MICROSCOPIC ANALYSIS OF METALS.

PART I.

METALLOGRAPHY

CONSIDERED AS A METHOD OF ASSAY.

DEFINITION.—Metallography, in the widest sense of the word, is the description of the structure of metals and of their alloys. It is not confined to the use of some single instrument—the microscope, for example — although the use of this instrument demands some special training, and for this reason tends to foster specialisation and specialists. In reality, in the examination of metals we begin by using our eyes. When our eyes have shown us all that can be seen, we reinforce them with glasses of gradually increasing power, until, at enlargements of about 2000 diameters, we are arrested by ultramicroscopic mysteries. But the eyes, and the optical instruments which extend their power, are themselves but incomplete means of investigation. They make, so to speak, a preliminary examination; the indications, which the visible characteristics—viz., shape, colour, or brilliancy—furnish, must be checked by chemical analysis, micro-chemistry, and crystallography, by the determination of physical or mechanical constants: in fine, by every means which permit the differentiation and identification of the substances, so far as these means, unfortunately restricted, are applicable to the subject under consideration.

The study of the metals and of their alloys is not without analogy with that of living organisms. Fig. 1, which represents one of the possible distributions of the carbide Fe_3C in steel, curiously recalls, at the first glance, a colony of bacilli and cocci. The similarity, in truth, is here quite accidental and superficial. But there are also more profound analogies. Our metals are neither simple bodies nor are they inert.

The ultimate chemical analysis of an alloy does not tell us how the elements present are combined among themselves, or whether they form isolated definite compounds or solutions, homogeneous or not. The proximate analysis which, in addition, is not often possible in the present state of chemistry, does not tell us how the constituents, supposed to be chemically separated, are individually organised or topographically distributed, as compared one with another. Histological organisation and anatomical distribution, supposing they are known, do not tell us what modifications the actual condition would undergo under the influence of certain changes of temperature or pressure.

Finally, these normal modifications, supposing them to be known in their turn, might be considerably disturbed by an infinitesimal quantity of some foreign impurity, sometimes inevitable, and the very presence of which is, at times, unsuspected.

SUBDIVISIONS OF METALLOGRAPHY.

Thus we are naturally led to establish in the study of metals several subdivisions quite analogous to those of medical science, and to speak of metallo-

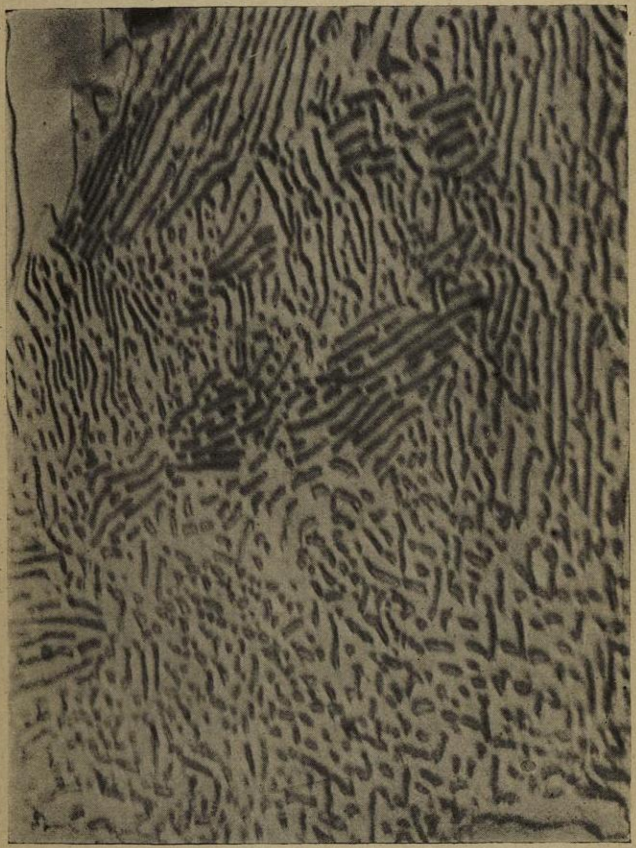

Fig. 1.—CEMENTATION STEEL. Polish-attack. [1] V × 1200 diameters.

