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Hot hardness of $(Fe,Cr)_3C$ and $(Fe,Cr)_7C_3$ carbides

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Hot hardness was measured on the primary carbides, $(Fe, Cr)_3C$ and $(Fe, Cr)_7C_3$, in unidirectionally solidified iron–carbon–chromium hypereutectic alloys with chromium more than 4.8 wt %. The hardness–temperature relation was represented by two Ito–Shishokin formulae, $H_v = A \exp(-BT)$, and thus was drawn by two lines on a semi-logarithmic graph. The inflection temperature where the two lines intersected was found at 730 to 860 K for $(Fe, Cr)_3C$ carbide containing 0 to 14 wt % Cr, increasing with an increase in the chromium concentration in the carbide, and at about 910 K for $(Fe, Cr)_7C_3$ carbide containing 36 to 76 wt % Cr. With increasing chromium concentration in each carbide, the hardness of the carbide increased and the thermal softening coefficients decreased. The effect of chromium on the hardness, the inflection temperature and the thermal softening coefficients was more pronounced for $(Fe, Cr)_3C$ carbide than for $(Fe, Cr)_7C_3$ carbide. Each of the thermal softening coefficients, $B_1 (T < T_t)$, $B_2 (T > T_t)$, the inflection temperature, T_t, room-temperature hardness, $H_v(T_{RT})$, and the hardness at T_t, $H_v(T_t)$, related linearly to the chromium concentration in the carbides, and hence the hot hardness of the carbides could be expressed as functions of temperature and chromium concentration in the carbides. The relationships between $H_v(T_{RT})$ and $H_v(T_t)$ and between the thermal softening coefficient, B_2, and the activation energy for creep, Q_c (kJ mol^{-1}), were represented by the following equations:

$H_v(T_t) \simeq 0.7 H_v(T_{RT})$, $B_2 = 1.26/Q_c$.

1. Introduction

In abrasive wear, a severer loss of materials occurs than in other types of wear, i.e. adhesive wear, corrosive wear and fatigue wear. Abrasive wear resisting white cast irons contain hard constituents in a relatively soft matrix, and the wear resistance of the material is severely influenced by the properties of the hard constituents as well as the shape and distribution of the constituents. Abrasive wear of white cast iron should be related to the hardness of iron carbides in the iron which are responsible for the wear resistance of the iron. Commercial white irons generally contain chromium as an alloying element, and M_3C and M_7C_3 type carbides are found in the alloyed iron. Room-temperature Vickers hardness numbers of the carbides are 1060 to 1240 for M_3C carbide and 1500 to 1800 for M_7C_3 carbide [1]. The carbides are harder than quartz, which has hardness values of 800 to 1000 and is one of the hard minerals.

Wear resisting materials suffer heat caused by friction on the surface and the surface temperature of the materials is sometimes raised significantly. High chromium steels and cast irons are also utilized where heat and corrosion resistance are required. The carbides are, therefore, important constituents in these materials. From this view point, information on hardness of carbides at elevated temperature is important. The hot hardness of cementite in unalloyed white cast iron has been investigated by two of the present

