CHAPTER V.

PRIMARY CONSTITUENTS OF CARBON STEELS.

I CALL every structural element a primary constituent when its micrographic reactions permit it to be considered as a species. These constituents, not including the slag, which is an impurity, nor the graphite, which does not appear normally in the usual conditions of the manufacture and treatment of steels, are really six in number. But the list is necessarily provisional, like that of the chemical elements, and for the same reasons. The progress of science brings discoveries, duplications, and confirmations.

FERRITE.

The chief constituent of carburised iron is the iron itself, pure, or at least relatively pure, for absolute purity is a myth. When iron is considered as a structural element of a complex whole, it is convenient to give it a particular name, and I have adopted that of "Ferrite," happily coined by Professor Howe in conformity with mineralogical nomenclature.

By polishing in bas-relief, ferrite at first assumes a specular polish. If this operation be long continued, it granulates and forms polyhedric grains, of which some are slightly in relief and some are in intaglio in respect of a given level.

Polish-attack produces the same effect, but more

rapidly.

Tincture of iodine yields the same results under the conditions previously defined. On continued etching, certain grains begin to colour yellowishbrown, more or less deeply. The extremities of the

grains are traced by dark lines in intaglio.

Nitric acid also marks the joints of the grains very well, but it colours or does not colour the preparation according to circumstances so complex and confused as to justify special investigation. If a polished section of extra-mild steel after etching in a bath of 2 per 1000 nitric acid (2 volumes of acid at 36° Baumé in 998 of water) be placed under the microscope, lighted by the vertical illuminator, and if etching be continued for half an hour, certain grains of ferrite become yellow and brown progressively, whilst others become dull without being coloured, or remain practically unaltered. The patina of the browned grains generally remains after wiping. On making the same experiment in 2 per cent. acid, the ferrite takes beautiful colours, differing in different grains and often in the same grain. These colourings are analogous to those which are produced by heating in air, and we obtain yellow, brown, purple, blue, green, or colourless grains with continual transformations. The patina acquired at the moment it is brought out of the liquid is more or less deteriorated by wiping. It is difficult to follow with the microscope the too rapid attack of a 20 per cent. acid; but an acid of this strength often furnishes a preparation, the ferrite of which is, after wiping, more or less eaten into, but not coloured. These facts lead one to believe

that the attack commences by the formation of a fine pellicle of oxide or of some other body, which tends to become dissolved in the bath. According as the formation of this patina at a given point appears more quickly or more slowly than its dissolution, the tints do or do not appear; and when they do, they can, under suitable circumstances, run up or down their ascending or descending scale. The phenomena are so complex that they cannot be foreseen exactly, even in the best observed cases. Nitric acid, although it may render excellent service with known steels—e.g. for determining the size of the grain and the final temperature at which it has been worked-is, for micrographic analysis, a dangerous reagent which has led me personally more than once into error, before I had thoroughly fathomed its manner of action. To say the least, its indications ought to be controlled by other means. This remark applies equally to all the acids.

The grains of ferrite are chiefly fragments of cubical crystals which develop around independent centres of crystallisation, and are mutually limited by roughly plane surfaces. Their structure can be revealed by the prolonged action of nitric acid diluted with varying proportions of water (Andrews 1 and Stead 2), by the double chloride of copper and ammonia (Heyn 3), or, better still, by a sufficiently long submersion in lukewarm 20 per cent. sulphuric acid, followed by cleaning in nitric acid. After such treatment, the surface of a certain grain may be formed parallel to either the face or the edge of a cube, or in any direc-

¹ Engineering, lx. p. 88 (1895).

tion whatever. The corrosion figures on this grain show squares, parallel lines, or have a confused aspect. Fig. 124 (vertical light, V × 400), which in reality



Fig. 124.—Ferrite. Strongly etched. Showing the orientation of the crystals. $V \times 400$ diameters.

represents the figures of growth of iron reduced from chloride of iron by hydrogen below 850°, gives a good idea of these corrosion figures. But, interesting as it may be in itself, the crystallographic study of iron

² Jour. of I. and S. Inst., part i. p. 145 (1898). ³ Mittheilungen aus den k. technischen Vers., pp. 310-331 (1898).

does not enter into the scope of this work. Micrographic analysis proposes rather to define ferrite as a whole without revealing details, and the reagents indicated have been chosen to that end.

CEMENTITE AND PEARLITE.