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[1] V = Vertical illumination.

graphy as **anatomical** (histological), **biological**, and **pathological**.

The first distinguishes and defines the different constituents of which an alloy may consist by observing their optical characteristics (*colour*, *brilliancy*), their chemical characteristics (*resistance to reagents, formation of surface films*), or their mechanical characteristics (*resistance to wear, to scarification*), and describes their forms, crystalline or otherwise, measures their absolute or relative dimensions, and examines the planes of weakness (*joints or cleavages*) which separate one from the other, or traverse each of them separately.

The second subdivision is occupied with determining how the composition, form, dimensions, and relations of the different constituents, determined in a fixed state in a given sample, are connected with possible conditions of calorific or mechanical treatment which the alloy under consideration may undergo during the process of its manufacture or employment.

The third subdivision deals with the influence of errors of treatment, and of the presence of impurities which constitute, as it were, a particular diathesis: at the same time, when effects have once been connected with their causes by a preparatory study, it often allows us to group them together again for the solution of the problems given by practical work.

It remains for these three divisions of metallography to be illustrated by appropriate examples. It will suffice, for this purpose, to make extracts from the work of those who have devoted themselves to the microscopic examination of metals, and who have, for the most part, brought the sum of their experience before the various societies and institutions which interest themselves in the results of such investigations. Hence I shall constantly refer to these works.

ANATOMICAL METALLOGRAPHY.

Bodies chemically homogeneous.—Let us take, to commence with, a simple body—*e.g.*, cast-silver.

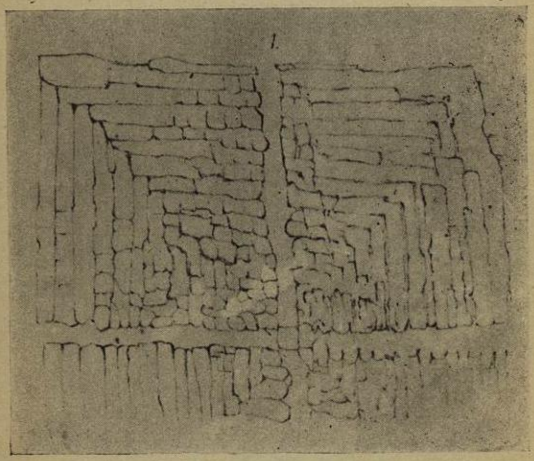

Fig. 2.—Cast-Silver (after Behrens). Not attacked.
V × 20 diameters.

Fig. 2 is a reproduction from a specimen of Professor Behrens,[1] whose work *Mikroskopisches Gefüge der Metalle und Legierungen* is a mine of information. It shows the skeleton of a cube, itself formed of little secondary cubes regularly juxtaposed. In addition, complete cubes, the length of whose sides varies from 0·05 mm. to 2 mm., are also grouped in series, or at least placed in tiers projecting from one corner and

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[1] *Op. cit.*, fig. 1, p. 40.

from the adjacent portions. It is easy to understand that the cleavages of these cubes are natural surfaces of fracture.

Let us now examine a hammered sample of mild steel. It contains $\mathrm{C}=0{\cdot}125$; $\mathrm{Si}=0{\cdot}03$; $\mathrm{S}=0{\cdot}026$; $\mathrm{P}=0{\cdot}019$; $\mathrm{Mn}=0{\cdot}31$. It is almost pure iron. With the exception of the filaments of carbide and of some small grains of slag, polishing on damp parchment with a little calcium sulphate, followed or not by etching with nitric acid or tincture of iodine, reveals, in the metal, a network of polygonal sections of polyhedric grains (fig. 3).

Fig. 3.—HAMMERED MILD STEEL (0·125 per cent. carbon). Attacked by dilute nitric acid. V × 100 diameters.

