# The Magnetic Transition Temperature of Cementite



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# X. *The Magnetic Transition Temperature of Cementite.* By S. W. J. SMITH, W. WHITE *and* S. G. BARKER.

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THE experiments described below were made upon a sample of steel kindly given to one of us, in 1908, by Prof. J. O. Arnold, of Sheffield. The steel had the following percentage composition :—

C=0·85, Si=0·05, Mn=0·06, S=0·03, P=0·02 and Fe (by difference)=98·99.

It was supplied in the form of rods, ½ in. in diameter, which nad been carefully annealed and were thus in a condition suitable for the extraction of the carbide of iron (cementite) from them by the method described by Arnold,* which we have followed.

Very little was known about the magnetism of cementite at the time when the material was obtained, and it was thought desirable to obtain further knowledge. It seemed obvious, for example, that a determination of the temperature at which iron carbide ceases to be magnetisable might prove useful in the attempts being made to analyse the effects of thermal treatment upon the properties of carbon steels.

An opportunity to carry out the intention of examining the thermomagnetic properties of cementite, by isolating it from the steel described above, did not present itself until last session, when the measurements given below were made in the Imperial College of Science.

In the interval the temperature at which cementite loses its magnetism had become known, approximately at least, through a measurement by Wologdine.† The material, suspended within a liquid of sufficiently high boiling point, formed a chain between the poles of an electromagnet, and the temperature to which the liquid could be raised before the chain broke down was observed to be 180°C.

Although this method is obviously only approximate, Wologdine appears to take the view that it is sufficient. He remarks that the loss of magnetic properties is progressive, and does not permit a more rigorous determination.

In the following year Maurain‡ found certain peculiarities,

* "Steel Works Analysis," 1898, pp. 326-330 ; also Chem. Soc. "Trans.," 1894, p. 788 ; "Journ." Iron and Steel Inst., 1910, Vol. I., p. 174.

† "Comptes Rendus," 1909, Vol. CXLVIII., p. 777.

‡ "Comptes Rendus," Vol. CL., 1910, pp. 777–780 ; also "Ann. de Chim. et de Phys." [8], Vol. XX., 1910, pp. 353–389.

at temperatures below 240°C. in the magnetisation curves of two steels containing about 0·2 and 0·9 per cent of carbon respectively. Discussing these peculiarities, he suggests that they are due to the thermomagnetic properties of cementite.

To account for the want of exact correspondence between his curves and the result given by Wologdine, he puts forward certain considerations to show why an exact correspondence is not always to be expected. These need not be given here, since we hope to show that the main cause of the discrepancy is the inexactness of Wologdine's result.

It is in fact misleading to regard 180°C. as a sufficient approximation to the temperature at which cementite loses its ferromagnetism. The actual temperature is much nearer 240°C.

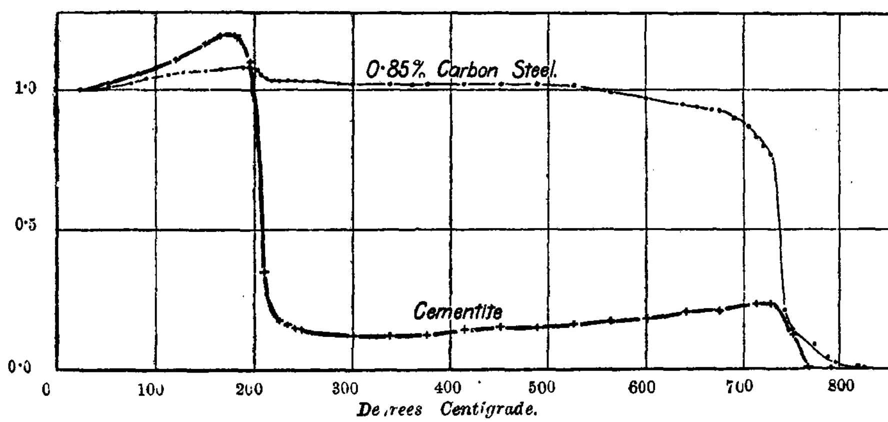


FIG. 1.

We may describe first some experiments which serve to indicate the extent to which we succeeded in extracting free cementite from the steel.

One of several sets of results is shown in Fig. 1. The thick-line curve refers to the cementite and the thin-line curve to a sample of the steel. The ordinates are magnetometer deflections at different temperatures, the deflection at the room-temperature being taken as the unit in each case.

The cementite was contained in a fused silica tube of about 0·5 cm. diameter and occupied about 20 cms. of its length. It was partially protected from the influence of the air by a plug of asbestos. A platinum rhodium thermojunction imbedded in the cementite was used to measure the temperature. The tube, placed along the axis of a magnetising solenoid kept cool by water circulation, was heated electrically. During the rise of temperature a steady current, sufficient to produce a field of about 100 units, traversed the solenoid. The silica tube lay at right angles to the meridian and pointed towards a magnetometer needle. The ordinates represent the deflections due to the cementite alone, other effects upon the needle being counterbalanced in the usual way.

