iron loses its ferromagnetism. Osmond had indulged in some quite brilliant speculation as to the crystal structures of the iron phases.

X-Rays were discovered by Röntgen in 1896. It was suspected that they had a wavelike motion similar to light but of a much smaller wavelength. Von Laue in 1912 suggested that if the atoms in a crystal were arranged in a regular pattern then they would be able to diffract X-rays. This was proved to be so in the same year by Friederich and Knipping. It is well known that if a beam of light is directed onto a plate containing a regular periodic pattern of small holes with the separation distance being about the same as the wavelength of light, then the transmitted light consists of (a) the direct beam of diminished intensity and (b) a number of weaker secondary beams. The same thing happens with a crystal and X-Rays and the secondary (diffracted) beams can be directly related to the positions of the atoms in the crystal. This discovery was brilliantly exploited by the two Braggs into a powerful tool for structure analysis; the work is regarded by many as the most important scientific achievement of the first half of the twentieth century. By means of this technique it was shown

that α -Fe is body centred cubic (Fig. 4) (Hull 1919); that β and δ -Fe are identical with α and that γ -Fe is face centred cubic (Fig. 4). Ferrite and austenite are interstitial solid

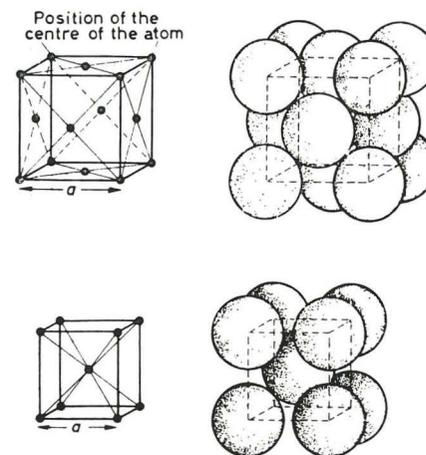


Figure 4. The arrangement of the atom in γ -iron (top) and α -iron (bottom). For γ -iron $a = 3.66\text{\AA}$ at 950°C and for α -iron $a = 2.86\text{\AA}$ at 20°C ($1\text{\AA} = 10^{-8}\text{ cms}$).

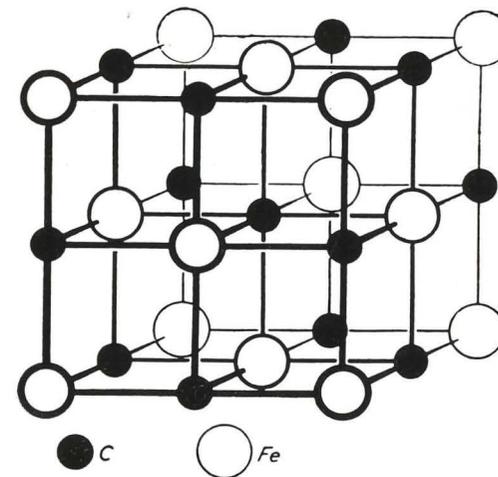


Figure 5. The positions of the carbon atoms in austenite. Only a small proportion of the available sites are actually occupied.

solutions of carbon in the α and δ modifications of iron respectively. In both structures the interstices are smaller than the carbon atoms and thus considerable distortion is present with the result that the solubility of carbon is limited. It was not until about 1942 that the position of the carbon atoms was finally established. In austenite the carbon occupies the sites shown in Fig. 5 (Petch 1942). Only a few of the sites marked are ever occupied (about 1 in 12 at saturation) but the occupation is random with the result that austenite remains f.c.c., the lattice parameter increasing with carbon content. Ferrite is peculiar in two respects (a) the carbon atom occupies interstices which are not the largest available and (b) the occupation of the chosen sites is not random with the result that the cubic cell is elongated in one direction and so becomes tetragonal. The maximum solubility of C in α -Fe is 0.02% so that the distortion is negligible. Careful work showed that martensite is simply supersaturated ferrite as shown in Fig. 6 (Petch 1942) with