The second constituent of steels is carbide of iron, foreseen by Karsten and Caron, and isolated more or less intact by F. C. G. Müller, Sir F. Abel, Osmond and Werth, Arnold and Read, and lastly, by Milius Förster and Schöne, and by Moissan. The results, taken together, tend to give this carbide the formula Fe₃C, the iron being capable of being replaced, in any proportion whatever, in special steels, by manganese or chromium. Professor Howe calls it "Cementite," and the carbon which is therein found combined in a definite composition has received the name of Carbon of Cementation (Caron), Annealing Carbon (Osmond and Werth), and Carbon of the Normal Carbide (Ledebur). It is, in fact, in cementation steels, and more generally in all steels cooled very slowly, that the cementite aggregates in particles of the largest size, and that it is the easiest to study.

Dr Sorby has shown that cementite can be obtained in two distinct forms-first, in rectilinear lamellæ relatively thick, which can be superposed like leaves (Independent Cementite): these groups often trace a continuous network, which divides the mass into grains, which are thus isolated from each other. Secondly, in finer lamellæ, usually curved, those of the same group being nearly parallel and interstratified with lamellæ of ferrite.1 This mixture has

been named "Pearlite" by Professor Howe, because it shows, with oblique light, the rainbow colours of mother-of-pearl, when the polishing or etching has eaten away to a convenient depth the readily soluble lamellæ of ferrite. The optical phenomenon involved has long been known, and has been explained by Fresnel.

Sorby subsequently showed that hard steels are mixtures of pearlite and independent cementite, soft steels mixtures of pearlite and ferrite, and, for an intermediate carbon content, the whole mass is composed of pearlite alone. This percentage of carbon has been fixed by Professor Arnold 1 at 0.90 in pure steels, which is practically exact, although it cannot be considered as having an absolute value. Not only does it vary with the amount of strange bodies present, but it is sufficient to examine a steel incompletely case-hardened and in which the carbon decreases gradually from the surface to the centre, in order to see that pure pearlite, unassociated with ferrite or independent cementite, is not reduced to a single line, but occupies a strip, the size of which corresponds to a variation of about 0.20 per cent. in the value of carbon between the appearance of the ferrite and that of the cementite.

Doubts have been raised as to the identity of the independent cementite and the cementite of the pearlite. Sorby was doubtful on this point, and I for a long time have shared this uncertainty. But the analyses of Professor Ledebur² have established the identity of its chemical composition. Arnold and

¹ Jour. of I. and S. Inst., p. 140 (1886); and p. 255 (1887).

Proc. Civ. Eng., t. exxiii., part i. (1895-96).
Stahl und Eisen, t. viii. p. 742, and t. xi. p. 294; Bull. Soc. d'Encouragement, 4º série, t. vii. p. 665.

The fact of these two forms of cementite having the same genesis, seems, as we shall see presently, to indicate unity. However, the hypothesis of several isomeric cementites, enunciated by Professor Camp-

bell,2 is not altogether excluded.

The characteristic property of cementite is its hardness, in the mineralogical sense of the word. Dr Muller³ compares it to that of felspar (No. 6 in the scale of Mohs), which seems to me correct. The variable figures, 45 to 47, indicated by Professor Behrens 4 are explained—the harder by the presence of chromium, the softer by the state of disaggregation to which allusion was just now made. This hardness, superior to that of all the other constituents of carbon steels (including hardened and annealed steels), allows the cementite to be easily isolated by polishing in bas-relief,5 provided that it is not scattered in a softer bed, in a state of division which exceeds the power of the microscope to define, and permits of no other control than that of immediate chemical analysis.

Polish-attack, so far as I have tried it, does not colour cementite.

Tincture of iodine, applied eight times, always



Fig. 125.—Cemented Steel (1.57 per cent. carbon). Polish-attack. V × 1000 diameters. (Typical cementite.)

under the conditions stated above, did not colour it, and left it shining with a silvery whiteness under perpendicular illumination.

Jour. Chem. Soc., t. lxv. p. 788 (August 1894).
Jour. of I. and S. Inst., part ii. p. 223 (1899).

³ Stahl und Eisen, t. viii. p. 292 (1888).

⁵ Polishing with emery is enough to bring out the principal charac-

The effect is the same, at ordinary temperatures, with nitric acid of 20 per cent. strength acting for



Fig. 126.—Cemented Steel (1.57 per cent. carbon). Polish-attack. $V \times 1000$ diameters. (Typical cementite.)

40 seconds at least, and with 2 per cent. acid for a much longer time.

