Diamond formation and behaviour of carbides in several 3d-transition metal–graphite systems

SHIGEHARU NAKA, AKIHIRO TSUZUKI, SHIN-ICHI HIRANO
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagaya University, Fiuo-cho, Chikusa-Ku, Nagaya, Japan

The formation of diamond and the behaviour of coexisting carbides with diamond in several 3d-transition metals (manganese, iron, cobalt, nickel)–graphite systems was studied under 7 GPa pressure up to 1700° C from the view-point of diamond formation. In the nickel–graphite and cobalt–graphite systems, no stoichiometric carbide was formed, but M_xC, which is thought to be the interstitial solid solution of carbon, was formed. In the iron–graphite system, on the other hand, the formation of two stoichiometric carbides, i.e. Fe_3C and Fe_7C_3, was found. In the manganese–graphite system, only one stoichiometric carbide Mn_7C_3, which is isostructural with Fe_7C_3, was formed. The diamond formation process in the presence of these transition metals is discussed in relation to the carbide formation.

1. Introduction

Diamond has been synthesized from graphite using some transition metals as a solvent–catalyst. In general, solvent–catalyst metals have been classified into two categories. The first is the metals which form no stoichiometric carbides under the condition for diamond synthesis. The second is the metals which do form stoichiometric carbides. The former consist of nickel, cobalt, platinum, etc. and the latter of iron, manganese, chromium, etc. Giardini and Tydings [1] proposed a relation between diamond formation and carbides. They supposed that diamond was simply precipitated from supersaturated solution with carbon in the nickel–graphite system and was associated with the formation of several stoichiometric carbides in the cobalt–graphite system. They, on the other hand, proposed in the iron or manganese–graphite system that the stoichiometric carbide with higher carbon content decomposed into the carbide with lower carbon content to precipitate diamond.

There have been strong doubts about the diamond formation mechanism in relation to the stability of the coexisting carbide, especially in the system where stable stoichiometric carbides are formed. In the present work, the formation of diamond and coexisting carbides are investigated systematically by use of a 3d-transition metal (nickel, cobalt, iron or manganese) in order to elucidate whether the diamond can be formed by the solution–precipitation process or the decomposition of the carbide.

2. Experimental details

The high temperature–high pressure experiments were carried out with a girdle-type high pressure apparatus. Fig. 1 shows the arrangement of the pressure cell. The pressure was calibrated at room temperature by the transition points of Bi_{I-II} (2.55 GPa), Tl_{II-III} (3.67 GPa), Ba_{I-II} (5.5 GPa) and Bi_{III-V} (7.7 GPa). The temperature was calibrated under 7 GPa pressure by the melting points of silver and gold, which were fixed according to the pressure effect on the melting point [2]. The estimated errors of pressure and temperature were ± 0.3 GPa and ± 50° C, respectively.

The starting materials were well crystallized graphite powders prepared from pitch cokes at 2800° C and highly pure metal powders of nickel,

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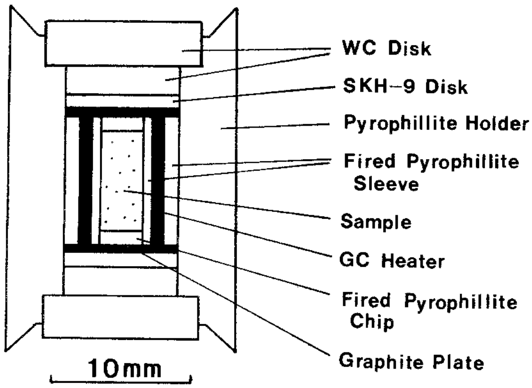

Figure 1 High pressure cell arrangement.

