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Hot hardness of cementite

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The hot hardness was measured on the (010) plane of primary cementite in unidirectionally solidified iron–carbon, iron–carbon–chromium, and iron–carbon–boron alloys at temperatures up to 973 K, using a hot hardness tester equipped with an indenter-heating system. The hardness of paramagnetic cementite against temperature was represented by the Ito–Shishokin relation. On the other hand, the hardness of ferromagnetic cementite deviated to low values from the Ito–Shishokin relation found for paramagnetic cementite. This deviation occurred from magnetostriction, because the thermal softening coefficient of cementite was found to relate to the thermal expansion coefficient regardless of the magnetic state similar to that found with fcc and bcc metals. Chromium and boron increased the hot hardness of cementite.

1. Introduction

The hot hardness of primary cementite in a hypereutectic iron–carbon alloy over a range of specimen temperatures up to 973 K was measured by one of the present authors [1, 2], and found that the hot hardness varied discontinuously at and around the Curie temperature (see Fig. 1). This variation, accompanied by the magnetic transformation of cementite, was observed using an old type hot hardness tester equipped with an unheated indenter. Gove and Charles [3] pointed out the importance of heating the indenter to prevent localized chilling on indentation and indicated that the magnitude of a localized chilling caused by use of an unheated indenter on the measurement of iron hardness at high temperature was greater than 100 K. These authors also examined the relationship between the hardness of cementite and temperature in the temperature range up to 973 K [4]. They found no abnormality in the hardness–temperature relationship at the Curie temperature (see Fig. 1). There was a significant difference between the hardness–temperature plots obtained by Yakushiji *et al.* [2] and by Gove and Charles [4], even when the effect of an unheated indenter used by the former authors was taken into account.

Therefore, it was necessary for the present authors to measure the hot hardness of cementite accurately using a heated indenter and to ascertain whether the hot hardness of cementite was affected by the magnetic transformation. In the present work, hot hardness was measured on primary cementite in unidirectionally solidified iron–carbon, iron–carbon–chromium and iron–carbon–boron hypereutectic alloys, in the temperature range from room temperature to 973 K. The effect of chromium and boron on the hot hardness of cementite was also investigated.

2. Experimental procedure

Iron–carbon, iron–carbon–chromium and iron–carbon–boron alloy melts were prepared from electrolytic iron, electrode graphite, electrolytic chromium of 99.99% purity, and boron of 99.5% purity by vacuum induction melting. Each melt was cast into an exothermic mould which was placed on a copper chill to solidify unidirectionally. The alloys were Fe–4.54% C, Fe–4.38% C–2.81% Cr, and Fe–3.72% C–0.70% B. Rectangular specimens with dimensions 5 mm × 5 mm × 10 mm for hot microhardness measurement were cut out of the castings. The top surface of the specimens was prepared so as to be perpendicular to the freezing direction as shown in Fig. 2, including the cross-section of primary cementite in plate form. The section of primary cementite on this surface, therefore, became parallel to the

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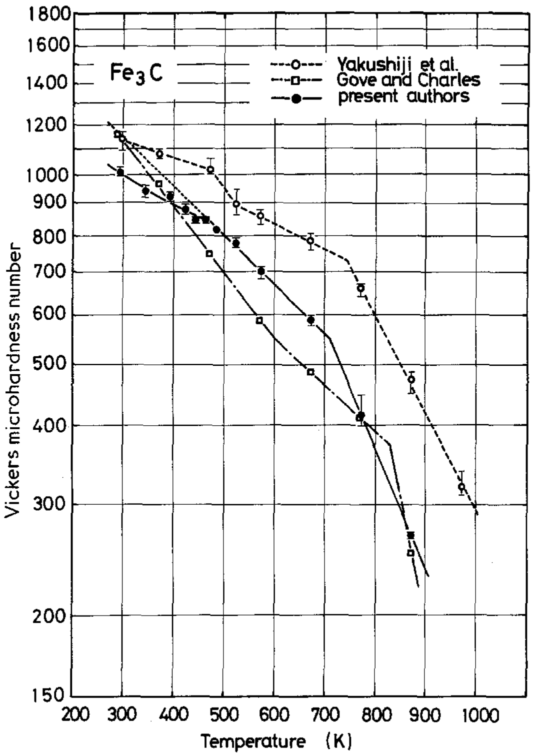

Figure 1 Hot hardness of cementite.