Stead has recently used with success Igewsky's reagent, consisting of 5 per cent. picric acid in

MICRO-ANALYSIS OF CARBON STEELS 175

alcohol, and finds it excellent for developing the structure of pearlite.

Figs. 125 and 126 (V×1000) of a case-hardened

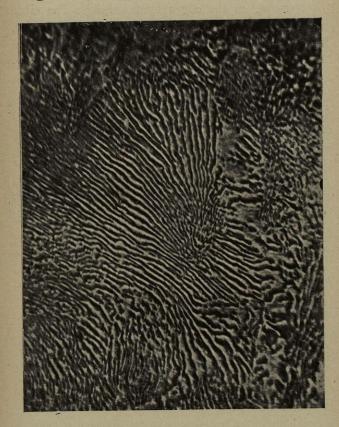


Fig. 127.—Pearlite in 1.00 per cent. carbon steel. Forged, heated, and cooled slowly from 800° C. Polished only. $V \times 1000$ diameters.

steel containing about 1.60 per cent. carbon and prepared by polish-attack, show mixtures of cementite and pearlite. In fig. 125 the pearlite is exceptionally distinct, the lamellæ of cementite being often thick enough to be measured. Photography, then, reveals them in the form of threads relatively clear, bordered on the right and left by dark strips corresponding to the rounding of the edges by polishing. The clear bands between the threads of cementite are ferrite. The independent cementite is a little less clear than the ferrite, but, as has been said, the respective clearness depends upon the focussing of the microscope. In fig. 126 the pearlite is very fine; the lamellæ of cementite no longer have a horizontal surface, and are reduced to rounded projections indicated by simple dark tracks along the edges of the projecting plates, the interstratified ferrite remaining clear. The independent cementite is in half-tone, and is distinguished by its form and dimensions - much greater in this case than those of the lamellæ of ferrite.

Fig. 127 is an example of pure pearlite in a steel of 100 per cent. carbon, forged, then reheated to 800° C., and submitted to simple polishing in bas-relief (V×1000).

SORBITE.

The types of pearlite just described are perfectly clear. This is not invariably the case. It often happens, either in polishing in bas-relief, or by polish-attack, or by etching with tincture of iodine, that part of the pearlite is free, while others are differently coloured in yellow, brown, and blue. Often very fine and deep lamellæ of cementite are found, which are more or less continuous: this is what fig. 128 (polish-attack, V×1500) ought to show, if the faintness of the original photograph

had been sufficiently reproduced. But, of the other strips of pearlite, no single one can be seen with any magnification: the surface, nearly uniformly



Fig. 128.—Sorbitic Pearlite (lamellar in 1.00 per cent. carbon steel. Polish-attack. V×1500 diameters.

tinted on the same grain, is only slightly granular (fig. 129: polish-attack, V×1500). In this last case I think that there is a distinct constituent, because it cannot be resolved into any two others, and I

Figs. 128, 129, and 130 have been taken from a

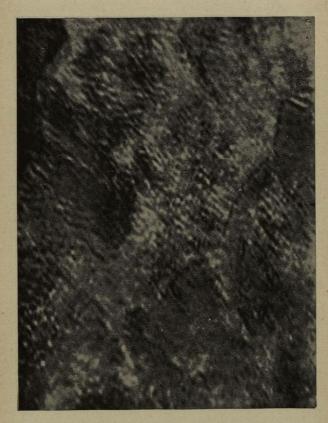


Fig. 129.—Sorbitic Pearlite (granular) in 1 00 per cent, carbon steel. Polish-attack. $V \times 1500$ diameters.

steel with 1.00 per cent. carbon, forged to 12 mm. round, then reheated to 860°, and cooled in about

MICRO-ANALYSIS OF CARBON STEELS 179

half an hour: it is the same steel as that of fig. 127. Sorbite is found side by side with pearlite in the same samples, and in fig. 130 one can see the juxtaposition



Fig. 130.—Pearlite passing into Sorbite in 1 00 per cent. carbon steel. Polish-attack. V $\times\,1500$ diameters.

of the free pearlite, and of the pearlite passing to sorbite. This circumstance, and the fact that the proximate chemical analysis has always, in similar steels, isolated the greater part of the carbon in the

¹ See footnote on page 292, and the remarks under the heading "Sorbite" on page 306.

state of cementite, seems to prove that there is not, from a physico-chemical point of view, a great difference between pearlite and sorbite. But sorbite may be obtained side by side with pearlite, by hastening the cooling without quenching, or by quenching a steel near the end of the critical interval, or, again, by reheating a quenched steel to about the same critical interval. For all these reasons sorbite may be considered as pearlite which has not been able to separate into ferrite and cementite by reason of lack of time, or from some other cause, and it seems to be true that it ought to contain a little more "hardening" carbon than free pearlite.