The steel (a short tube) was examined in the same way as the cementite, the same apparatus being used to determine its temperature.

A glance at the curves shows a very pronounced drop (about 90 per cent.) in the magnetism of the cementite between 180°C. and 250°C. There is also a corresponding but very much smaller drop (about 5 per cent.) in the magnetism of the steel (which contains about 13 per cent. of cementite).

A comparison of the curves suggests that the isolation of the cementite was not quite complete, and that it still contained a small quantity of admixed steel. One or two attempts were made, without success, to obtain a specimen of cementite which would not exhibit any appreciable magnetism above 250°C. The failure may have been due to the fact that the susceptibility of the cementite beyond the transition temperature, although relatively very small, is still appreciable. It is much more likely, however, that the effects observed were due mainly to partial decomposition of the cementite after its isolation. We noticed that successive heatings of the cementite occasioned successive increases in the magnetisability above 250°. The cementite of Fig. 1 had been heated to 800° five times before the measurements to which the curve corresponds were made.

We now attempted to fix the transition temperature of the cementite more accurately and to find whether the change was reversible. The procedure was as before except that a copper constantan thermocouple was used to measure the temperature.

The lower half of Fig. 2 is a specimen of the results obtained during heating and cooling between 20°C. and 300°C. In this case the deflection was about 50 per cent. less at 250° than at 200° and the magnetic change was seen to take practically the same course during the rise and fall of temperature. It will be seen that the intensity of magnetisation was distinctly greater at 230° than at 240°. The arrangement was not sufficiently sensitive to decide whether there was any appreciable difference between the readings at 240° and 250°. A shorter and wider tube was used to contain the cementite in this experiment It was not noticed until the work had been completed that it would have been better to have used the tube already described.

The upper half of Fig. 2, arranged for comparison, shows the behaviour of the steel over the corresponding range in the same apparatus. The scale of ordinates, arbitrary as before, is arranged so that the drop between 200° and 250° (in this case roughly 10 per cent.) is about the same in actual length as the larger (50 per cent.) drop in the cementite.

The upper and lower curves taken together serve to show

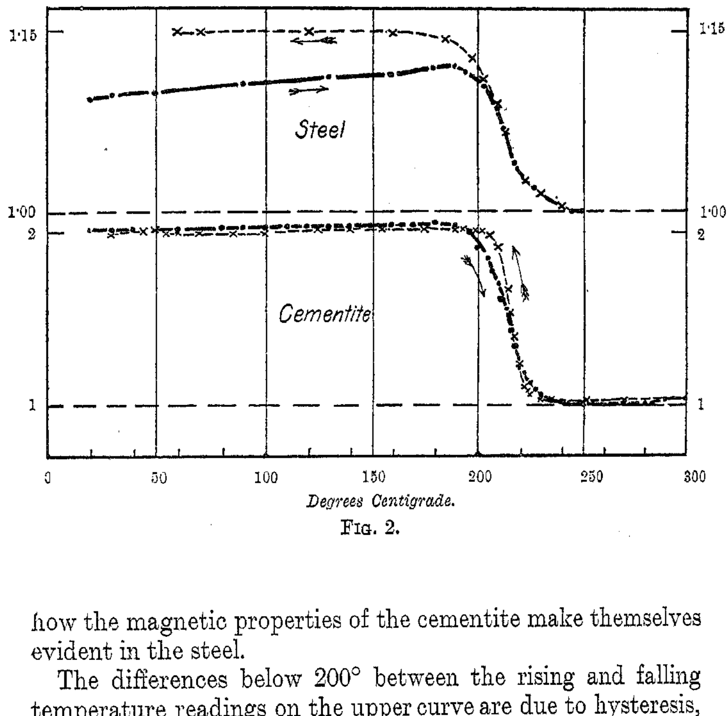


Fig. 2.

how the magnetic properties of the cementite make themselves evident in the steel.

The differences below 200° between the rising and falling temperature readings on the upper curve are due to hysteresis, and arise from the method of experiment. A small ring was constructed from a portion of one of the rods, and the permeability of the material in different fields was measured by the ballistic method.

The results for fields of 14 and 3·3 C.G.S. units respectively are shown in Fig. 3. Rising temperature observations are marked by dots and falling temperature observations by crosses. The ordinates in this figure give the approximate intensities of magnetisation in C.G.S. units, the scales for the stronger and weaker fields being shown on the left and right respectively.