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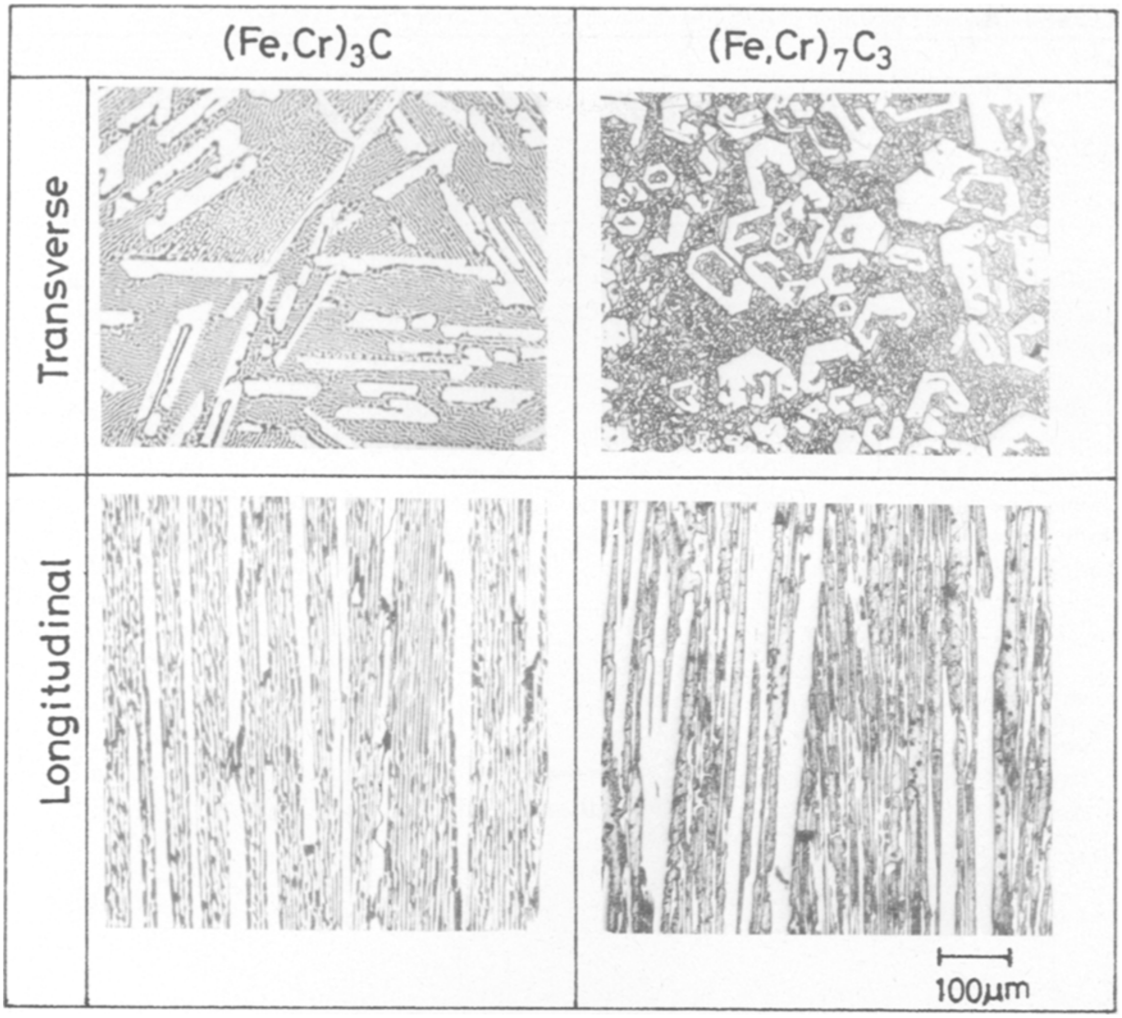

Figure 1 Microstructures of $(Fe, Cr)_3C$ and $(Fe, Cr)_7C_3$ carbides on transverse and longitudinal sections of alloys Fe–C–5Cr and Fe–C–30Cr.

authors [2]. However, the effect of chromium on the hot hardness of cementite and M_7C_3 carbide is unknown. In the present work, the hot hardness of $(Fe,Cr)_3C$ and $(Fe,Cr)_7C_3$ carbides was measured in the temperature range up to 1173 K on the primary carbides in unidirectionally solidified iron–carbon–chromium hypereutectic alloys and the relation between the hardness and the chromium concentration in the carbide was examined.

2. Experimental details

Iron–carbon–chromium hypereutectic alloys were prepared from electrolytic iron, electrode graphite and electrolytic chromium of 99.9% purity by vacuum induction melting and then by casting the melts into steel moulds of inside diameter 10 mm. Each casting was unidirectionally solidified by zone melting at a zone-travelling velocity of 2.5×10^{-7} m sec^{-1} under an argon atmosphere. The chemical composition of the alloys is given in Table I, including two chromium levels of $(Fe,Cr)_3C$ carbide, and three chromium levels of $(Fe,Cr)_7C_3$ carbide. Microstructures of both types of carbide on the transverse and longitudinal sections of two alloys are shown in Fig. 1. Micro-vickers hardness was measured on the (010) plane of primary $(Fe,Cr)_3C$ carbide and on the (001) plane of primary $(Fe,Cr)_7C_3$ carbide on the transverse section in vacuum. The load applied to the indenter was 50 g and the loading duration was 30 sec. The hardness value, which was determined as an average of 10 indentations, was measured as a function of temperature in the

TABLE I Chemical composition of alloys and chromium concentration in primary carbides

Alloy	C %	Cr %	Primary carbide	Cr % in carbide
Fe–C–5Cr	4.73	4.80	$(Fe,Cr)_3C$	7.58
Fe–C–10Cr	4.44	9.35	$(Fe,Cr)_3C$	14.2
Fe–C–20Cr	4.96	20.2	$(Fe,Cr)_7C_3$	36.1
Fe–C–30Cr	4.83	29.2	$(Fe,Cr)_7C_3$	58.5
Fe–C–40Cr	4.47	39.0	$(Fe,Cr)_7C_3$	76.5

range from room temperature to 973 K for $(Fe,Cr)_3C$ carbide and to 1173 K for $(Fe,Cr)_7C_3$ carbide.