It has been said that sorbite is an unimportant constituent, and several authors have not distinguished it from pearlite. But if we remember that sorbite, although it can only remain present in annealed steels up to a certain point, is essentially characteristic of "negative" quenchings, and that this procedure considerably improves the mechanical qualities of the steel, it would appear as legitimate and as necessary to distinguish sorbite from pearlite as it is to distinguish steels cooled naturally in air from steels which have been submitted to "negative" quenching (such as oil-hardening), double quenching, or tempering above blue heat. In my opinion the present methods of the manufacture of rails, etc., will probably appear primitive in the future, and I hope that the greater quantity of pearlite in our steel will be replaced in future practice by sorbite.

From the point of view of micrography, sorbite is characterised by the absence of striæ and by the property of colouring rapidly by polish-attack or by tincture of iodine, after the application of the first drop of tincture, even when that is diluted with its own volume of alcohol. It is easily seen in figs. 125 and 126 that all the transitions between sorbite and pearlite occur as the separation of the cementite is more or less advanced.

MARTENSITE.

The fourth constituent is that which is generally obtained by quick quenching in cold water from a temperature a little superior to the maximum temperature of the critical interval; it is not new, but the structure of it was not known. Dr Sorby 1 speaks, but with great reserve, of an extremely fine grain. Professor Behrens² mentions, in certain samples which he examined, the existence of a soft polygonal network; but he subsequently admitted that this network is the result of a beginning of superficial decarburisation. The researches of Professor Martens 3 apply to steels more or less soft, and show the unequal distribution of carbon in these metals, but not the ultimate strucure of the hard portions. I published, in 1891,4 a photograph of medium hard quenched steel, which showed in oblique light, after slight etching by nitric acid, a clear enough wavy appearance; but I misinterpreted this observation. In short, as the grain of the fracture diminishes by quenching so far as to disappear entirely to the eye in steels of high carbon content, I was convinced that the structure of quenched steels tended towards an amorphous state. It is, however, as we shall shortly

¹ Jour. of I. and S. Inst., p. 276 (1887).

² Op. oit., p. 151.

³ Trans. Amer. Inst. Eng., t. xxiii. p. 59.

⁴ Jour. of I. and S. Inst., part i. pl. viii. (1891).

see, very crystalline. A good example is afforded in steel with 0.45 per cent. carbon, heated to 825°, which, after slow cooling to 720°, is quenched in a freezing mixture at -20° . The structure only appears vaguely after polishing in bas-relief, from which it follows that the hardness of the mass is about uniform: polish-attack produces a good development (fig. 131, V×1000). There are then seen faintly engraved groups of needles, or, rather, of rectilinear fibres, arranged parallel and sometimes separated by grains of a vermicular or worm-like character. Three systems of fibres, respectively parallel to the three sides of a triangle, cross frequently in the same region, and characterise, according to the opinion which Michel Lévy has given me, crystallites of the cubic system. I shall call this constituent "Martensite" after the name of Professor Martens, who founded in Germany, in 1878, an independent centre of metallographic research, and has since followed these studies

Martensite, isolated by polish-attack, is generally colourless, or only a pale yellow. On the other hand, the first drop of tincture of iodine causes a yellow, brown, or black coloration, according to the amount of carbon, the fibres always coming out bright.

with perseverance, talent, and success.

In the presence of these inequalities of coloration and attack, it may be doubted whether martensite really is a primary constituent. But the observed facts can be equally explained by the juxtaposition of fibres and the tendency of these fibres to throw the carbon out of their organism. The most recent facts tend to support the second hypothesis, without, however, eliminating all doubt. It is thus in previously polished samples of steels, with very

variable contents of carbon, that the characteristic forms of martensite appear by simply annealing in an atmosphere of hydrogen.

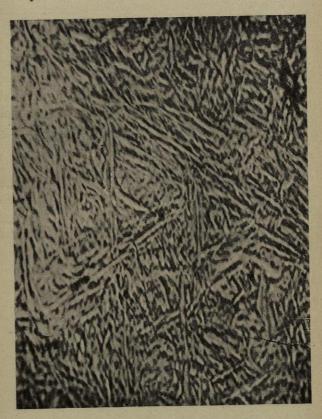


Fig. 131. - MARTENSITE in 0.45 per cent. carbon steel. Polish-attack. V×1000 diameters.