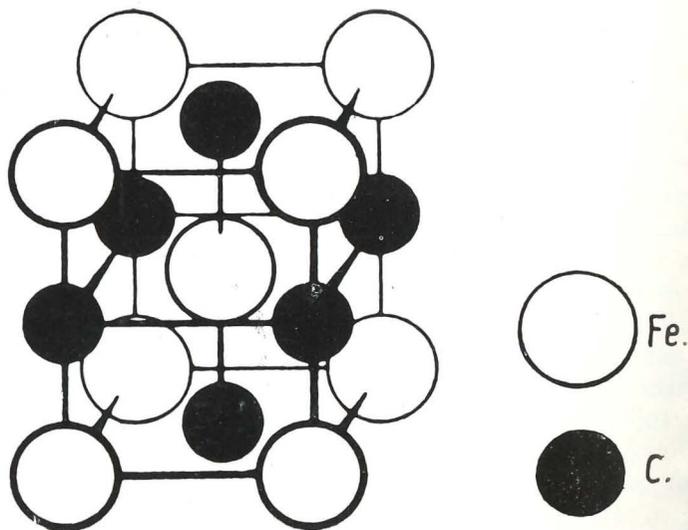


Figure 6. The positions of the carbon atoms in ferrite.

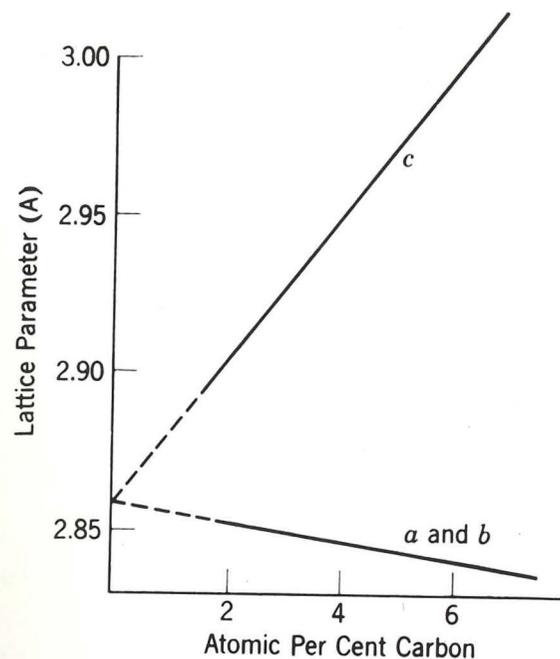


Figure 7 The variation of the lattice parameters of martensite with carbon illustrating that martensite is supersaturated ferrite.

the result that in medium or high carbon steel the tetragonal distortion is appreciable. In Fig. 7, the values of the tetragonal parameters of martensite are shown as a function of the carbon content. It is seen that extrapolating to zero carbon gives $c=a$, i.e. the cell is b.c.c. This value of 'a' corresponds with the lattice parameter of pure α -Fe.

The Mechanism of Hardening

Having established the structure of the phase responsible for the hardness, it still remained to explain why martensite is hard. The interest in this waned in the pre-war years probably due to two factors (a) physical metallurgists became increasingly interested in how martensite formed from austenite and (b) at that time it had so far proved impossible to understand the mechanical properties of even simple single crystals of pure metals and no doubt the feeling

existed that there was little point in trying to understand a complex situation.

In order to appreciate the later work, it is first necessary to consider briefly the source of strength in crystals. The force required to initiate plastic deformation in a crystal is found to be 1000 — 10,000 times smaller than the force calculated to cause one perfect plane of atoms to slide past another 'en bloc'. To overcome this dilemma, Taylor, Orowan and Polanyi independently in 1934 suggested that crystals contain extended line defects, called dislocations, which are interior sources of weakness. The simplest type of dislocation is shown in Fig. 8, from which it can be seen

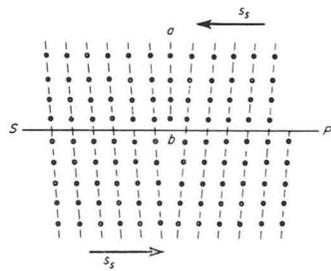


Figure 8 (a). An edge dislocation

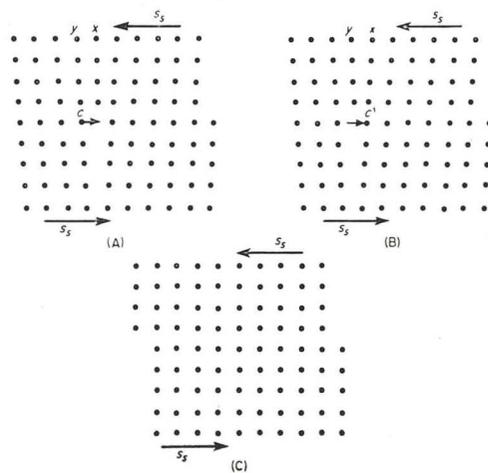


Figure 8(b). three stages in the movement of an edge dislocation through a crystal