3. Results

Hardness values of $(Fe,Cr)_3C$ and $(Fe,Cr)_7C_3$ carbides are plotted on a logarithmic scale against temperature in Fig. 2. The relationship between hardness and temperature was expressed by the Ito–Shishokin formula

$$H_v = A \exp(-BT) \qquad (1)$$

where H_v is the Vickers hardness, T the temperature, A and B constants. The hardness–temperature relation usually consists of two lines and thus has two sets of A and B values. It has been described that the concave curve found at low temperatures for M_3C type carbides free from chromium and with the lowest chromium concentration is attributed to the ferromagnetism of the carbides [2]. The inflection point where two lines intersect must correspond to about half the melting point of a carbide, as is the case for metals. The hardness and the temperature at the

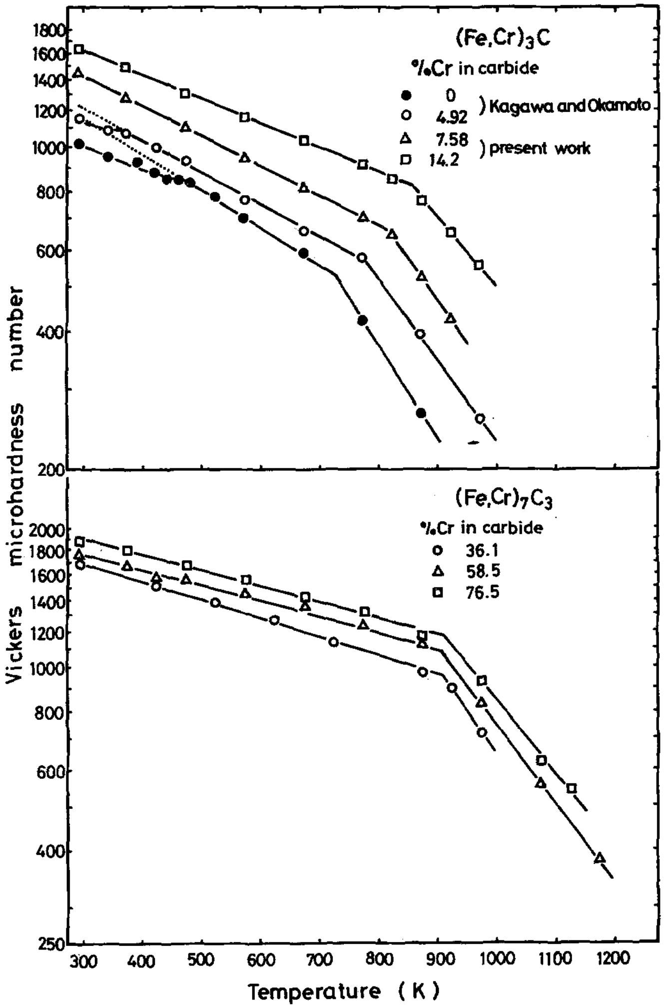

Figure 2 Hot hardness of (a) $(Fe,Cr)_3C$ and (b) $(Fe,Cr)_7C_3$ carbides.

TABLE II Summary of the results obtained

Alloy	A_1	A_2	$B_1 \times 10^3$	$B_2 \times 10^3$	T_t(K)	$H_v(T_{RT})$	$H_v(T_t)$
Fe–C	1207	4260	1.79	4.63	730	1013	520
Fe–C–3Cr	1264	4249	1.60	3.99	780	1148	561
Fe–C–5Cr	1487	6513	1.49	4.20	820	1445	659
Fe–C–10Cr	1666	14930	1.20	3.40	860	1622	821
Fe–C–20Cr	2236	24235	0.94	4.50	911	1674	953
Fe–C–30Cr	2197	34655	0.75	3.92	908	1755	1086
Fe–C–40Cr	2425	33303	0.80	3.68	910	1881	1166

inflection point shifted to higher values with increasing chromium concentration in the carbides. The values of constants, A and B, the hardness, $H_v(T_{RT})$, at room temperature (T_{RT}), the hardness, $H_v(T_t)$, and the temperature, T_t, at the inflection point, are listed in Table II, where the subscripts 1 and 2 are used to denote the results below and above the inflection points, respectively.

The chromium concentration of the primary carbides determined by electron microprobe analysis is given in Table I. The relations between chromium concentrations in carbide and alloy are shown for the two types of carbide in Fig. 3.