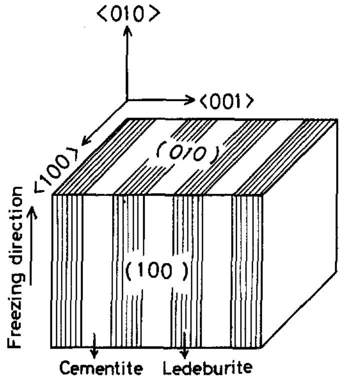

Figure 2 Schematic illustration of the structure of the specimens for hardness measurement.

(010) plane of cementite. Hardness measurement of cementite was carried out on this plane in vacuum. The width of the primary cementite plates was 30 to 60 μm. The hot hardness tester used was equipped with an indenter-heating device, the temperature of the indenter being controlled to be the same as that of the specimen. The load applied to the Vickers hardness indenter was 50 g for Fe–C alloy and 100 g for Fe–C–Cr and Fe–C–B alloys. The loading duration was 30 sec. A hardness value at every temperature up to 973 K was determined as the average of more than 10 indentations.

3. Results

The hot hardness values of each cementite in the three alloys were plotted on a logarithmic scale against temperature in Figs 1 and 3. Each of the plots of log hardness against temperature is composed of one curve and two lines. In general, these plots for a metal without any transformation are represented by the following Ito–Shishokin formula:

$$H_{\mathrm{V}} = A \exp(-BT),$$

where H_{V} is the Vickers hardness, T the temperature, A and B constants, having one set of values at low temperature and another set of values at high temperature. In this case, the plots of log hardness against temperature consist of two lines and the inflection point where the two lines intersect has been observed to be at the point corresponding to half the melting temperature of the metal. As the temperature of the metal is elevated, it has been stated that the controlling mechanism for deformation is changed from slip to diffusion at the inflection temperature.

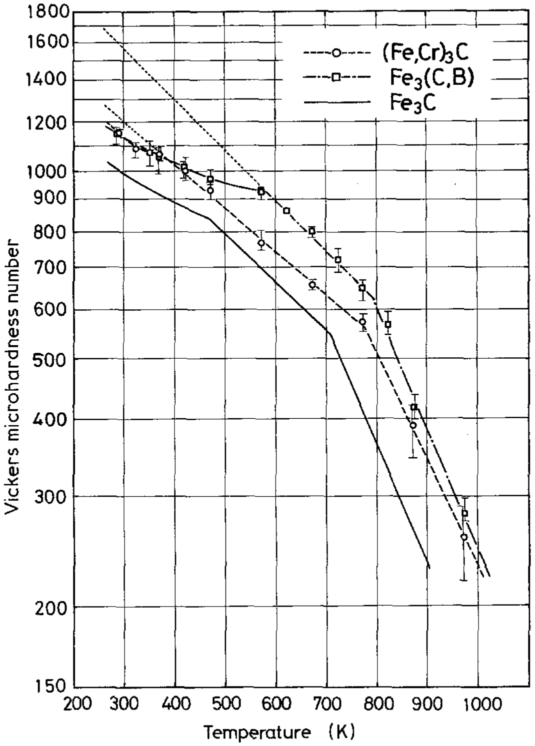

Figure 3 Hot hardness of cementite containing chromium or boron.

In the plot of log hardness against temperature for each cementite type there is a temperature at which a curve found at low temperatures, including room temperature, intersects with the line on the low-temperature side of the Ito–Shishokin relation. This temperature is concluded to correspond to the Curie point. For example, the intersecting temperatures for the cementites in the iron–carbon and iron–carbon–chromium alloys are about 473 and 365 K, respectively. On the other hand, the Curie points for the cementites without any alloying elements and with 5%* chromium should be 467 and 350 K, respectively, from the data obtained by the present authors [5, 6], agreeing with the above-mentioned intersection temperatures within experimental error.

The cementite in the iron–carbon–boron alloy has an intersection temperature at 583 K. If this temperature is equal to the Curie point, its cementite will contain ~ 1.5% boron. Nicholson [7] has shown that increasing the boron concentration in cementite raises its Curie point as opposed to chromium which lowers it.