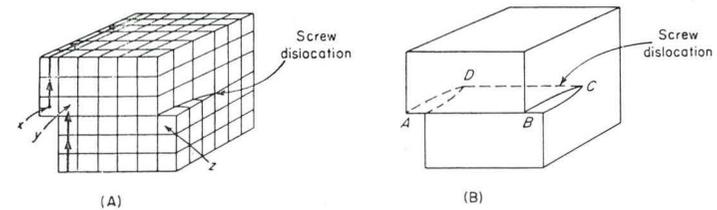


Figure 9. Two representations of a screw dislocation. Notice that the planes in this dislocation spiral around the dislocation like a left-hand screw.

that the passage of one dislocation across the crystal produces a deformation equal to one lattice spacing. It can be shown that the force required to do this is very much less than that required to make one plane slide over another. A second type of simple dislocation is shown in Fig. 9. In real crystals the actual dislocations are likely to be combinations of these two.

Dislocation theory did not attract much attention from physical metallurgists for a number of years. For example Cottrell's book, *Theoretical Structural Metallurgy* published in 1948 and generally regarded as a pioneer in the new fundamental approach to physical metallurgy, did not even mention them. Barrett's book, *Structure of Metals* which was devoted almost exclusively to structural aspects of metallurgy gave four pages to a so-called detailed treatment of dislocation theory. The situation changed very rapidly in the half dozen years following the end of the war. During this time it was shown that dislocations provided a rational explanation of discontinuous yielding in iron (Cottrell and Bilby 1948) and the growth of crystals from the vapour phase (Frank 1952), two phenomena which had hitherto been utterly baffling. The simplicity and generality of the ideas were extremely convincing and all that most practical minded metallurgists required to be finally convinced was some direct evidence of the existence of these dislocations. This was not long in coming. Following Frank's suggestion that crystals grown from the vapour grew by the spiralling

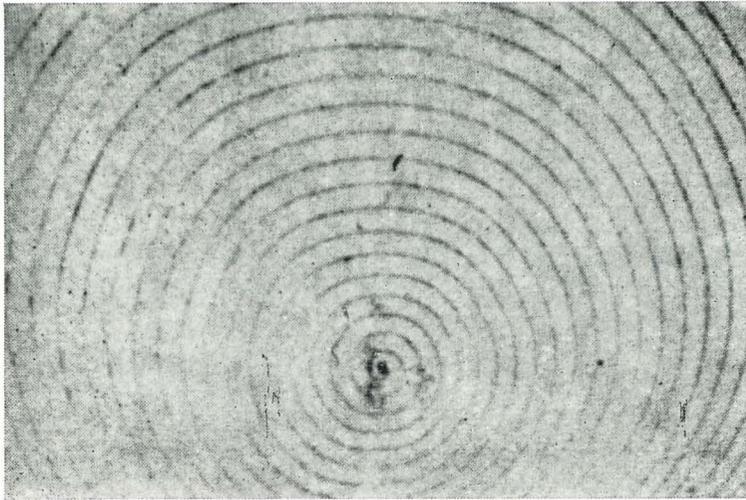


Figure 10. Growth spiral on silicon carbide. Magnification 60.

