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High temperature and pressure preparation and properties of iron carbides Fe_7C_3 and Fe_3C

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The formation regions of Fe_7C_3 and Fe_3C were determined at high temperature and high pressure in the iron–graphite system. Fe_7C_3 formed at relatively higher pressures and Fe_3C at lower pressures. Both Fe_7C_3 and Fe_3C were isolated from coexisting excess carbon powders by a magnetic method. Fe_7C_3 had a Curie point of 250° C and a saturation magnetization of $120\,\mathrm{emu\,g^{-1}}$ at room temperature and Fe_3C had those of 210° C and $125\,\mathrm{emu\,g^{-1}}$. Fe_7C_3 decomposed to Fe_3C and carbon at 600° C, but to α-Fe and carbon at 700° C at atmospheric pressure, and Fe_3C to α-Fe and carbon at 700° C. The substitution of other metals (Cr, Mo and W) for iron in these carbides leads to changes in the thermal stabilities and the magnetic properties.

1. Introduction

Iron is one of the group VIII transition metals and used as solvent–catalyst for diamond synthesis. The behaviour of iron with carbon has been known to differ from cobalt and nickel in points of the formation of several carbides under atmospheric and high pressure conditions. Among iron carbides, Fe_3C (cementite), which is metastable to α-iron and graphite at atmospheric pressure, has been known to exist in white cast iron and also to form at high temperature and high pressure. The other carbide, Fe_7C_3 [1], which was previously believed to have the composition of FeC [2, 3] is formed only in small amounts under specific conditions such as hydrocarbon synthesis in the presence of iron, but is found to be stable at high pressure [3, 4].

The properties of Fe_3C were investigated in detail by metallurgists but those of Fe_7C_3 have not been studied as much because of the difficulties of preparation. Fe_7C_3 is suggested to be isomorphous to Cr_7C_3 and Mn_7C_3 [1] and have a ferromagnetic Curie temperature of about 250° C [2], compared with 210° C of Fe_3C [5]. Other properties, however, have not been measured. The formation and the stability of Fe_7C_3 have been reported to be critical to the diamond formation process in the iron–graphite system at 7 GPa [6].

In this work, the formation regions of Fe_7C_3 and Fe_3C were examined under high pressure and high temperature conditions to prepare the pure carbides by subsequent magnetic separation from the residual excess graphite. The Fe_7C_3 and Fe_3C prepared were observed under a scanning electron microscope (SEM) and their magnetic properties and thermal stabilities at atmospheric pressure were measured. The effect of substitution of other metals for iron on the properties was also investigated.

2. Experimental details

A girdle-type high pressure apparatus was used for the preparation of the iron carbides Fe_7C_3 and Fe_3C. Fig. 1 shows the arrangement of the pressure cell used. The determination of the formation region of each carbide and the preparation of Fe_7C_3 were carried out by the smaller cell (Fig. 1a), which enables higher pressures to 8 GPa to be generated. Fe_3C was prepared by

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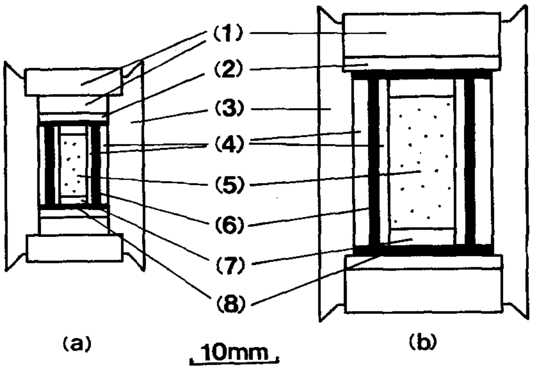

Figure 1 High pressure cell arrangement for girdle-type high pressure apparatus: (a) cell for higher pressure treatment; (b) cell for lower pressure treatment. (1) WC disk, (2) SKH disk, (3) pyrophyllite, (4) fired pyrophyllite sleeve, (5) sample, (6) graphite or GC heater, (7) fired pyrophyllite chip, (8) graphite plate.

use of the larger cell (Fig. 1b). The pressures were calibrated at room temperature by the transition points of bismuth, thallium and barium [7] in the smaller cell and bismuth and thallium in the larger cell. The temperature–applied electric power relation was determined by the melting points of silver, gold and nickel, which were calibrated by the pressure dependence [8, 9].