The dotted curve in the figure represents the behaviour of the steel after quenching from about 1000°C., in a field

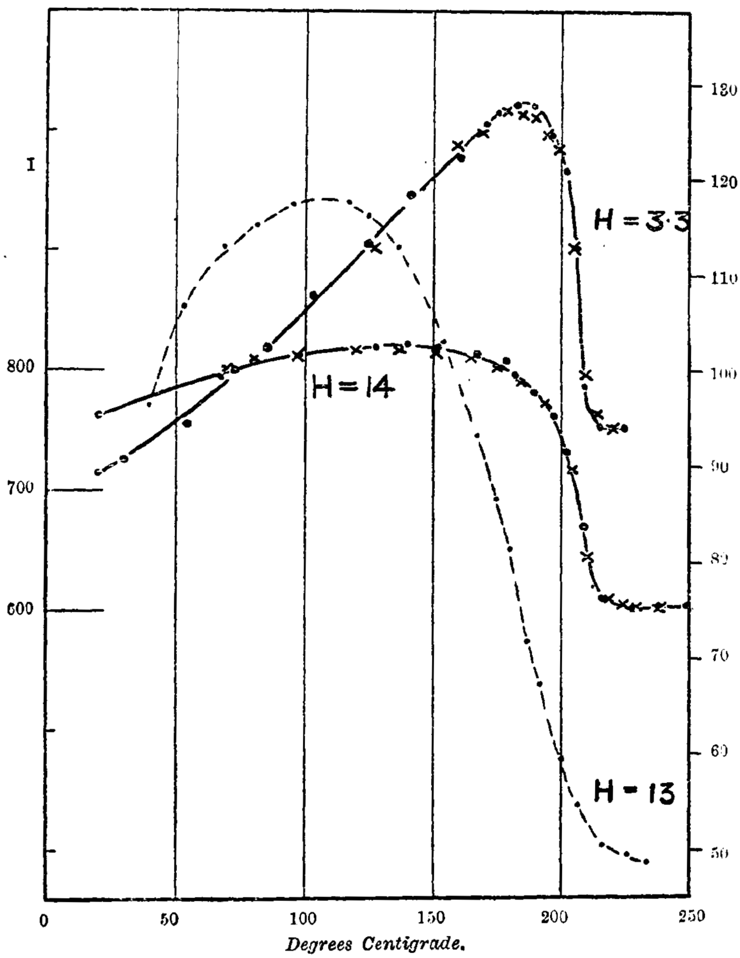


FIG. 3.

**H** = 13 C.G.S., during heating from 40°C. to 235°C. It is one of a series of results which we hope to describe at a later date. The scale of **I** for this curve is the same as that for the annealed steel in the field **H** = 3·3.

In conclusion we may indicate a modification of Wologdine's method, which has some obvious advantages and may be useful in other cases. It affords a very simple way of confirming the cementite curve of Fig. 2.

A small quantity of the material is dropped into a test tube containing melted paraffin wax. This tube, preferably surrounded by a thin copper sheath open at the sides, is placed between the conical pole pieces of an electromagnet, the bottom of the tube being a few centimetres below the pole ends. The temperature of the tube is raised to about 300°C. by a small Bunsen burner placed in a recess at the bottom of the sheath, and observations are made while, after lowering or removing the burner, the material cools. Successive experiments are made with different exciting currents in the electromagnet coils.

When the current is above a certain value the cementite rises from the bottom of the tube into the space between the pole pieces, immediately after the circuit is completed, although the temperature is still 300°C. The magnetic susceptibility of the (partially decomposed) particles is sufficient to enable the field to raise them against gravity.

Lowering the current step by step, a range of field strengths is reached over which the cementite does not rise until a temperature, quite sharply marked in each case, is attained. This temperature lies between about 240°C. and 200°C. for the range of fields in question—the particles rising sooner the higher the field.

In any field weaker than that which causes it to rise at 200°C., the cementite remains at the bottom of the tube even when the temperature has fallen below 100°C.

These results are clearly in agreement with Fig. 2, and show how the beginning and the end of the interval, over which the susceptibility of the cementite varies rapidly, can be fixed quite easily. The same arrangement can be used to show the presence of cementite in " cast-iron " filings.

ABSTRACT.

The temperature at which cementite (carbide of iron) loses its ferromagnetism is determined sufficiently accurately for purposes of thermomagnetic analysis and examples are given to show the possibility of using the thermomagnetic properties of cementite to determine whether that substance is present in any iron-carbon alloy.

## DISCUSSION.

Prof. S. P. THOMPSON has communicated the following remarks upon this Paper : The authors do not say how they in fact extracted the cementite from the steel experimented upon, neither do they give any analysis of its composition. The steel used is stated to contain 0·85 per cent. of carbon. It therefore contained little free cementite, since a steel of that composition is nearly a pure pearlite with a slight excess of ferrite. It would be interesting to know whether similar results are obtained with cementite derived from a steel containing a higher percentage of carbon, and therefore consisting of cementite and pearlite.