These grains are not, properly speaking, crystals at all, since they have neither plane faces nor geometrically regular forms. They are not, however, all identical; polishing on parchment does not wear them away uniformly; nitric acid and iodine do not attack them equally. These differences are, at least partially, due to the crystalline arrangement of the mass—an arrangement which varies between neighbouring grains, and yet remains constant throughout an individual grain. To bring out this structure, it is advisable to etch rather deeply with dilute and lukewarm sulphuric acid. The grains, cut in sections parallel to two of their axes, show little cubes regularly superimposed, very much like those of silver (fig. 4).

Fig. 4.—HAMMERED MILD STEEL (0·125 per cent. carbon). Attacked by dilute sulphuric acid. V × 600 diameters.

BIBLIOTECA

If the section be parallel to a single axis only, the etched grain appears lamellar (fig. 5), and the exposed structure becomes confused when the section is not parallel to any axis of the grain. We have therefore a double network of weak cleavage planes: one due to those in the mass of the grains themselves, the other to the demarcation of adjacent grains, variously orientated. These interspaces form a natural locale for the gases which may be set free at the moment of solidification or later, and are ready formed lines along which fissures may open or extend under

Fig. 5.—Hammered Mild Steel (0·125 per cent. carbon). Attacked by dilute sulphuric acid. V × 1000 diameters.

mechanical influence. All the efforts of metallurgists must then tend, if not towards eliminating these sources of weakness, which is impossible, at least towards minimising them by diminishing the proportion of the gases, by checking the liberation of these gases, by preventing the free play of the crystalline forces, by accelerating cooling, and, in a word, by every means adapted to making the contact surfaces smaller and less discontinuous.

We see that a body, homogeneous in the eyes of the chemist, may be very complex from a structural point of view; but chemically homogeneous bodies are themselves the exception, and we generally have at an early stage to differentiate the chemically distinct constituents.

Bodies chemically heterogeneous.—The simplest case is that in which the constituents do not possess the same colour, which enables us to recognise them on the first inspection of a plane section. Figs. 6 and 7 represent two alloys of gold and aluminium, which contain respectively:

Au = 85; Al = 15 (fig. 6).
Au = 54; Al = 46 (fig. 7).

Both contain a common constituent which was discovered by Sir William Roberts-Austen, and is of a beautiful purple colour; it is a definite compound with the formula $AuAl_2$, which possesses the very rare property of having a fusion point above that of the least fusible of its two components. During solidification it first isolates in crystallites, which appear black in the photograph; the spaces are filled up with the material, separating out during the second stage of solidification, the proportions and the nature of which vary with the composition of the alloy.

When the constituents, as generally happens in the case of metals, do not possess distinctive colours of their own, we may try to colour them artificially.

Tincture of iodine, for example, will allow us to

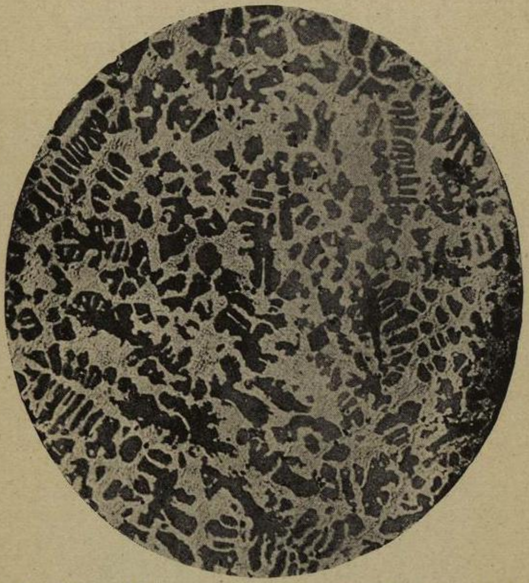

Fig. 6.—GOLD = 85 per cent. ; ALUMINIUM = 15 per cent. Cast. Polished only. V × 1000 diameters.

distinguish lead, in many of its mixtures, by the formation of its iodide, which is yellow. But the precipitates thus produced by a chemical reaction do not always adhere to the constituent reacting and very rarely resist the wiping of the surface of the object.[1] It is perhaps best to fix them, as H. Le Chatelier has advised, beneath a fine covering of

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[1] In cases when the objects have to be wiped or rubbed with a linen fabric to dry the surfaces.

gelatine impregnated with a suitable reagent, and applied to the surface which we wish to study. This operation can be performed and followed under the microscope.