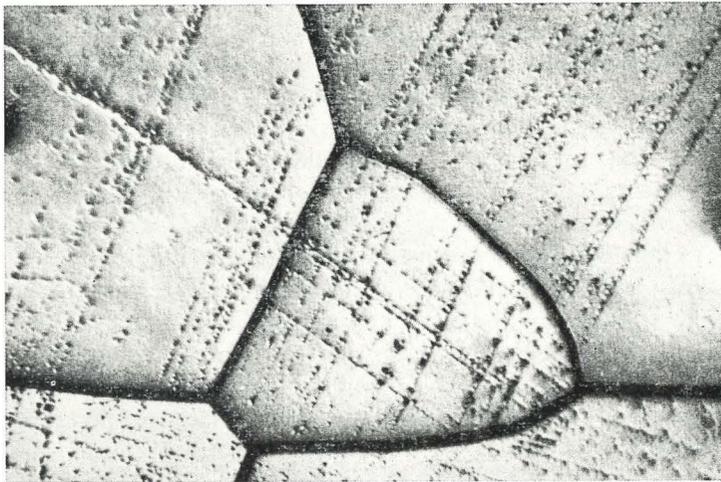


Figure 11. Dislocation etch pits in silicon iron (x 900)

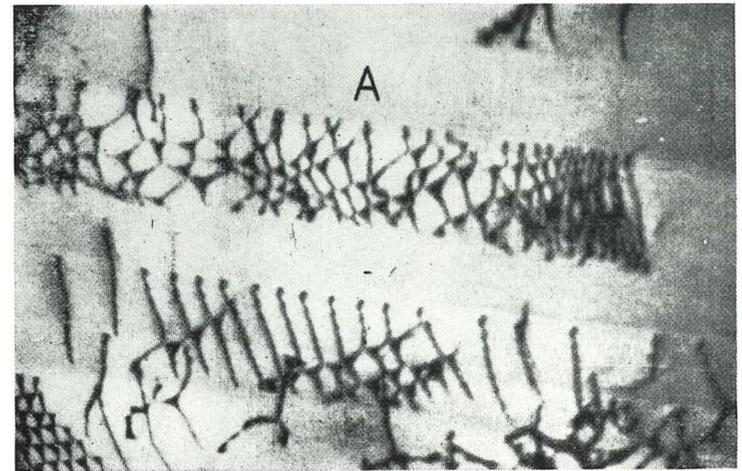


Figure 12. Dislocations in stainless steel (x 44,000)

movement of a screw dislocation where it emerges from the surface, spiral growth patterns were found in a number of materials (Fig. 10). Careful etching was found to give pits which could be demonstrated to be the point of emergence of dislocations (Fig. 11). There were several other experiments which all gave convincing evidence of dislocations but the most convincing proof of all came when the technique of thin film electron microscopy was developed.

For the present purpose electrons may be considered to be similar to light except that they are of much smaller wavelength and thus capable of much higher effective magnifications. The specimen must be in the form of a very thin film ($\approx 1000\text{\AA}$ thick) which is prepared by dissolving thin sheets of the metal to be examined. One of the first pictures taken by this technique is shown in Fig. 12 and clearly shows the dislocations on two slip planes. Since that time a vast amount of effort has been devoted to the study of dislocations in metals and the ways in which the mechanical properties are related to them.

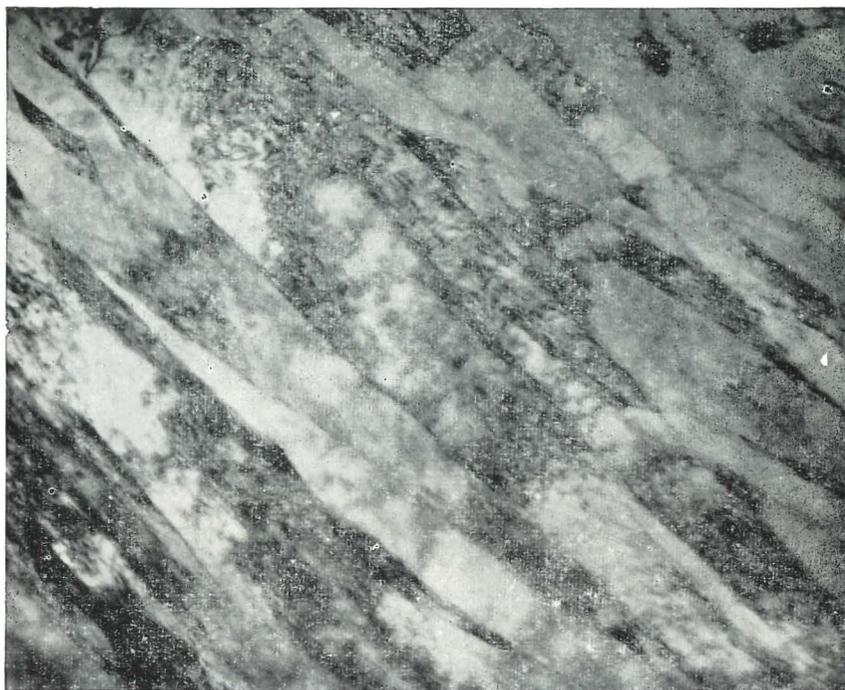


Figure 13. 0.1% C steel quenched to produce martensite. Needles have formed rather than plates and there is no internal twinning (x 80,000)