Prof. J. O. ARNOLD remarked that he had read the valuable and interesting Paper by Dr. Smith and Messrs. White and Barker with much pleasure, since the physical results obtained agreed in a remarkable manner with hundreds of thermo-metallurgical observations made in the Sheffield University laboratories. In Fig. 1 the sudden drop in the magnetism of the nearly saturated steel was coincident with the thermal transformation of pearlite to hardenite, which commenced about 728°C. and was complete at 732°C. In other words, at Osmond's combined range $A_c$ (1-2-3). In connection with the chemical-physics of the case it was well to remember that the cementite experimented upon by the authors was "B" cementite precipitated in the mass on cooling at 695°C. "A" cementite or the cementite of supersaturation commenced to precipitate at about 900°C., and though the chemical formula of both varieties was $Fe_3C$, containing 6·6̇ per cent. carbon, the physical properties were different. Arnold and Read had shown by electrolysis that the "A" carbide was electronegative to the "B" or low temperature cementite dealt with by the authors.

The SECRETARY : In reply to Prof. Thompson's first remark, it should be said that full details of the method of preparing cementite which we employed are given in the book to which we refer. A specimen chemical analysis is also referred to. For convenience in working we used considerable quantities of the material, and there is no doubt that it was not quite pure. Fig. 1, while showing the effect of these impurities, is sufficient to establish the particular property of cementite about which we have written.

The question of the chemical individuality of cementite is frequently raised. It is tersely summarised by Prof. Arnold on p. 268 of Vol. I. of the "Journal" of the Iron and Steel Institute for 1911. The present experiments indicate a new thermomagnetic proof of the thesis which Prof. Arnold there maintains. Already a fair number of materials containing widely different percentages of carbon (and including cast-irons) have been examined thermomagnetically. In every case, in which a sufficient number of observations has been made, peculiarities have been observed between 150°C. and 300°C. Hopkinson makes no mention of such peculiarities in his well-known Papers ; but if his curves be examined it will be seen that he made scarcely any measurements in the region in which the presence of cementite is disclosed.

Prof. Thompson raises the question of possible differences between the cementite existing as patches in hyper-eutectoid steels and the lamellar cementite of pearlite, and suggests extraction of the "structurally free" cementite from a high carbon steel. It has to be remembered that much of the carbon of high carbon steels is apt to separate as graphite during annealing, and that, even if this difficulty were overcome, the task of separating two kinds of cementite between which there is no very sharp line of demarcation would still remain. A steel containing twice as much carbon as that we used would still contain almost as much of our cementite as of the other. A question similar to Prof. Thompson's has been considered from the chemical point of view by Saniter amongst others. So far as he could decide, free—*i.e.*, isolated—cementite has the same chemical composition whether relatively coarse-grained or fine. Without committing ourselves, we should be inclined to think that, except perhaps when the carbide is very finely divided, no considerable variation of the present property with size is likely. The question turns upon the relative importance of the surface properties. Prof. Arnold's remarks upon the electrochemical difference between the two kinds of cementite are very interesting in this connection. Surface energy sometimes plays an important part in electrolytic phenomena, and it would produce a difference between the two cementites of the kind which Profs. Arnold and Read have observed. Unless the surface energy is an important modifying influence it seems to us that two structurally different kinds of cementite cannot exist in equilibrium with ferrite except at one particular temperature. Otherwise (as may be the case) the usual interpretation of the phase rule must apparently fail when applied to iron and iron carbide.

Prof. Arnold's expression of interest in the steel curve of Fig. 1 makes us regret that, to avoid confusion, we omitted from that figure the magnetometer deflections observed during cooling. The magnetism of the steel increased as rapidly between 700 deg. and 690 deg. during cooling as it fell near 730 deg. during heating. In contrast with these phenomena, there was no appreciable difference between the temperatures at which the magnetism of the cementite was lost and regained. The eutectoid change is accompanied by changes in distribution of the carbide and iron in the material. The cementite change, on the other hand, is apparently of the same type as that which occurs in iron itself.

The cooling curve of the cementite of Fig. 1 (also omitted to avoid confusion) is instructive with regard to the impurities which the material contained. Part of the magnetism reappeared as soon as the temperature fell below about 770 deg. There was a similar small accession of magnetism at about 690 deg. The main portion of the magnetisability returned between 300 deg. and 200 deg. in the same way as it had disappeared.

There are many questions of interest arising out of the thermomagnetic properties of cementite. The present Paper deals only with one of them. We hope to return to others.