A second method consists of forming an adherent

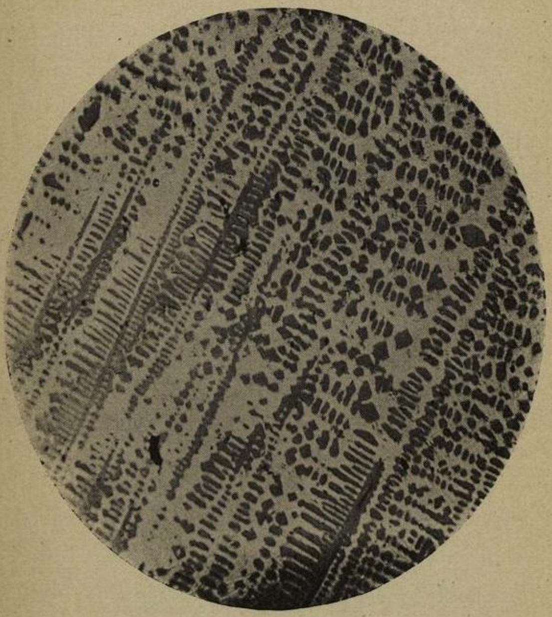

Fig. 7.—GOLD = 54 per cent. ; ALUMINIUM = 46 per cent. Cast. Polished only. × 100 diameters.

surface film, too thin to possess a colour of its own, but capable of giving, with reflected light, a coloration varying with the thickness of the layer. These are the temper colours, oxide films or patinas. As they do not form on unoxidisable metals, and do not appear simultaneously, other things equal, on metals unequally oxidisable, this process is of frequent application.

In this manner Professor Martens obtained the beautiful figures of spiegeleisen, which illustrate his earliest papers,[1] and were one of the first successes of budding metallography. The metal under consideration was formed of two constituents: a definite carbide $(Fe.Mn)_3C$, and a solution of carbon (or of carbide) in the remainder of the alloy. The definite carbide was relatively slightly oxidisable, and took, after a certain amount of heating at a certain temperature, a yellow colour, for example, whilst the solution had already turned to blue. Colours induced by this method have the great advantage of not being attenuated under high enlargements. Wedding,[2] Behrens,[3] and Guillemin[4] have all made frequent use of them; they are a great help in the study of alloys of copper.

When the constituents are of too small dimensions to be discernible even under the microscope, the difference in depth formed by an unequal etching again gives rise to decomposition of reflected light; as the etching becomes deeper, there appear successively (in normal light) yellow, brown, blue, and black colorations, which must not be confounded with the preceding, as they do not show, like them, the presence of a *patina*. From this we deduce a third method, which extends the power of the microscope to a certain point, but teaches only one fact, viz., that the constituents under consideration are not uniformly acted upon. It is in this manner that we

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[1] *Zeitschrift des Vereins Deutscher Ingenieure*, 1878, Taf. xxiv. and xxv.

[2] *Jour. of I. and S. Inst.*, 1885, p. 187.

[3] *Loc. cit.*, *passim*.

[4] *Commission des Méthodes d'essai des matériaux de construction*, 1st Session, Reports, t. ii. p. 19.

identify sorbite in untempered steels (portions not striated in fig. 8), and troostite in steels tempered half-hard at certain temperatures (dark bands of fig. 9).

Fig. 8.—FORGED STEEL (1·24 per cent. carbon). Reheated to 800°. Polish-attack. V × 2000 diameters.