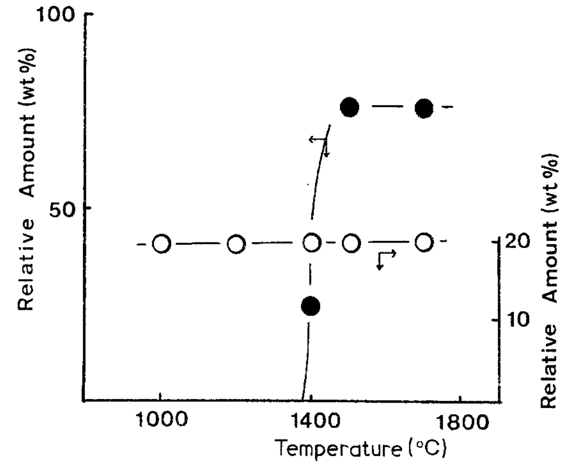

Figure 2 Changes in relative amounts of crystalline phases formed by the mixture of 80 wt % graphite–20 wt % nickel under 7 GPa pressure for 10 min: diamond (•); Ni_xC (○).

cobalt, iron and manganese. The mixture of 80 wt % graphite and 20 wt % metal (about 95 at % carbon and 5 at % metal) was placed in the pressure cell. The pressure was raised to 7 GPa and then the whole of the girdle-type pressure cylinder was kept cool in a water jacket. The temperature was increased to the desired value by passing the electric current through a glassy carbon heater. After holding for 10 min, the electric current was cut off and the sample was quenched down to room temperature. The treated specimens were identified by an X-ray diffraction method and the magnetic properties of the specimen were also measured. The relative amounts of the crystalline phases were determined by the calibration curve of the X-ray diffraction intensities, which was obtained beforehand (by the correction for the preferred orientation of the crystalline phases to the relationship between the X-ray diffraction intensities) with a certain amount of crystalline phase in the mixture. The X-ray diffraction lines used for the measurement of the relative intensity were 1 1 1 for diamond and 0 0 2 for graphite.

3. Results and discussion

3.1. Diamond formation in nickel–graphite system

In the nickel–graphite system, no stoichiometric carbide was observed in agreement with the previous report [1] and nickel interstitial solid solution of carbon (f c c type) was found to form. It was reported that the diamond syntheses by use of nickel include the carbide Ni_xC ($x > 4$) which has a larger lattice constant than that of nickel metal itself [3]. Fig. 2 shows the changes in the relative amounts of crystalline phases in the treated specimen with increase in the heat-treatment temperature at 7 GPa pressure. The amount of Ni_xC was not changed up to 1700° C. The diamond could be detected at 1400° C and its amount increased rapidly with increase in temperature. The yield of diamond was above 70 wt % of the sample above 1500° C. The change of lattice constant of Ni_xC is shown in Fig. 3. The lattice constant increased gradually up to 1400° C and steeply increased at higher temperature, followed by the approach to the constant value at 1700° C.

The nickel reacts with graphite to form low carbon content carbide Ni_xC (with large x) at lower temperature and, above the nickel solid solution–diamond eutectic temperature, diamond

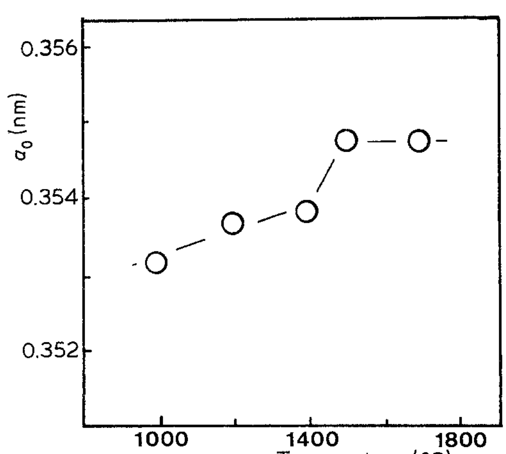

Figure 3 Change of lattice constant (a_0) of Ni_xC with heat-treatment temperature.