Whatever it may be, martensite keeps its form as well in the carburised regions hardened by quenching extra soft steel as in the hardest steels, with this difference only, that when the metal contains less carbon,

the needles are longer and better differentiated, other things equal. These are the forms which characterise it and enable it to be recognised under variations in its hardness: it is certainly not a definitely segregated combination of carbon and iron: it represents the crystalline organisation, under the influence of carbon, of one of the allotropic modifications of iron. However, the forms in which we find it through rapid cooling may be pseudomorphic, and I do not put them forward as a sufficient argument in favour of the real presence of the corresponding allotropic variety in the hardened metal.

Professor Howe has proposed for quenched steels (considered from a structural point of view) the name of "Hardenite." This name, on account of its very etymology, cannot be used to mean a constituent of variable hardness, and this is why I have adopted that of Martensite. But it may be useful to keep the word Hardenite, and to restrict it to Martensite saturated with carbon, in which well-defined sense it is now generally used.

TROOSTITE.

The fifth constituent has been obtained by quenching steels during the critical interval Ar_{1'2'3}—that is to say, during the course of transformation. Suppose we take a metal with 0.45 per cent. of carbon, heated to 825°, cooled slowly to 690°, and then quenched in water at ordinary temperature. Polishing on rouged parchment then shows on it projections in relief, fragments hollowed out, and, between the two, a border of variable size and of intermediate hardness. After the polish-attack, it is evident that the hard

projections are martensite, and the soft parts hollowed out ferrite. As for the interposing borders, they are yellow, brown, blue, or black: but these colours form



Fig. 132.—Troostite and Martensite in 0.45 per cent. carbon steel. V × 1000 diameters.

irregular marblings and develop less quickly than in the case of sorbite (fig. 132, $V \times 1000$). Their structure is almost amorphous, slightly granular, and mammillated. In a hard steel, quenched during the critical interval, the ferrite is replaced by troostite, itself surrounded by sorbite.

Tincture of iodine, either on the first or second application, acts like the polish-attack.

By calling this fifth constituent "Troostite" I have sought to do homage to one of our French masters, who has rendered eminent services to metallurgical science.

Even in the conditions of quenching stated, troostite is not an absolutely necessary constituent: it may be absent, the more so when the steel is very soft. In hard steels it passes insensibly to sorbite, while its boundaries with martensite are absolutely definite.

Another means of preparing troostite consists in quenching the steel, at a temperature higher than that of the critical interval, in a liquid less active than cold water—for instance, in oil or in boiling water. With cold water we get the same result if we increase the sizes of the pieces. In short, it is enough to diminish the energy of the quenching in order to eliminate the martensite structure: and we get troostite. But the hardness is not proportionately diminished, and the troostite, like martensite, may pass through nearly the whole scale of the hardness of steels, according to the content of carbon and the rate of cooling.

If the dimensions of the pieces submitted to quenching are so great that the cooling is not uniform—for example, in the case of a steel of 1 per cent. carbon — one would obtain martensite on the surface, troostite in the centre, and a mixed intermediate zone.

Tempering also tends to transform martensite to troostite.

AUSTENITE.

If we consider all the circumstances which usually affect the hardness of steel after quenching—viz. the content of carbon, the initial temperature of quenching, the chilling power of the bath and the influence of mass,-not only is the hardness of the martensite not increased when the carbon exceeds a certain amount, but a new constituent, much softer, which can be scratched with a sewing-needle and by apatite, perhaps even (but this is doubtful) by fluor-spar, appears near it. I have dedicated this constituent to Sir W. Roberts-Austen, and called it "Austenite."

To obtain it, the temperature of the steel must be above 1000°, the temperature of the quenching bath a little below or just at 0° C., and the proportion of carbon must exceed 1.10 per cent. With carbon steels I have never obtained pure austenite, but mixtures with martensite or hardenite. The amount of austenite increases with the amount of carbon from 1.10 per cent. (when it is absent) to about 1.60 per cent. or 1.80 per cent., when there may be 70 per cent. present. Beyond that, no matter what is done, it produces a separation of cementite, so that the proportion of dissolved carbon is diminished, and consequently the proportion of austenite no longer increases.

Contrary to what one would expect, austenite differentiates badly from hardenite by polishing in bas-relief, particularly if it is abundantly present.

Polish-attack does not colour it, but in the long run eats into it.