Colorations, natural or artificial, are not the only resources of anatomical metallography. We can make use of the mechanical properties of bodies. Behrens has prepared a whole series of needles of regularly varying hardness, with which he scratches the surface of a polished section[1]; such a needle may scratch one constituent and not another. In the

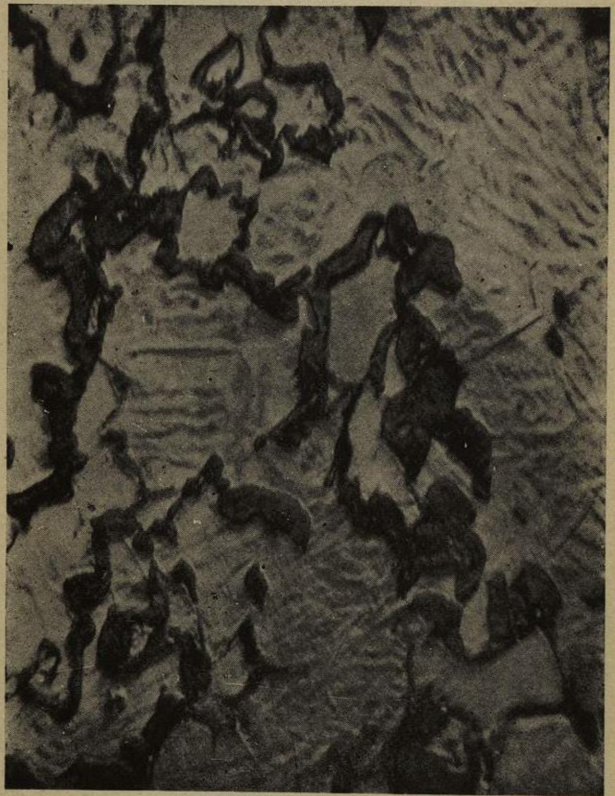

Fig. 9.—FORGED STEEL (0·45 per cent. carbon). Heated, and quenched at 730°. Polish-attack. V × 1000 diameters.

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[1] *Loc. cit.*, pp. 21–27.

bronzes, the composition of which is represented by the formula $CuSn_3$ or $CuSn_2$, Professor Martens has been able not only to determine, but to measure with the sclerometer, the hardness of each of the structural constituents.[1]

However, the resistance to scratching does not depend only on the nature of the bodies, but also on their absolute dimensions; a layer of glass sufficiently thin may be, if not scratched, at least cut, by the finger nail. The method is only applicable, therefore, to fairly coarse structures. But equivalent information may be obtained, in the case of more delicate structures, by rubbing on a soft layer with the help of very fine powders. Fig. 10 is a photograph of some hard steel (1·24 per cent. carbon) forged into a round bar 12 millimetres in diameter, the forging of which has been finished at about a dull red heat. A transverse section has first been polished; then the polishing has been continued on damp parchment sprinkled with a very small quantity of rouge; the iron is hollowed out, and has left in relief the carbide of iron Fe_3C, which, in the sample under consideration, is divided into a multitude of little rounded grains. The grains of carbide appear dark on a clear ground or light on a dark ground, according as the objective is a little above or below the focussing point. The photograph was taken in the first of these positions. The same result would be obtained by etching the metal by an acid which etches the iron without appreciably dissolving the carbide, but as the iron, in being attacked, has its polish removed in a very irregular manner, the preparations are often lacking in definition. The two

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[1] *Mitteil. aus den K. techn. Versuchsanstalten*, t. viii. p. 236.

methods can be combined by replacing the water, in the polishing on parchment, by an extract of liquorice-root, which, by the help of repeated rubbing, slightly dissolves the iron without taking away its polish. The device is useful in bringing out clearly that curious constituent of slowly cooled steels, *pearlite*, the discovery of which has done so