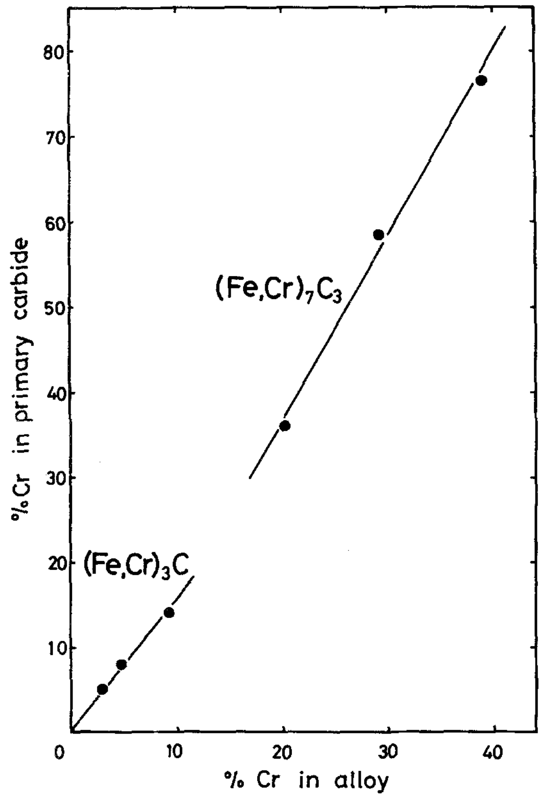

Figure 3 Relationship between chromium concentrations in carbide and in alloy.

The relations were almost linear and the ratio of the chromium concentration in the carbide to that in the alloy was about 1.5 for (Fe, Cr)$_3$C carbide and about 1.9 for (Fe, Cr)$_7$C$_3$ carbide. Hardness values given in Fig. 2 were plotted against chromium concentration in the carbides in Fig. 4. The chromium concentration dependence of the hardness was larger for (Fe, Cr)$_3$C carbide than for (Fe, Cr)$_7$C$_3$ carbide. The former carbide can contain chromium up to about 15 wt% and the lowest chromium concentration in the latter carbide is about 36 wt% [3]. It is noted that the room-temperature hardness of (Fe, Cr)$_3$C carbide containing 15 wt% Cr is comparable to that of (Fe, Cr)$_7$C$_3$ carbide containing 36 wt% Cr, although it has been reported that M$_7$C$_3$ carbide is harder than M$_3$C carbide [4].

The values of A_1, A_2, B_1, B_2, T_t, $H_v(T_{RT})$ and $H_v(T_t)$ given in Table II were plotted against the chromium concentration of the carbides in Fig. 5. There existed a good correlation between each of them, excluding the A_2 value for (Fe, Cr)$_7$C$_3$ carbide, and the chromium concentration, while poor correlations were observed between the A_2 value and the chromium concentration because the A_2 value was extrapolated from limited data. With increasing chromium concentration in the carbides, the values of B_1 and B_2 decreased, while the other values increased. The effect of chromium on these values is more pronounced for (Fe, Cr)$_3$C carbide than for (Fe, Cr)$_7$C$_3$ carbide. The hot hardness values of (Fe, Cr)$_3$C and (Fe, Cr)$_7$C$_3$ carbides were formulated as a function of the chromium concentration in the carbides as follows.

For (Fe, Cr)$_3$C, $T_C < T < T_t$ (Curie point, $T_C = 200 - 24.55[\%\mathrm{Cr}]$ [5], $T_t = 726 + 9.24[\%\mathrm{Cr}]$):

$$H_v = (1006 + 45.08[\%\mathrm{Cr}])\exp\{-(1.80 \times 10^{-3} - 4.158 \times 10^{-5}[\%\mathrm{Cr}])(T - 293)\} \qquad (2)$$

$T > T_t$:

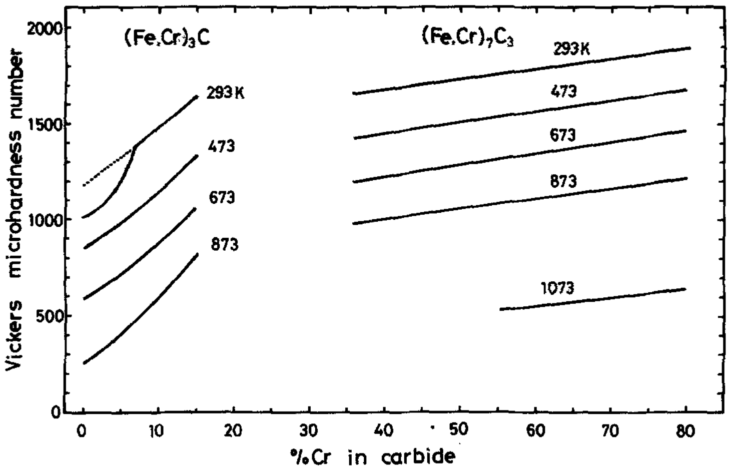

Figure 4 Effect of chromium on the hardness of (Fe,Cr)$_3$C and (Fe,Cr)$_7$C$_3$ carbides.