Starting graphite was a graphitized pitch coke which was prepared from pitch coke at 2800° C. Highly pure electrolytic iron powder was used in the mixture sample with graphite. In order to prepare Fe_7C_3 graphite was mixed in excess to iron to avoid the coexistence of the ferromagnetic Fe_3C. Chromium, molybdenum and/or tungsten powder were also used in order to substitute iron. The mixture sample was packed in the high pressure cell and the pressure was raised to the desired value at room temperature. Subsequently the electric power was applied and kept constant for a given time. After heat treatment the sample was quenched to room temperature under pressure. The high temperature and high pressure treatments were conducted at pressures from 3 to 8 GPa and temperatures up to 1700° C.

The specimens prepared were identified by X-ray powder diffraction. Since the iron carbides were ferromagnetic at room temperature, their separation from residual excess graphite powder was carried out by a magnetic separation technique in acetone. The prepared iron carbides were observed under a scanning electron microscope. The ferromagnetic Curie temperatures of the iron carbides were measured by a Faraday-type magnetic balance and the saturation magnetization, residual magnetization and coercive force were measured by a vibrating sample magnetometer (VSM).

3. Results and discussion

3.1. Formation regions of Fe_7C_3 and Fe_3C

The mixture of 80 wt% graphite and 20 wt% iron (ca. 95 at% carbon and 5 at% iron) was treated at pressures of 3 to 8 GPa and temperatures of 1000 to 1700° C for 10 min. Fig. 2 shows the formation diagram of the carbides. Iron first reacted with graphite to form Fe_3C around 1000° C over the whole pressure region up to 8 GPa in this work. At pressures below 5 GPa, no carbide other than Fe_3C was found, and Fe_7C_3 formed by the reaction of Fe_3C with excess graphite at higher pressures above 5 GPa, as shown in Fig. 3. In the iron–graphite system diamond formation was observed above 7 GPa and is considered to proceed through precipitation from supersaturated iron–carbon solution above the peritectic temperature of Fe_7C_3. Fe_3C did not change even by higher temperature treatments of the lower pressure condition, in which Fe_3C could be melted. These facts may suggest that Fe_3C formed more readily from iron–carbon solution than Fe_7C_3.

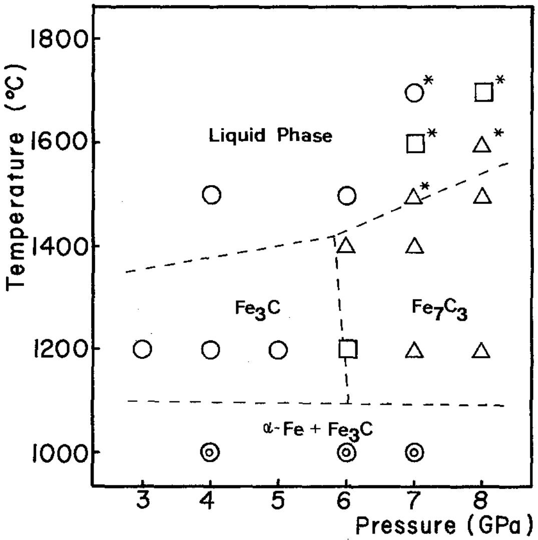

Figure 2 Formation diagram of iron carbides in excess carbon (80 wt% graphite and 20 wt% iron) by high temperature and high pressure treatment for 10 min. α-Fe + Fe_3C (◎); Fe_3C (○); Fe_7C_3 (△); Fe_3C + Fe_7C_3 (□). (*) indicates coexistence of diamond.

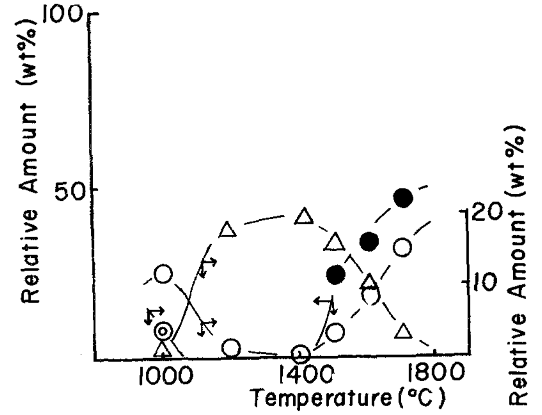

Figure 3 Changes of relative amounts of crystalline phases formed by the mixture of 80 wt % graphite and 20 wt % iron at 7 GPa for 10 min. α-Fe (◎); Fe_3C (○); Fe_7C_3 (△); diamond (●).