In simple terms a metal is hardened if the movement of dislocations is impeded.* This can be done in several ways:

- (a) by anchoring the dislocations by means of segregation or precipitation of foreign atoms;
- (b) by the presence of dispersed particles of a second phase which act as obstacles to dislocation movement;
- (c) by distorting the lattice through the presence of foreign atoms;
- (d) by refining the grain size or substructure which results in an increased interaction between the dislocations as they pile-up against the boundaries;

*Here we neglect those materials produced artificially having few dislocations

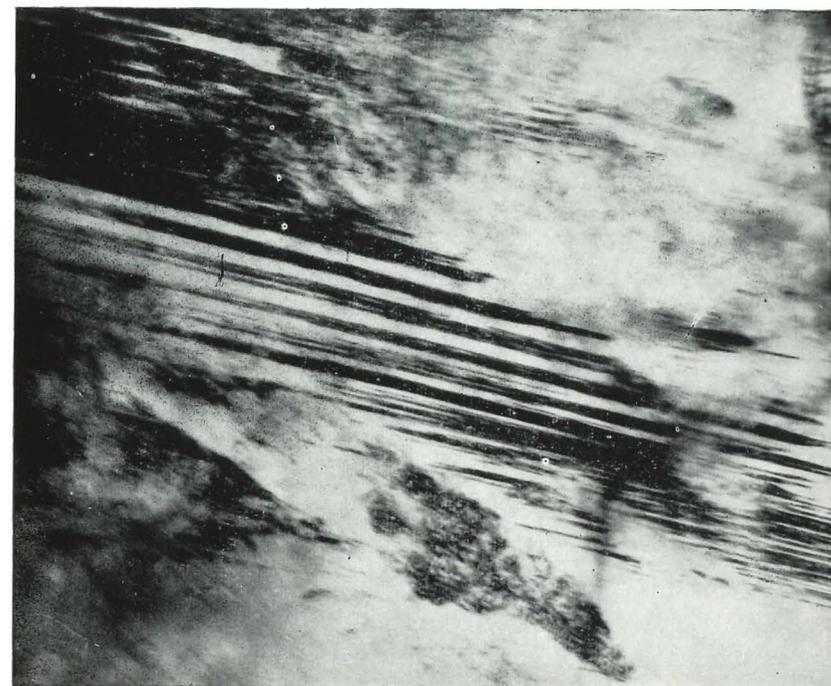


Figure 14. 1.0% C steel quenched to produce martensite. Twins having a minimum thickness of 20 Å have been formed (x 80,000)

- (e) by creating more dislocations which interact with each other. Since the dislocations are generated during plastic deformation this is the reason why metals get harder as they are deformed.

All of these sources of hardening have been recognised.

The contribution of electron microscopy

Kelly and Nutting (1960) examined quenched plain carbon steels in the electron microscope. In low C steels martensite occurs as long needles with a heavy dislocation density (Fig. 13), whereas at high C contents the martensite consists of plates internally divided into twinned crystals, (Fig. 14). It is known that the hardness increases very rapidly

with C content. These authors suggested that this increase is due to the increasing proportion of internally twinned martensite, i.e. to (d) above. This suggestion aroused almost as much opposition as the β iron theory. Careful measurements by Radcliffe and Schatz (1963), Winchell and Cohen (1963) and Roberts and Owen (1965) indicated that the increasing hardness is due to the increasing supersaturation of C atoms producing solid solution hardening, (c) above. The C atoms in the b.c.c. structure cause extensive tetragonal distortion, which was shown by Fleischer and Hibbard (1963) to cause severe impediment to dislocation movement. However, the argument is not yet completely settled. A suggestion has been made that C atoms segregate to dislocations during the quench giving a hardening contribution due to (a) above.