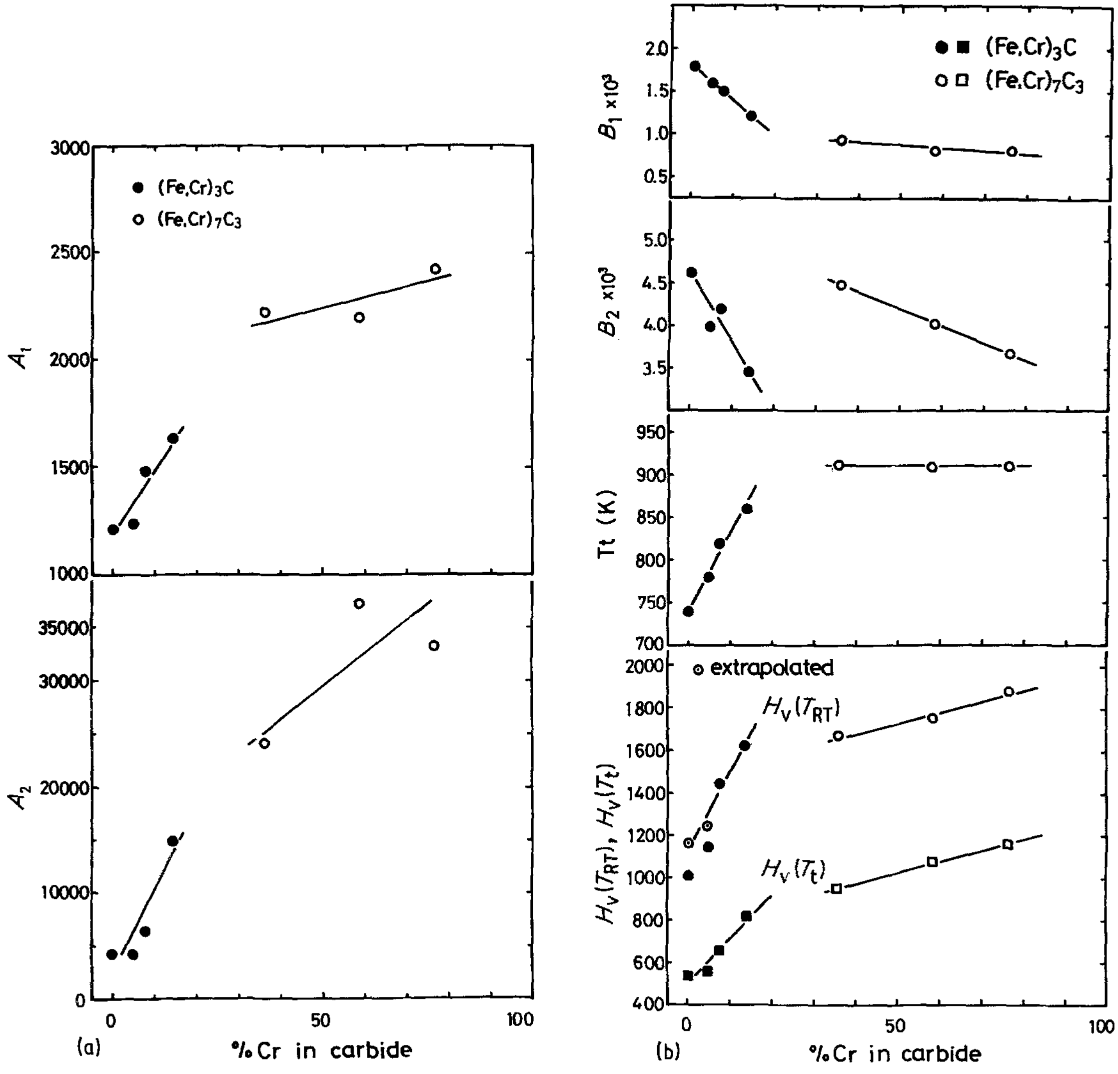

Figure 5 Variations of thermal softening coefficients, inflection temperature, T_t, room-temperature hardness, $H_v(T_{RT})$, and hardness $H_v(T_t)$ at inflection temperature with chromium concentration in carbides.