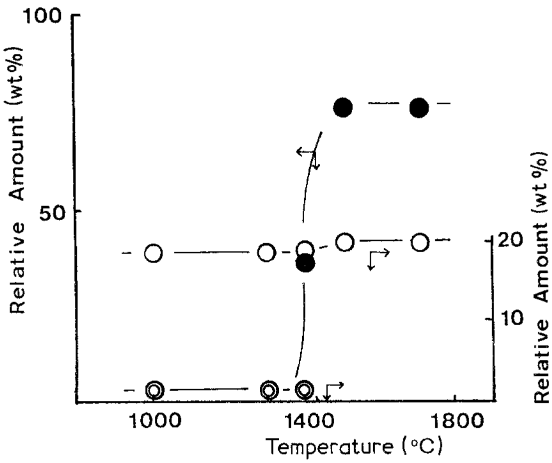

Figure 4 Changes in relative amounts of crystalline phases formed by the mixture of 80 wt% graphite–20 wt% cobalt under 7 GPa pressure for 10 min: diamond (•); α-cobalt (◎); Co_xC (○).

is formed from supersaturated solution, as suggested by Strong and Hanneman [4] from the nickel–carbon phase diagram under 5.4 GPa pressure. On quenching, the same carbon content Ni_xC is solidified. The nonstoichiometric carbide Ni_xC is ferromagnetic and has lower Curie temperature than nickel metal itself.

3.2. Diamond formation in cobalt–graphite system

As in the nickel–graphite system, no stoichiometric carbide was detected in the cobalt–graphite system and β-cobalt interstitial solid solution of Co_xC (f c c type) was formed. Fig. 4 shows the relative amounts of the crystalline phases with increase in the heat-treatment temperature. At low temperature, a trace amount of α-cobalt (h c p) coexisted with the f c c type of Co_xC, but it disappeared when a large amount of diamond was formed. The diamond formation began at 1400° C and its amount increased abruptly with increase in temperature. The yield of diamond was above 70 wt% in the specimens treated above 1500° C. The change of lattice constant of Co_xC is shown in Fig. 5. The change was similar to that in the case of Ni_xC.

These results indicate that Co_xC is formed by reaction of cobalt with graphite at low temperature, and that diamond is formed from the supersaturated solution, as in the nickel–graphite system. α-cobalt was found to disappear when the epitaxial growth of Co_xC took place on diamond during the solidification. The lattice constant of

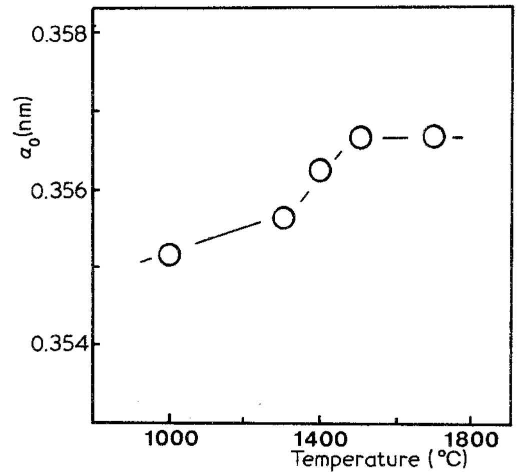

Figure 5 Change of lattice constant (a_0) of Co_xC with heat-treatment temperature.

Co_xC above 1500° C was close to that of diamond. This fact might reflect the superior wettability of cobalt in the liquid phase sintering of diamond powder [5]. It was not possible to measure the Curie temperature of Co_xC in this work up to 900° C, but its value was expected to be lower than that of the cobalt metal itself.

3.3. Diamond formation in iron–graphite system

In the iron–graphite system, two stoichiometric carbides, i.e. Fe_3C and Fe_7C_3, were formed. Fig. 6 shows the relative amounts of the crystalline phases with increasing temperature. Iron reacted with graphite to form Fe_3C at around 1000° C,

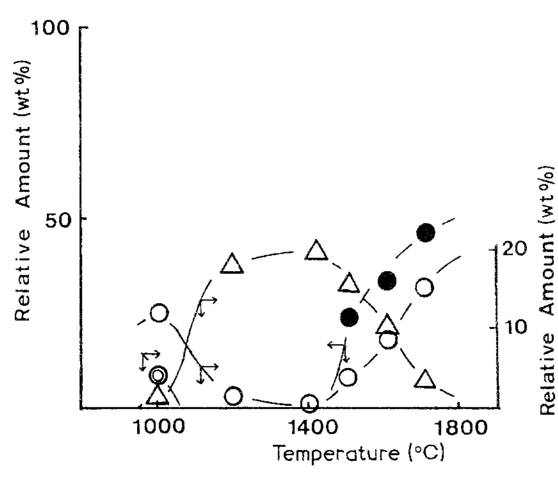

Figure 6 Changes in relative amounts of crystalline phases formed by the mixture of 80 wt% graphite–20 wt% iron under 7 GPa pressure for 10 min: diamond (•); α-iron (◎); Fe_3C (○); Fe_7C_3 (△).