On tempering the carbon atoms are rejected from solid solution. At first the hardness increases slightly due to the formation of ϵ carbide, $\frac{\text{Fe}}{2.4}\text{C}$, which causes hardening by mechanism (b). Eventually this transforms to Fe_3C and the depletion of solute leads to complete softening (Fig. 15.)

Materials Science

Finally a brief word about the future. Prognosticating about further development is bound to be a very subjective, not to say unreliable business. However, we are told that history goes in cycles and thus before one looks forward it is as well to look back. In many ways metallurgy was the progenitor of chemistry and physics as we have indicated. Indeed the study of the reaction between lead and oxygen played a considerable part in the early development of chemistry. Eventually, being more general sciences, these two outgrew metallurgy. Physical metallurgy developed by mixing some of the principles of chemistry and physics with the principles of mechanics. We are now going through a period when a new, more general science than physical metallurgy is developing. This has been called materials science.

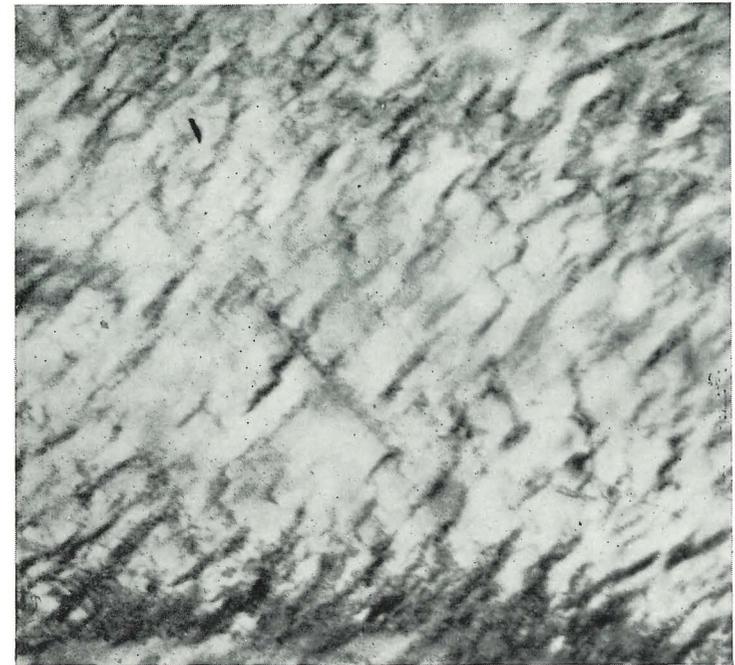


Figure 15 a. 1.0% C steel quenched and tempered for 1 hour at 200°C, showing large precipitates along the twin boundaries, as well as small unidentified precipitates across them.

There is as yet no clear and universally accepted definition of what materials science is, of its place in future scientific development or how best the universities should expand into the new discipline. The subject has been much in vogue in the United States for a number of years, one motivation for this being the favour with which money-granting governmental organizations looked upon projects in the area. Unfortunately some of these were little more than physical metallurgy masquerading under a flag of convenience. In this country a number of university departments have made tentative moves in the direction of materials science, sometimes at post graduate level. Out of these explorations has come the conviction that a new



Figure 15(b). 1.0% C steel quenched and tempered for 1 hour at 300°C, showing cementite lying along the twins.

subject based upon the relationship between the properties and structure of engineering materials will play an important part in the future. There is, of course, a very good practical reason for this, namely, the fact that modern engineering is increasingly resorting to non-metallic materials such as ceramics, cermets and plastics. The use of resin-bonded fibreglass is already widespread. The volume of production of plastics is already greater than all the non-ferrous metals put together. However, the potential of these new materials has not yet been fully exploited because they are not yet completely understood. Since modern physical metallurgy grew because of the need to understand the behaviour of metals, it is clear that there is a considerable incentive for the establishment of materials science.

Although not the only one, physical metallurgy is one of the best starting points for this new science. We now have a fair qualitative understanding of the strength of metals in terms that are completely general and applicable to non-metallic solids. All that is needed to convert physical metallurgy into materials science is a willingness to broaden our interests and faith in the concepts that have been developed over the years and proved so useful in understanding metals.