3.2. Preparation of Fe_7C_3 and Fe_3C

A mixture rich in carbon, 80 wt % iron and 20 wt % graphite, was employed in this work so that all the iron reacted completely with graphite during heat treatment. Fe_7C_3 was synthesized at 7 GPa and 1400° C for 20 min in the pressure cell of Fig. 1a and Fe_3C was synthesized at 3 GPa and 1300° C for 20 min (Fig. 1b). Both Fe_7C_3 and Fe_3C were separated from the mixture specimen of a desired carbide and excess graphite powder by a magnetic separation.

The X-ray powder diffraction profiles of the prepared Fe_7C_3 and Fe_3C are shown in Fig. 4. The profile of Fe_7C_3 (Fig. 4a) coincided well with that reported by Herbstein and Snyman [1], which was indexed by the hexagonal unit cell of a_0 = 688 pm and c_0 = 454 pm, and also the X-ray diffraction profile of Fe_3C (Fig. 4b) agreed with that reported by Lipson and Petch [10], which was indexed by the orthorhombic unit cell of $a_0 = 452$ pm, $b_0 = 509$ pm and $c_0 = 674$ pm. Fig. 5 shows the SEM photographs of Fe_7C_3 (Fig. 5a) and Fe_3C (Fig. 5b). Both Fe_7C_3 and Fe_3C did not show any specified morphologies.

3.3. Properties of Fe_7C_3 and Fe_3C

Both Fe_7C_3 and Fe_3C were ferromagnetic at room temperature. Table I indicates the magnetic properties of Fe_7C_3 and Fe_3C measured in the present work. The Curie temperatures of Fe_7C_3 and Fe_3C agreed with previous reports [2, 5]. Magnetization of Fe_7C_3 was saturated at about 12 kOe but that of Fe_3C was saturated at about 16 kOe at room temperature, as shown in Fig. 6. Saturation magnetizations of Fe_7C_3 and Fe_3C were 120 and 125 emu g^{-1}, respectively, and their residual magnetizations and coercive forces were considerably smaller. The saturation magnetization of Fe_3C was only reported to be 137 to 141 emu g^{-1} at 50° C [11], which was derived by the extra-

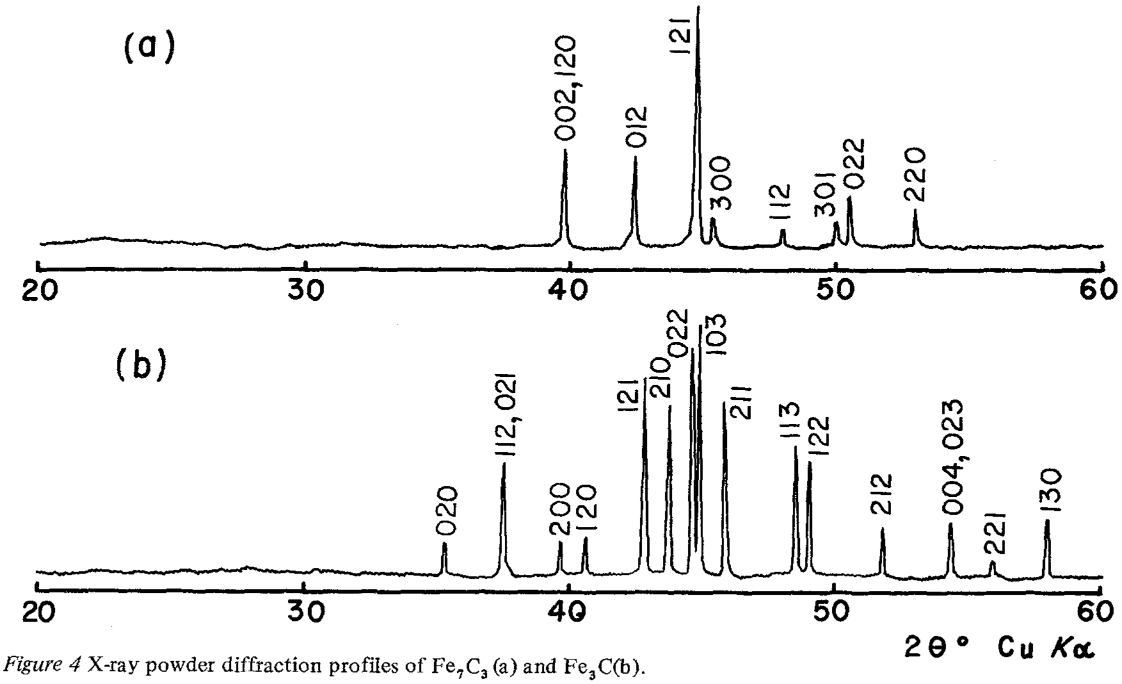

Figure 4 X-ray powder diffraction profiles of Fe_7C_3 (a) and Fe_3C(b).