The hot hardness of paramagnetic cementite that exists above the Curie point can be well represented by the Ito–Shishokin formula. The inflection temperatures for the cementites in the iron–carbon, iron–carbon–chromium, and iron–carbon–boron alloys are observed to be about 710, 775, and 793 K, respectively. Both the cementites containing chromium and boron are hardened as compared with the cementite in the iron–carbon alloy, and boron gives higher hardness values than chromium above 365 K.

On the other hand, the plot of log hardness against temperature for ferromagnetic cementite is concavely curved, and not linear. The hot hardness of ferromagnetic cementite is smaller than the values expected from the extrapolation of the hardness for paramagnetic cementite, which is illustrated by dotted lines in Figs 1 and 3. However, Yakushiji *et al.* [2] have shown the hardness of cementite to change discontinuously at and around the Curie point, whereas Gove and Charles [4] have obtained a log hardness–temperature plot which shows no change accompanied by the magnetic transformation. The latter authors also observed that upon indenting below about 470 K cementite frequently cracked, and thus the cementite had anomalously low hardness values. In the present study, however, no cracks were observed even on indenting at room temperature. The concave plots for ferromagnetic cementite, therefore, could not be attributed to cracking and should be due to the intrinsic nature of the ferromagnetic cementite.

4. Discussion

Primary cementite, which is formed at high temperatures in cast iron, has a carbon concentration lower than eutectoid cementite with stoichiometric composition [5, 6, 8]. When primary cementite is annealed below the eutectoid temperature, ferrite precipitates from it and the composition of the cementite approaches that of stoichiometry [8]. In addition to this, the Curie temperature of the cementite increases by about 20 K. The cementite, therefore, must be hardened by the heat-treatment, as described by Collins and Woodford [9] who have shown that the hardness of eutectic cementite equilibrated with iron solid solution at a lower temperature becomes larger than that of eutectic cementite formed at higher temperatures. In the present work, as-cast specimens were used for hardness measurement. Precipitation of ferrite in cementite as mentioned above occurred after 1 h holding at 773 K, and 30 min holding at 873 K for iron–4.3% carbon alloy [10]. Chromium retarded the ferrite precipitation [10]. The holding period employed in the present experiments was 20 min at each temperature and the effect of ferrite precipitation on the hardness of cementite might be small although the heat treatment was cumulative.

Petty and O'Neill [11] have investigated the hardness of metals in relation to their physical properties. They indicated the relationship shown in Fig. 4 where the thermal softening coefficient, which was equal to B at low temperatures in the Ito–Shishokin formula, was directly proportional to the thermal expansion coefficient, and the proportional constants depended on the types of atomic packing of the metals regardless whether the material was ferromagnetic or paramagnetic. The reason why the coefficients of thermal softening and thermal expansion for a material are closely related to each other may be due to the fact that both the coefficients are connected with the thermal variation of the atomic bonding energy of the material. To confirm the relationship found by Petty and O'Neill the hot hardness of the Invar alloy iron–36 wt % nickel whose Curie point was ~ 500 K [12], was investigated. The alloy ingot

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*The chromium concentration of the cementite was determined by electron microprobe analysis.

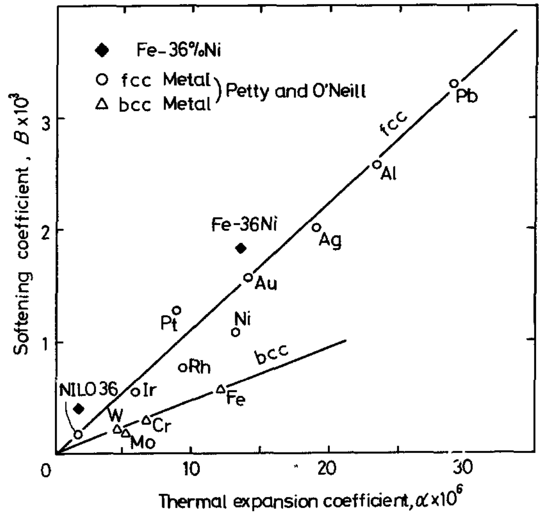

Figure 4 The relationship between the softening coefficient, B, and the thermal expansion coefficient, α, of metals and the iron–36% nickel alloy.