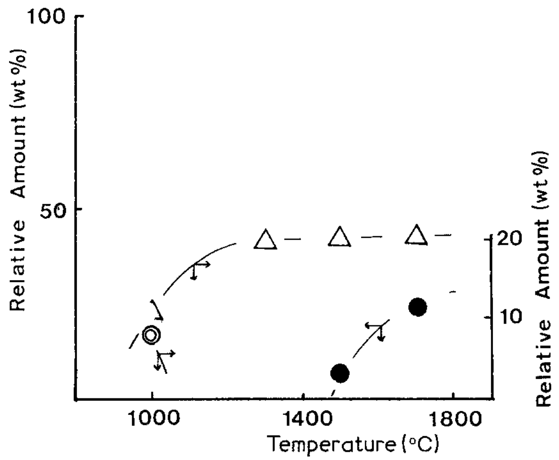

Figure 7 Changes in relative amounts of crystalline phases formed by the mixture of 80 wt % graphite–20 wt % manganese under 7 GPa pressure for 10 min: diamond (•); α-manganese (◎); M_7C_3 (△).

then Fe_3C changed into Fe_7C_3 by further reaction. The diamond was found to form at 1500° C and Fe_3C was reformed at higher temperature. The yield of diamond was about 50 wt % in the specimen treated at 1700° C. The behaviour of Fe_3C and Fe_7C_3 depends on pressure, so that detailed study of the behaviour of iron carbides in relation to diamond formation is necessary. Under 7 GPa pressure, the iron carbide Fe_7C_3 was found to melt incongruently and diamond might form from iron–carbon solution above the peritectic temperature of Fe_7C_3. The Curie temperature of Fe_3C was 210° C and that of Fe_7C_3 was 250° C in agreement with reported values [6].

3.4. Diamond formation in manganese–graphite system

In the manganese–graphite system, only one stoichiometric carbide Mn_7C_3 was formed at 7 GPa, although $Mn_{23}C_6$ is a stable phase under atmospheric pressure [7]. The relative amounts of the crystalline phases is shown in Fig. 7. Manganese reacted with graphite to form Mn_7C_3 at around 1000° C. The diamond formation took place at 1500° C. The yield of diamond was about 20 wt % in the specimen at 1700° C. Mn_7C_3 did not change to the other kind of carbide in the entire temperature range used in this work. Giardini and Tydings [1] proposed that MnC, which was richer in carbon than Mn_7C_3, was formed and decomposed to Mn_7C_3 and diamond. In this work any indication of the formation of MnC was not observed. Mn_7C_3 probably melts congruently, so diamond should be precipitated from the manganese–graphite solution above the Mn_7C_3–diamond eutectic temperature. A carbide poorer in carbon than Mn_7C_3 may exist, though it was not detected in this work with the carbon-rich composition.

4. Summary

Diamond was synthesized from the mixture of graphite and metal powder of nickel, cobalt, iron or manganese under 7 GPa pressure. The formation and behaviour of their carbides were found to be classified into two groups. Nickel and cobalt form only nonstoichiometric carbides M_xC with graphite; on the other hand, iron and manganese form stoichiometric carbides. In the former, the metal–carbon system have only one eutectic point (liquid → diamond + M_xC). Among the latter, manganese has stable carbide Mn_7C_3. But iron, which forms easily metastable Fe_3C under atmospheric pressure, has two carbides of Fe_3C and Fe_7C_3 at 7 GPa pressure. The stability range of Fe_7C_3 is not so wide that the change of carbide phase from Fe_7C_3 to Fe_3C could be detected at the temperature where diamond is formed. These differences certainly reflect the difference in the interactions between metal and carbon, which are related to the number of 3d-electrons in metals.

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