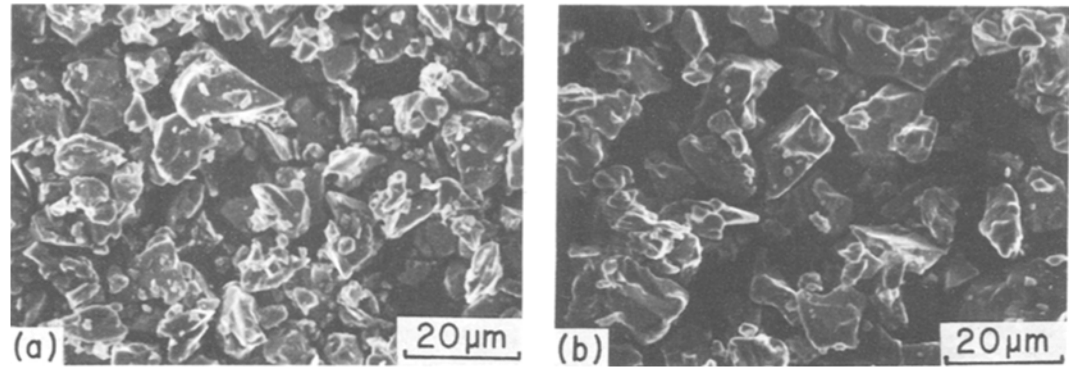

Figure 5 SEM photographs of Fe_7C_3(a) and Fe_3C(b).

polation of the data up to 9.73 kOe to infinite magnetic field.

Thermal stabilities of Fe_7C_3 and Fe_3C at atmospheric pressure were determined in a flow of nitrogen. Fe_7C_3 and Fe_3C were treated to various temperatures for 1 h. Fe_7C_3 remained intact at 500° C but decomposed to Fe_3C and a trace of α-iron at 600° C, while Fe_3C did not decompose at these temperatures. Both Fe_7C_3 and Fe_3C dissociated to α-iron and carbon at higher temperatures above 700° C. These results show that Fe_7C_3 decomposes at 600° C intermediately to metstable Fe_3C instead of stable α-iron, but to stable α-iron at higher temperatures where Fe_3C also decomposes to α-iron.

3.4. Formation of solid solution of Fe_7C_3 and Fe_3C with chromium, molybdenum and tungsten

The formation of Fe_7C_3 solid solution was previously reported by the authors [12]. Solid solutions of iron carbides were prepared by the use of chromium, molybdenum and tungsten. The mixture of 80 wt% graphite and 20 wt% metals was treated at 7 GPa for 10 min. Table II shows the resultant phases and the Curie temperature of the carbides formed. Chromium is known to form Cr_7C_3 isomorphous to Fe_7C_3. Fe_3C phase formed at low chromium content but Fe_7C_3 phase was stabilized with 25 wt% chromium, even at 1700° C. The partial substitution of molybdenum and tungsten for iron resulted in the Fe_3C phase, while the addition of chromium to these metals favoured the formation of the Fe_7C_3 phase. The Curie temperatures of the Fe_7C_3 phase were lowered from 250° C of pure Fe_7C_3 to 125° C of Fe_7C_3 solid solution containing 85 wt% iron, 5 wt% chromium, 5 wt% molybdenum and 5 wt% tungsten. The Fe_7C_3-type structure was stabilized by the substitution of chromium for iron. The magnetic interactions of magnetic atoms in a solid solution phase are different from pure Fe_7C_3 and make the Curie temperature lower.