was homogenized at 1373 K for 20 h before the hardness measurement. The log hardness–temperature plot obtained is shown in Fig. 5 together with the thermal expansion data from Touloukian *et al.* [13]. It consists of two lines which intersect at the Curie point, denoted by T_c. The thermal softening coefficient, B, for the ferromagnetic state is much smaller than that for the paramagnetic state. The small value of B for the ferromagnetic state has already been reported by Petty and O'Neill. Thermal expansion data for the Invar alloy also show that the thermal expansion coefficient is much smaller for the ferromagnetic state than for the paramagnetic state, the so-called Invar property. The dotted curve in the figure was extrapolated from the values above the Curie point. The mean values of thermal softening and thermal expansion coefficients in the temperature range between 293 and 473 K were calculated for

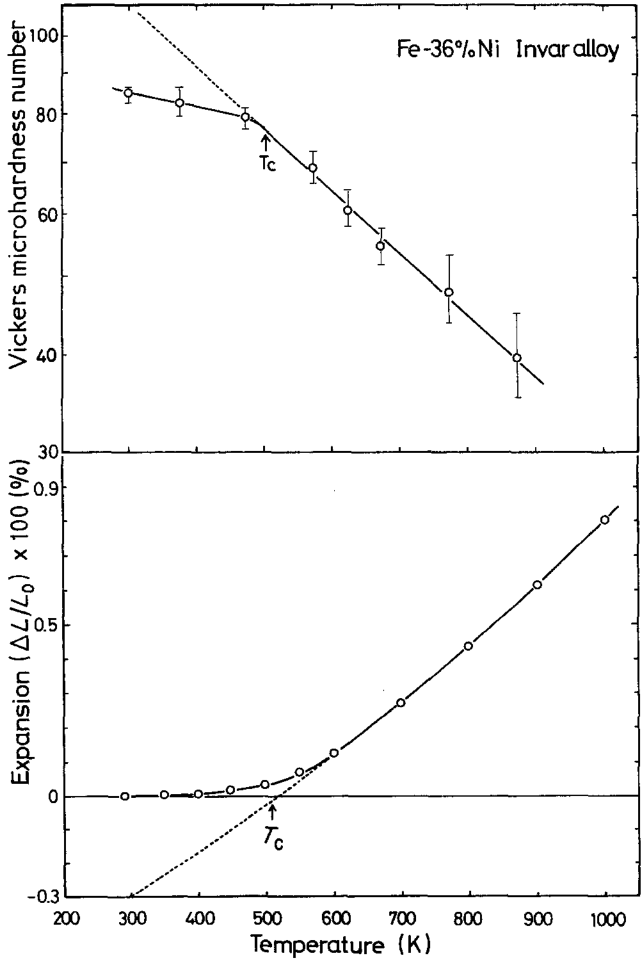

Figure 5 Hot hardness and thermal expansion of the iron–36% nickel alloy.

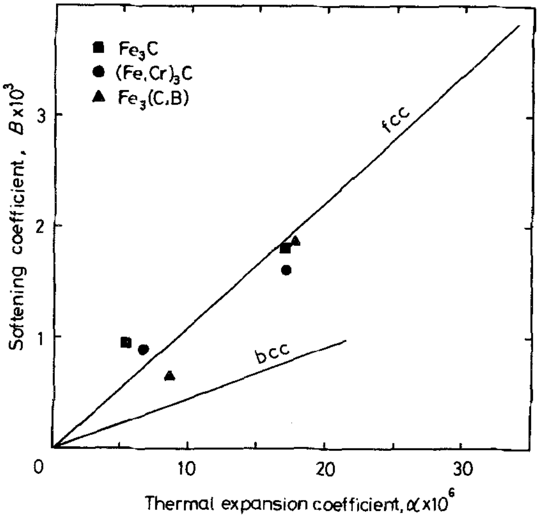

Figure 6 The relationship between the softening coefficient, B, and the thermal expansion coefficient, α, of cementites.

the ferromagnetic and paramagnetic states of the Invar alloy and could be plotted as one in a group of f c c metals in Fig. 4.

According to the relation given by Petty and O'Neill, the thermal softening coefficient of cementite should be smaller for the ferromagnetic state than for the paramagnetic state, because of a small thermal expansion coefficient for the former, which results from magnetostriction.