The relationship between pure and applied research

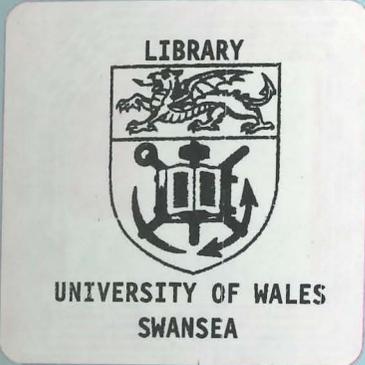
By way of conclusion I should like to say a short word about a problem that in my opinion is the major one facing academics and industrialists in the future, and it has little to do with science but a lot to do with people. It is almost a cliché now to say that in these days of mass communication the great trouble is lack of communication between individuals. Modern physical metallurgy has produced two different types: the one interested in pure research to be found in the universities and research institutions and the other located in industry who is devoted to solving immediate short or long term problems, usually by empirical 'let's try it and see' methods. The former have lost all contact with the latter and even more regrettably, frequently look upon the work with some contempt—'hack metallurgy' is an often used term of derision. The latter group have long since despaired of even understanding the former. Both approaches have their place. Empirical research is still the quickest and most economical means of solving commercial problems. The best approach is empirical research based upon the best available scientific knowledge and the best empirical researcher is the one who has a proper understanding of fundamental principles. Something must be done to arrest this dichotomy. It is a problem that would repay active consultation between the universities and industry.

BIBLIOGRAPHY

- W. F. Barrett, 1873. *Phil. Mag.* **46**, 472.
 J. A. Brinell 1905. *Iron and Steel Mag.* **9**, 16.
 R. L. Fleischer 1962. *Acta Met.* **10**, 835.
 G. Gore 1869. *Proc. Roy. Soc.* **17**, 260.
 H. M. Howe 1890. *The Metallurgy of Steel.*
 A. W. Hull 191. *Phys. Rev.* **49**, 540.
 P. M. Kelly and J. Nutting 1960. *Proc. Roy. Soc.* **259A**, 45.
 A. Martens 1878. *Zeit des Vereines deutsche. Ingenieure* **22**, 11.
 E. Orowan 1934. *Zeit. Physik* **89**, 634.
 F. Osmond 1901. *Microscopic Analysis of Metals.* London.
 F. Osmond and J. Werth 1885. *Ann. des Mines* **8**, 5.
 N. J. Petch 1942. *J. Iron and Steel Inst.* **147**, 221.
 M. Polanyi 1934. *Zeit Physik* **89**, 660.
 R. A. F. de Reaumur 1722. 'L. Art de convertir le fer forge en acier'
 Paris. Eng. Trans. by C. S. Smith, Chicago
 1956.
 M. J. Roberts and W. S. Owen 1965. *Iron and Steel Inst. Spec. Rep.*
 No. 93, 171.
 W. Rosenhain and J. Humfrey 1913. *J. Iron and Steel Inst.* **87**, 219.
 H. C. Sorby 1886. *J. Iron and Steel Inst.* 140; 1887 *ibid* 254.
 G. I. Taylor 1934. *Proc. Roy. Soc.* **A145**, 362.
 D. K. Tchernoff 1868. *Zapiski Russ. Tekh. Obshestva* **399** Eng. Trans.
Proc. Inst. Mech. Eng. 1880, 286.
 A. Westgren and G. Phragmen 1922. *J. Iron Steel Inst.* **105**, 241; 1924,
109, 159.
 P. G. Winchell and M. Cohen 1962. *Trans. Am. Soc. Metals* **55**, 347.

ACKNOWLEDGEMENTS

- Permission to reproduce the following figures is gratefully acknowledged:
 Figure 1, 2 and 3 are reproduced from *The Micro-structure of Metals*,
 by J. Nutting and R. G. Baker, published by the
 Institute of Metals in 1965.
 Figures 13 and 14 are reproduce from a paper by P. M. Kelly and
 J. Nutting in the Proceedings of the Royal Society,
 259 A, 45 (1960).
 Figure 15 is reproduced from a paper by P. M. Kelly and
 J. Nutting in the Journal of the Iron and Steel
 Institute, 1961, Vol. 197, page 199.



Printed in Great Britain by
CROWN PRINTERS
(JONES AND SON)
MORRISTON
SWANSEA