TABLE I Magnetic properties of Fe_7C_3 and Fe_3C at room temperature

	Fe_7C_3	Fe_3C
Curie point (° C)	250 ± 5	210 ± 5
Saturation magnetization (emu g^{-1})	120 ± 3	125 ± 3
Residual magnetization (emu g^{-1})	0.9 ± 0.1	0.9 ± 0.1
Coercive force (Oe)	35 ± 5	40 ± 5

4. Conclusion

In the iron–graphite system two stoichiometric carbides, i.e. Fe_7C_3 and Fe_3C (cementite) were formed at high temperature and high pressure. Only Fe_3C formed at pressures below 5 GPa, and Fe_7C_3 formed above 5 GPa by the reaction of preformed Fe_3C and excess graphite. Both Fe_7C_3 and Fe_3C were able to be obtained as pure carbide under the appropriate conditions of 7 GPa and 1400° C and 3 GPa and 1300° C for 20 min, respectively. These prepared carbides could be separated from residual excess graphite by a magnetic separation by using their magnetic property. The X-ray powder diffraction profiles of Fe_7C_3 and Fe_3C prepared at high temperature and high pressure agreed well with previous reports.

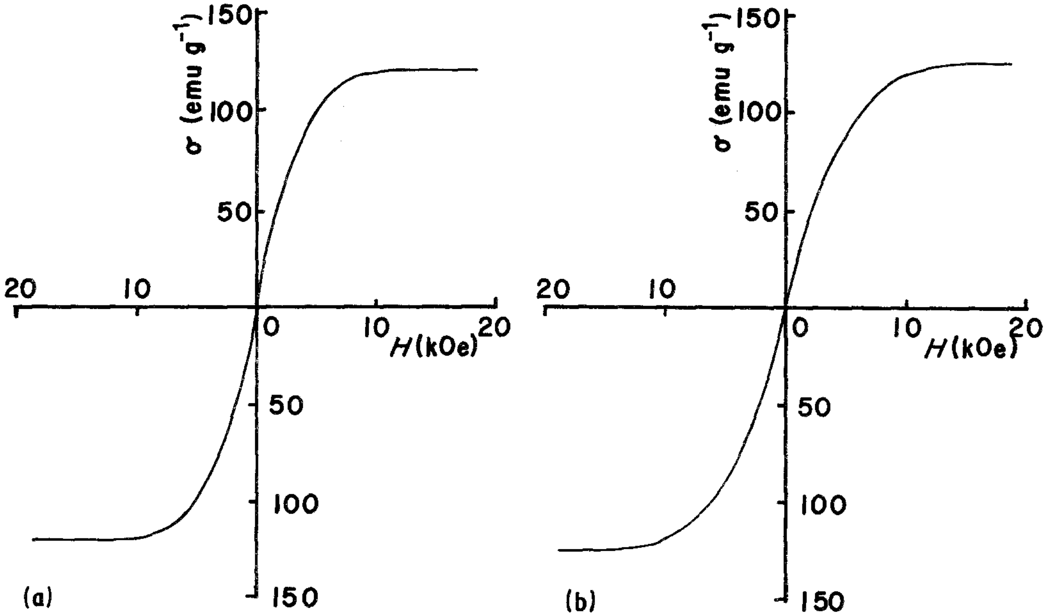

Figure 6 Magnetization–magnetic field curves of Fe_7C_3(a) and Fe_3C(b) measured by VSM.

The Curie points and saturation magnetization at room temperature were 250° C and 120 emu g^{-1} for Fe_7C_3 and 210° C and 125 emu g^{-1} for Fe_3C. Both Fe_7C_3 and Fe_3C had small residual magnetizations and coercive forces. At atmospheric pressure they decomposed to α-iron at 700° C. The substitution of chromium, etc. for iron favours the thermal stability of the Fe_7C_3 phase and influences the magnetic properties.

The stabilities of Fe_7C_3 and Fe_3C in the diamond stable region should be important in the diamond formation process in the iron–graphite system.

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TABLE II Formation of iron carbides solid solution from the mixture of 80 wt % graphite and 20 wt % metals at 7 GPa for 10 min

Metal composition (wt %)	Treatment temperature (° C)	Formed phases	Curie point (° C)
Fe95Cr5	1500	Fe_7C_3 + D	200
Fe95Cr5	1700	Fe_3C + D	180
Fe75Cr25	1700	Fe_7C_3 + D	190
Fe90Cr5Mo5	1700	Fe_7C_3 + D	170
Fe90Cr5W5	1700	Fe_7C_3 + D	175
Fe90Mo5W5	1700	Fe_3C + D	150
Fe85Cr5Mo5W5	1200	Fe_7C_3 + Metal	240
Fe85Cr5Mo5W5	1700	Fe_7C_3 + D	125

D: Diamond.

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