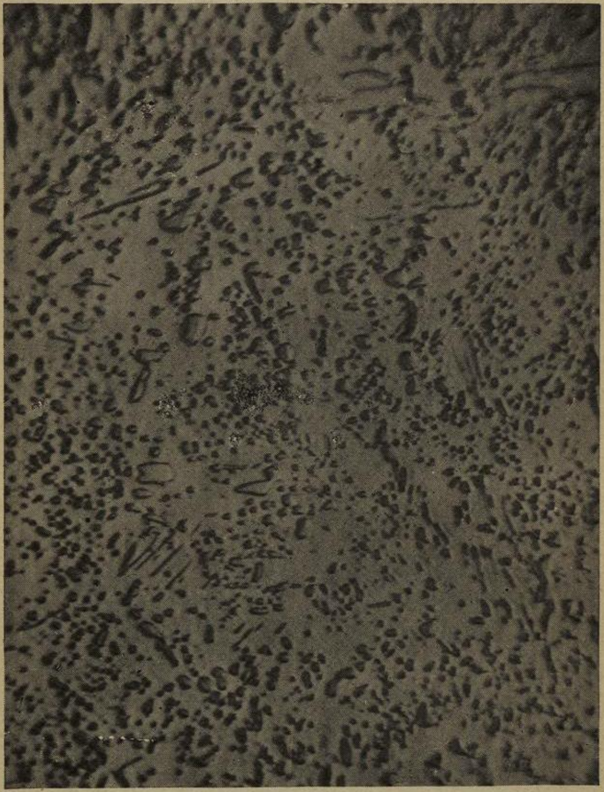

Fig. 10.—FORGED STEEL (1·24 per cent. carbon). Polished in bas-relief. V × 1000 diameters.

much honour to the late Dr Sorby, the pioneer of microscopic metallography.[1]

This constituent is a mixture of iron and of the carbide Fe_3C in alternate layers, generally curved (fig. 11); the thickness of a pair of layers probably does not exceed $\frac{1}{1000}$ mm. on an average; it may be much less. The unequal relief of the two components causes, on account of the decomposition of the light, iridescent reflections similar to those of pearl; whence the name pearlite, proposed by Professor Howe with the assent of Dr Sorby, and universally adopted to-day.

Causes of Error.—The different methods which have just been enumerated, and serve to distinguish two constituents, do not always furnish conclusive indications. A chemically homogeneous body may offer a very variable resistance to chemical or mechanical action according to its crystalline arrangement, and according to its degree of density. We have seen examples of this above. It is easy enough to mistake for two different constituents two different aspects of a single constituent; and confusions of this kind have certainly been made more than once. The scepticism sometimes shown in connection with the statements of metallographers has in principle, therefore, some justification; investigators should check themselves by multiplying their experiments, and should only give, as facts, concordant results obtained from several different methods. This necessary verification has taken place in numerous cases. It has been said, for example, that the aspect of pearlite under the microscope does not indicate the existence of two different bodies, but only the lamellar struc-

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[1] *Jour. of I. and S. Inst.*, 1886, p. 140.

ture of a single body, with a slighter or deeper attack of the cleavages. The objection, in itself, is reasonable, but these hard layers of carbide of iron which are seen under the microscope in a section of a steel have been chemically isolated by Müller,[1] by Abel

Fig. 11.—Cementation Steel. Polish-attack. V × 1500 diameters. (*Typical lamellar pearlite.*)

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[1] *Stahl und Eisen*, t. viii. p. 292 (1888).

and Deering,[1] Osmond and Werth,[2] Arnold and Read,[3] and by Mylius, Förster, and Schöne,[4] and it is no longer possible to deny it an independent existence. As, on the other hand, the carbide Fe_3C, isolated by the best methods from steels cooled very slowly, contains almost the whole of the carbon, it cannot be doubted that the second constituent, ferrite, is almost pure iron.

This would no longer be necessarily the case after quicker cooling, even without quenching. The ferrite would then include a certain proportion of carbon under a form chemically discernible, that of hardening carbon. Thus we see that micrography and chemistry constantly help each other. The one indicates the existence of a mechanical mixture, and the other tries to determine its nature; or, to put it another way, analysis separates certain definite constituents which micrography can only locate.

BIOLOGICAL METALLOGRAPHY.

General Considerations.—In the preceding section we have seen what methods permit of differentiating the different structures of a chemically homogeneous body, and the different constituents of a chemically heterogeneous mixture. This distinction made, the determination of the forms and dimensions do not present any difficulties, and we are to some extent commencing biological problems—that is to say, problems connecting the changes of structure with their causes.

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[1] *Ann. de Chim. et de Phys.*, 5e série, t. xxx. p. 499.
[2] *Ann. des Mines*, 5e série, t. viii. p. 19 (1885).
[3] *Jour. of the Chem. Soc.*, t. lxv. p. 788 (1894).
[4] *Zeitschr. für anorg. Chem.*, t. xiii. p. 38 (1896).