$$H_v = (510 + 20.42[\%\mathrm{Cr}] \exp \{-(4.56 \times 10^{-3} - 7.030 \times 10^{-5} [\%\mathrm{Cr}])[T - (726 + 9.24[\%\mathrm{Cr}])]\} \quad (3)$$

For $(\mathrm{Fe,Cr})_7\mathrm{C}_3$, $(T_t \simeq 910)$, $T < T_t$:

$$H_v = (1481 + 5.06[\%\mathrm{Cr}])\exp\{-(1.052 \times 10^{-3} - 0.360 \times 10^{-5} [\%\mathrm{Cr}])(T - 293)\} \quad (4)$$

$T > T_t$:

$$H_v = (766 + 5.30[\%\mathrm{Cr}]) \times \exp \{-(5.239 \times 10^{-3} - 2.030 \times 10^{-5} [\%\mathrm{Cr}])(T - 910)\} \quad (5)$$

4. Discussion

The hot hardness test is available for industrial use to estimate high temperature mechanical properties of materials. The correlations of hardness with tensile strength, yield point, compressibility, creep characteristics, elastic modulus, and electrical and magnetic properties have been investigated by many workers [6–11]. On the other hand, some quantitative researches on the hardness–temperature relationship of materials have been developed [12–18]. The relationship for a pure metal has been represented in the form of Equation 1 given by Ito [16], Shishokin [17] and Westbrook [19], consisting of two lines which intersect at about half the melting point of the metal.

Values of A_1 which are the extrapolated hardness values at absolute temperature zero are considered as an intrinsic hardness of the concerned materials and may relate to the inherent strength of interatomic bonds in the crystal lattice and thus correlate with the melting point of the crystal. Westbrook [19] has indicated that there exists a linear relationship between the A_1 value and the melting point for pure metals and that the slope depends on crystal structure. A correlation between the B_1 value and the reciprocal melting point has been found by Westbrook [19]. Furthermore, the inflection temperature, T_t, has been described to be about half the melting point of a metal. In the case of carbides, for example, the melting point of $\mathrm{Fe_3C}$ carbide is 1500 K [20] and the ratio of the inflection temperature to the melting point is about 0.5, the value having been observed for pure metals. Therefore, room-temperature hardness, $H_v(T_{RT})$, should relate to the hardness, $H_v(T_t)$, at the inflection point. Values of $H_v(T_{RT})$ were plotted against values of $H_v(T_t)$ in Fig. 6, where the data points for pure metals [21] were involved. The slope of the log–log plot of $H_v(T_{RT})$ against $H_v(T_t)$ was about unity and the relation was represented by

$$H_v(T_t) \simeq 0.7 H_v(T_{RT}) \quad (6)$$

The deformation is controlled by slip below the inflection temperature and is governed by diffusion above it [22]. Petty and O'Neill [10] have indicated that a linear relation exists between the reciprocal of the thermal softening coefficient below the inflection temperature, B_1, and the activation energy, Q_d, for self-diffusion of pure metals. On the other hand, Kumagai and Kayaba

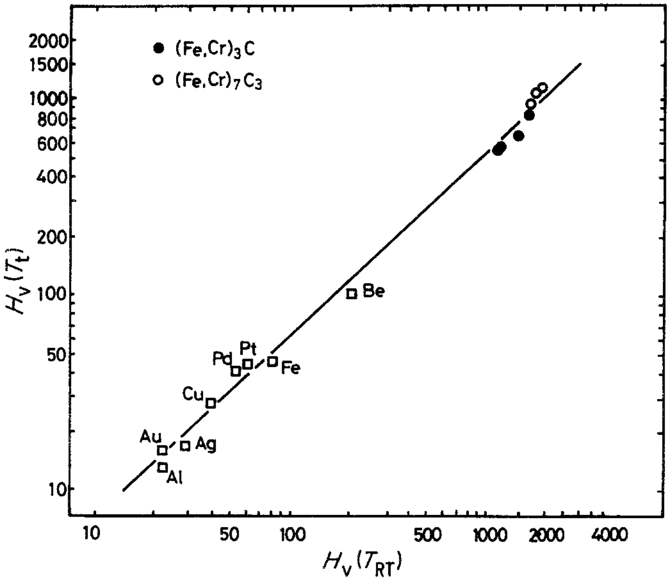

Figure 6 Relation between room-temperature hardness $H_v(T_{RT})$ and hardness $H_v(T_t)$ at inflection temperature.