Tincture of iodine at once colours hardenite and austenite. The colorations of the two constituents



Fig. 133.—Austenite and Hardenite in 1.57 per cent. carbon steel. Polish-attack. $V \times 250$ diameters.

instance, a blue coloration may belong to hardenite in one grain, and to austenite in another.

The best agent for etching is dilute hydrochloric acid (10 per cent. solution), which colours hardenite and not austenite (fig. 133, V×250). The attack requires several minutes, and does not influence each grain with the same speed: there is more regularity



Fig. 134.—Austenite and Hardenite in 1.57 per cent. carbon steel. Polish-attack. $V \times 1000$ diameters.

obtained by having the specimen connected, by means of a platinum wire, with the positive pole of a bichromate cell, a strip of platinum placed in the acid being connected with the negative pole. In this way the specimen becomes the anode, and the platinum the cathode.

Fig. 134 represents the same preparation magnified



Fig. 135. — Austenite Steel after plain polishing and placing in liquid air revealing the transition to Martensite. $V \times 250$ diameters. (Typical martensite structure.)

1000 diameters after polish-attack. The hardenite has been coloured brown, which has allowed a good photograph to be taken; but there is an abnormal fact —the coloration only appears on a little part of the

borders. This point has probably been accidentally tempered.

It is seen that the hardenite forms barbed laminæ with, generally, a mesial rib, slightly visible on the photograph. These laminæ are often parallel in two principal oblique directions in the interior of the same

grain. Austenite constitutes the remainder.

Another property quite characteristic of austenite is that at a very low temperature it is transformed, with increase of volume, into hardenite. It is sufficient to immerse in liquid air for a few minutes a previously polished section containing austenite to produce the change: the austenite swells in slight relief above the hardenite (fig. 135, $V \times 250$).

Note on the Relative Softness of Austenite.

Doubt having been frequently expressed as to the reliability of the method of determining the relative hardness of austenite compared with that of hardenite, it may be useful to explain how the demonstration may be effected.

I first obtained a bar of steel containing 1.55 per cent. of carbon in its interior, and a gradually

decreasing amount towards the outside.

A small piece was forged into a bar having the dimensions 19 mm. × 9 mm. × 10 mm. This was heated to 1050° C., and quenched in mercury at a temperature of -9° C. When cold, one of the surfaces was ground down to remove the outer layer where superficial decarburisation had been effected during the reheating. It was then polished, but was not subjected to any attack by etching reagents. A pointed sewing-needle was then repeatedly drawn across it from end to end with even pressure.

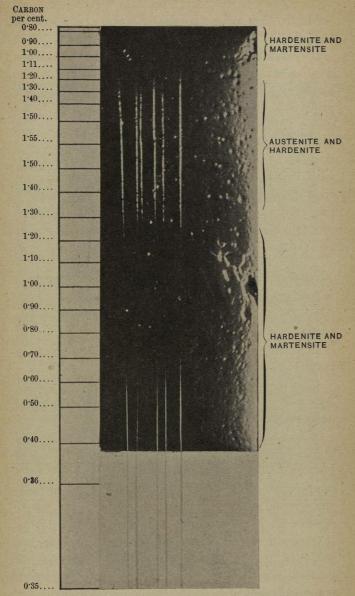


Fig. 135A.

The photograph (fig. 135A), taken when the object was illuminated by oblique rays of light, indicates clearly enough that the needle scratched the steel in the region where the carbon was between 0.37 per cent. and 0.70 per cent., and that it would not scratch it where the carbon varied between 0.70 per cent. and 1.20 per cent. It commenced again to scratch it feebly in the region of 1.25 per cent. carbon, and continued to scratch it with a gradually increasing depth till 1.45 per cent. carbon was present, and apparently continued to scratch it with equal ease till the carbon reached the maximum of 1.55 per cent. carbon, after which the material gradually got harder and harder with the diminishing carbon, until at a point where it approached 1.15 per cent. carbon it was too hard for the needle to make any impression.

Judging from the relative distinctness of the scratches, it is clearly shown that in the region of highest carbon the metal is more readily scratched than where it is only 0.37 per cent.

The central portions where the needle readily scratches contain austenite.

The question as to the relative hardness of the needle does not arise, for the scratches were all made by the same needle, and they all indicate, beyond the slightest shade of doubt, that austenite is considerably softer than hardenite. It resembles, in some of its properties, Hadfield's manganese steel after quenching, for both can be scratched with a needle, although they cannot be cut or machined by the hardest tool steels. Austenitic steel is relatively little susceptible to magnetic influences compared with hardenite, although not to the same extent as manganese steel.