Fig. 6 shows the relationship between the thermal softening coefficient, B, and the thermal expansion coefficient, α, for each cementite in the specimens. The thermal expansion coefficients of the cementites were evaluated as mean values in the temperature range to 100 K below the Curie points from the plots of unit cell volume against temperature shown in Fig. 7 [6, 14]. In the figure, the dotted curves, which show the unit cell volume of paramagnetic cementite at low temperatures, were drawn by the same method as described previously [6]. As seen from Figs 1 and 3, the values of B for ferromagnetic cementite were not constant in the temperature range up to the Curie point. Therefore the mean values of B and α in the same temperature range to 100 K below the Curie points as the thermal expansion were calculated for ferromagnetic cementite. In Fig. 7, B was plotted against α. Although the data are scattered around a line passing through the origin, considering experimental error, it is concluded that B for cementite is related to α and that the relationship is independent of the magnetic state. Thus, it is reasonable that the hardness values for ferromagnetic cementite were lower than those expected from extrapolation of the data for paramagnetic cementite.

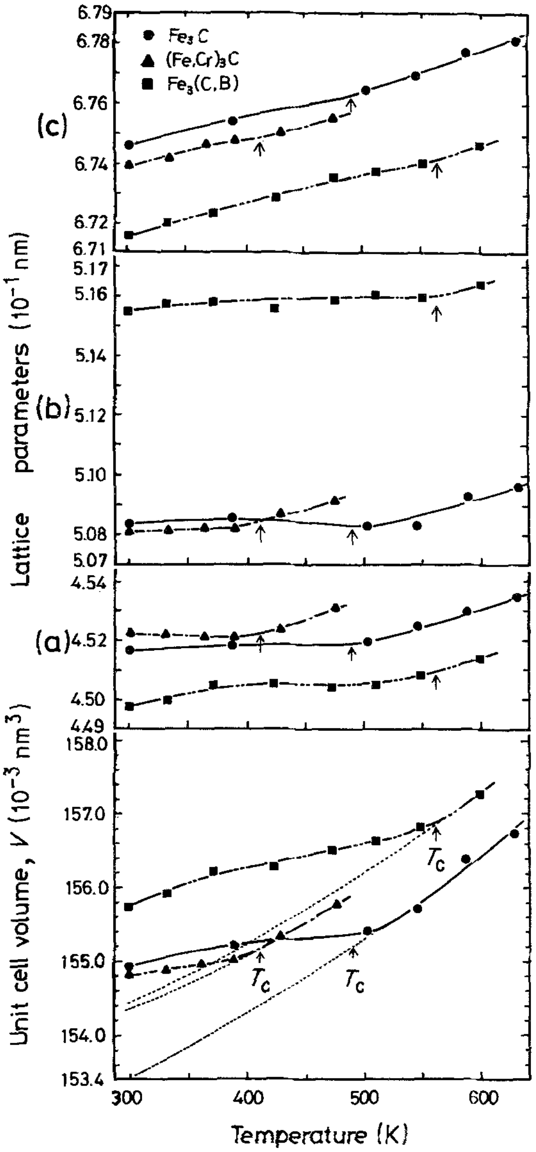

Figure 7 The variation in lattice parameters and unit cell volume of cementites with temperature.

It has been reported that the relationship of Young's modulus to temperature can be represented by a similar formula to the Ito–Shishokin relation for hardness and that a plot of Young's modulus against temperature has an inflection point at about half the absolute melting temperature of the metal. These facts suggest that there is a close connection between hardness and Young's modulus. Petty and O'Neill [11] have indicated that the hardness of fcc and bcc metals was proportional to Young's modulus regardless of the magnetic state. Drapkin and Fokin [15] estimated Young's modulus of cementite at temperatures up to 773 K from the data on Young's modulus for iron–carbon alloys with different carbon contents and showed that it became a maximum at and around the Curie point and was influenced by the magnetic state in a similar way to that of the hot hardness.

5. Conclusion

The hardness of primary cementite in iron–carbon, iron–carbon–chromium, and iron–carbon–boron alloys was measured in the temperature range up to 973 K. The hot hardness of paramagnetic cementite was represented by the Ito–Shishokin formula. The inflection temperature in the log hardness against temperature plot for the cementite in the iron–carbon alloy was observed at about 710 K. Either addition of chromium or boron into the iron–carbon alloy increased the hot hardness of cementite and raised the inflection temperature to a high value. The thermal softening coefficient of ferromagnetic cementite was confirmed to become smaller than that of paramagnetic cementite. This could be attributed to a small thermal expansion coefficient of the ferromagnetic cementite, which was due to magnetostriction. It was, therefore, concluded that the hardness of cementite was affected by the magnetic transformation.

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