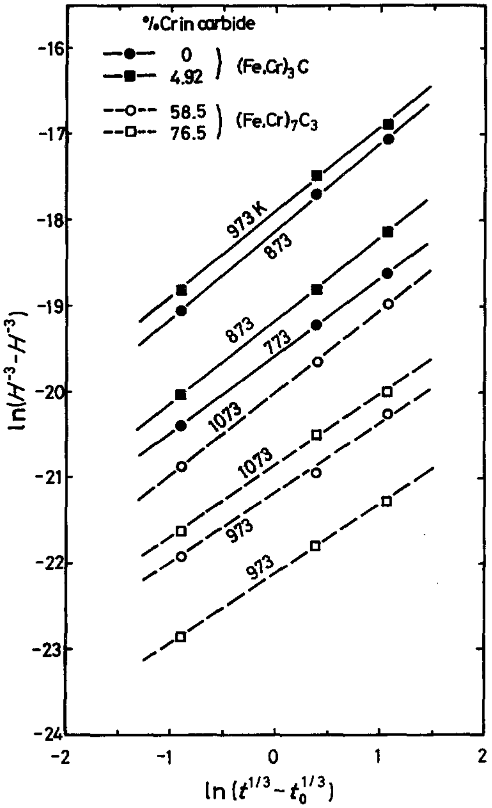

Figure 7 Log–log plots of $(H^{-3} - H_0^{-3})$ against $(t^{1/3} - t_0^{1/3})$ for carbides from time-dependent hardness measurements.

[23] have pointed out that the reciprocal of the thermal softening coefficient above the inflection temperature, B_2, for pure metals is also proportional to the activation energy, Q_d. It has been indicated that the activation energy for self-diffusion is almost equal to that for creep, Q_c, in pure metals [24]. Therefore, to examine the relation between the activation energy for creep and the thermal softening coefficients, B_1 and B_2, of the carbides used, the time-dependent hardness of the carbides was measured to determine the activation energy for creep. A hardness–time relation has been represented by the following equation [25]:

$$H^{-3} - H_0^{-3} = k(t^{1/3} - t_0^{1/3}) \exp(-Q/3RT) \quad (7)$$

where H is the hardness at time t, H_0 the hardness at time t_0 when it attains the full load, Q the activation energy, R the gas constant, T the temperature, and k a constant. From Equation 7, we obtain,

$$\ln(H^{-3} - H_0^{-3}) = \ln k + \ln(t^{1/3} - t_0^{1/3}) - Q/3RT \quad (8)$$

The hardness of (Fe,Cr)$_3$C and (Fe,Cr)$_7$C$_3$ carbides was measured at different loading durations. The load was 50 g and the time, t_0, was 6 sec. Log–Log plots of $(H^{-3} - H_0^{-3})$ against $(t^{1/3} - t_0^{1/3})$ for the carbides are shown in Fig. 7. The plots were linear and the slopes at different temperatures were approximately unity. From the interval between the two lines for each carbide, the activation energy was calculated and is given in Table III. The values of the activation energy for creep of (Fe,Cr)$_3$C and (Fe,Cr)$_7$C$_3$ carbides ranged between those for self-diffusion of γ-iron and of chromium [26], and increased with increasing chromium concentration in each carbide. In Fig. 8, the reciprocals of B_1 and B_2 were plotted against the activation energy determined from time-dependent hardness measurements. The data for pure metals from the literature [19, 21] are included in this figure. According to Kumagai and Kayaba [23], the relationship between the reciprocal of B_2 and the activation energy Q_d for pure metals is given by

$$B_2 = 0.75/Q_d \quad (9)$$

while Petty and O'Neill [10] have indicated that the relationship between the reciprocal of B_1 and the activation energy for creep may depend on

TABLE III Activation energy for M$_3$C and M$_7$C$_3$ carbides in Fe–C and Fe–C–Cr alloys determined from time-dependent hardness measurements

Specimen	Carbide	Activation energy for creep Q_c (kJ mol^{-1})
Fe–C	Fe$_3$C	254
Fe–C–3Cr	(Fe, Cr)$_3$C	269
Fe–C–5Cr	(Fe, Cr)$_3$C	290
Fe–C–30Cr	(Fe, Cr)$_7$C$_3$	313
Fe–C–40Cr	(Fe, Cr)$_7$C$_3$	330
		Activation energy for self-diffusion Q_d (kJ mol^{-1})
Gamma iron		270
Chromium		309

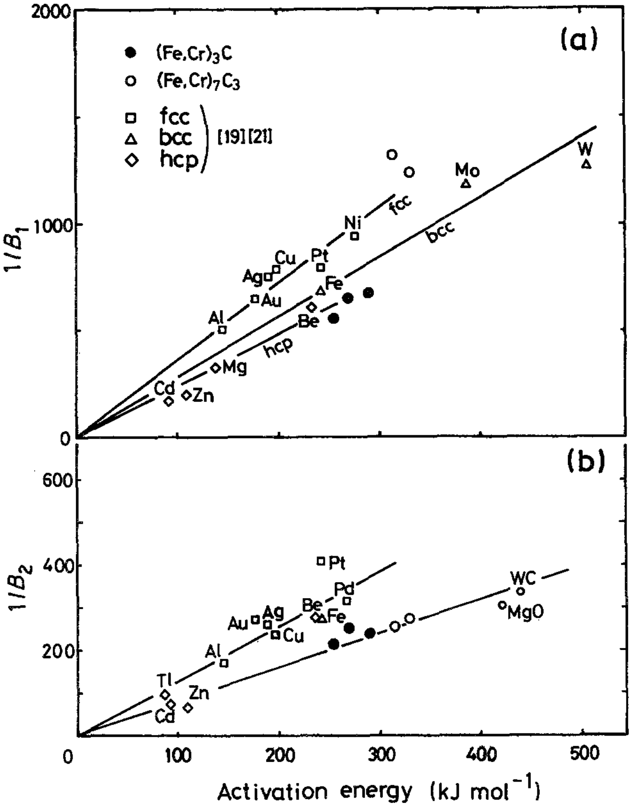

Figure 8 Relations between each of the reciprocal of thermal softening coefficients, $1/B_1$ or $1/B_2$, and the activation energy for self-diffusion or creep.

the crystal structure. In Fig. 8a, concerning B_1, the data points for $(Fe,Cr)_3C$ of orthorhombic structure fall near the line for hcp metals, while those for $(Fe,Cr)_7C_3$ of hcp structure are close to the relation for fcc metals. Even though the carbides had a crystal structure similar to that of pure metals, both materials would not belong to the same group, because the carbides involve covalent bonds but pure metals have only metallic bonds. In Fig. 8b, concerning B_2, the relationship for pure metals appears to be independent of the crystal structure of the metals, and the result for the carbides, WC(hcp) [9] and MgO (NaCl type) [9] deviates from the line for pure metals. The plots for these carbides appear to follow the relation

$$B_2 = 1.26/Q_c \qquad (10)$$

The correlation between the activation energy and the melting point for pure metals depends on crystal structure. The activation energy for M_7C_3 type carbides is given by the following equation:

$$Q_c = 0.17T_m \qquad (11)$$

where T_m is the melting point of the carbide. The value for Fe_3C deviates a little from the relation given by Equation 11. From Equations 10 and 11, the thermal softening coefficient, B_2, is related to the melting point in the following equation:

$$B_2 = 7.41/T_m \qquad (12)$$

It is, therefore, concluded that for $(Fe,Cr)_3C$ and $(Fe,Cr)_7C_3$ carbides, there is a close relationship between the thermal softening coefficient, B_2, and the activation energy for creep or the melting point of the carbides as given in Equations 10 and 12, and that the coefficient, B_2, can be estimated from these relationships.

5. Conclusion

On a semilogarithmic graph, the hardness–temperature relation for $(Fe,Cr)_3C$ and $(Fe,Cr)_7C_3$ carbides in hypereutectic iron–carbon–chromium alloys with chromium more than 4.8 wt% was represented well by two lines which intersected at an inflection point and were expressed by the Ito–Shishokin formula. With an increase in chromium concentration in each type of carbide, hardness of the carbides increased and the inflection temperature, T_t, was raised from 730 to 860 K for $(Fe, Cr)_3C$ carbide with 0 to 14 wt% Cr, while the inflection temperature for $(Fe, Cr)_7C_3$ carbide with 36 to 76 wt% Cr varied little at and around 910 K. The thermal softening coefficients, inflection temperature, T_t, room-temperature hardness $H_v(T_{RT})$ and hardness at the inflection temperature, $H_v(T_t)$, of M_3C or M_7C_3 carbide related linearly to the chromium concentration. Therefore, a relationship between $H_v(T_{RT})$ and $H_v(T_t)$ was obtained and was expressed by $H_v(T_t) \simeq 0.7 H_v(T_{RT})$. The activation energy for creep of these carbides was determined from time-dependent hardness measurements. It appeared to agree with the activation energy for self-diffusion of iron in the case of $(Fe,Cr)_3C$ carbide and with that of chromium in the case of $(Fe,Cr)_7C_3$ carbide. A relation existed between the activation energy and the reciprocal of the thermal softening coefficient above T_t, B_2, and hence the B_2 value depended on the melting point of carbide.

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