Reports of the Academy of Sciences of the USSR

PHYSICS

1970

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1970. Volume 192, No. 4

UDC 536.424

PHYSICS

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ON THE ROLE OF CARBIDE Fe_3C IN THE SYNTHESIS OF DIAMOND

The synthesis of diamonds using a number of metals (Ta, Fe, Ni, Co, Mn) as "catalyst-solvents" is accompanied by the formation of carbides ($^{1-6}$), concerning whose role in this process there are very different views ($^{6-8}$).

In the opinion of Giardini and Tydings (^{2}), the mechanism of the diamond-synthesis reaction in carbide-forming systems (to which they assign Fe–C, Co–C, and Mn–C) consists in the successive formation of carbon compounds with increasing stoichiometric carbon content, which leads to the formation of the "final" carbide, which decomposes into a carbide depleted in carbon and carbon crystallizing as diamond (at the corresponding pressure and temperature). For the Fe–C system, for example, the authors propose the following scheme for obtaining diamonds:

$$\alpha\mathrm{Fe} \to \alpha(\mathrm{Fe},\mathrm{C}) \to d(\mathrm{Fe}) + \mathrm{Fe_3C} \to \gamma(\mathrm{Fe},\mathrm{C}) \to \mathrm{Fe_3C} \to \mathrm{Fe_2C} \to \mathrm{FeC}$$

where $\alpha(\mathrm{Fe},\mathrm{C})$ is ferrite, $d(\mathrm{Fe})$ is pearlite, and FeC yields diamond; with increasing temperature in the presence of excess carbon, the process is directed toward Fe_3C.

However, analysis of the data presently available makes it possible to doubt the correctness of this scheme. Thus, theoretical calculations ($^{9-13}$) and experimental works (^{10,11}) have shown that cementite Fe_3C becomes a stable phase under the influence of pressure. From comparison of the region of cementite stability (Fig. 1a) and the region of diamond stability (Fig. 1b), it follows that cementite should be stable in the region of diamond synthesis.

Table 1

Results of experiments on diamond synthesis in the iron–graphite system at different ratios of iron and graphite
($P = 60$ kbar, $T = 1500^\circ$)

Iron : graphite ratio, at. %	Duration of synthesis, min	Experimental results
90 : 10	2.5	Diamonds not obtained
80 : 20	5	Same
75 : 25	2.5	Same
75 : 25	5	Same
70 : 30	2.5	Several diamond crystals
70 : 30	4.0	Diamonds not obtained
65 : 35	2.5	Diamonds synthesized
60 : 40	2.5	Same
50 : 50	2.5	Same
45 : 55	1.5	Same
10 : 90	2.5	Same

Calculation (11) showed that the formation of Fe_3C in saturated austenite is accompanied by a decrease in volume both relative to graphite and to diamond; consequently, high pressure will promote this process.

In view of the fact that the solubilities of cementite and diamond, as thermodynamically stable phases, in the region of diamond synthesis will be lower than the solubility of graphite, diamond and cementite will separate from a solution of carbon in molten iron; i.e., the formation of Fe_3C must accompany diamond synthesis.

Our investigations confirmed this assumption. Figure 2 shows the arrangement of the starting materials—plates of pressed iron powder or Armco iron and a heater made of spectrally pure graphite—in the reaction zone of the high-pressure chamber. The pressure was determined from known phase transitions in Bi, Tl, and Ba (14); the effect of heating on the change in pressure was not taken into account; the temperature was measured with thermocouples. Experiments carried out at high pressure showed that cementite is readily formed on the surface of an iron plate already at temperatures such as 1000° (15), and also simultaneously with diamond, i.e., at $T = 1500^\circ$ and a pressure of 60 kbar. Iron carbides other than Fe_3C were not observed by us.

It was also investigated how Fe_3C* behaves under the action of high pressures and temperatures. A smooth change in its electrical resistance upon heating and the absence of iron lines in the x-ray pattern of the final product indicate that decomposition of Fe_3C does not occur under these conditions.

Fig. 1. *a*—equilibrium line of the reaction
$Fe_3C \rightleftharpoons 3Fe + C$ (graphite);

Fig. 1

Figure 1: Fig. 1

b—diamond-graphite equilibrium line

In order to check the assertion of Giardini and Tydings about the course of the diamond-forming reaction through Fe_3C, we carried out experiments in the Fe_3C-graphite system. Fe_3C carbide powder was pressed into a pellet and placed in the reaction zone by the method indicated in Fig. 2. In none of the experiments carried out in the Fe_3C-graphite system in the region of diamond growth at pressures of $\sim$ 60 kbar and a temperature of 1500-1600° were diamonds synthesized.

The experimental data obtained by us cast doubt on the possibility of diamond formation in the Fe-C system according to the scheme proposed by Giardini and Tydings. It may be considered that the formation of Fe_3C carbide is a reaction accompanying diamond synthesis.

The scheme of successive reactions in the iron-graphite system in the region of diamond stability may be represented as follows:

$$\alpha \mathrm{Fe} + \mathrm{C} \to \alpha(\mathrm{Fe}, \mathrm{C}) \to \alpha(\mathrm{Fe}, \mathrm{C}) \to \gamma(\mathrm{Fe}, \mathrm{C}) \to \gamma(\mathrm{Fe}, \mathrm{C}') \to \gamma(\mathrm{Fe}, \mathrm{C})$$

$$\begin{array}{cccc} \downarrow & \downarrow & \swarrow & \searrow \\ \mathrm{Fe_3C} & \mathrm{Fe_3C} & \mathrm{Fe_3C} & \text{diamond} \end{array}$$

Increase of temperature in the presence of excess carbon.

Since the formation of cementite in the region of diamond synthesis has thermodynamic and kinetic advantages over the formation of diamond, and in composition it corresponds to 75 at.% iron and 25 at.% carbon, the question of the ratios of iron to carbon (graphite) at which diamond synthesis in the Fe-C system begins was of interest.

Mixtures of iron and graphite powders of various proportions prepared for this purpose were placed in the reaction zone of the chamber with independ— by heating (Fig. 3). From the results given in Table 1 it is seen that, at an atomic ratio of iron to graphite of 75 : 25, only cementite is formed, and there are no diamonds; several crystals were obtained at Fe : C = 70 : 30, while diamonds are synthesized steadily only beginning with the ratio Fe : C = 65 : 35.

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* Kindly provided by A. A. Zhukov (VNII EKMASH).

Fig. 2. Reaction zone of the direct-heating chamber; labels: graphite, metal, graphite.

Figure 2: Fig. 2. Reaction zone of the direct-heating chamber; labels: graphite, metal, graphite.

Fig. 3. Reaction zone of the chamber with independent heating; labels: graphite, reaction volume, insulator.

Figure 3: Fig. 3. Reaction zone of the chamber with independent heating; labels: graphite, reaction volume, insulator.

It follows from this that the ratio of metal and graphite in the iron-graphite system is of just as great importance for synthesis as the correspondence of the pressure and temperature of the reaction to the region of diamond synthesis. In conclusion we note that, in connection with the stability of Fe_3C at high pressures and temperatures, it should be considered that the diamond-synthesis region (see Fig. 1) is bounded on the left by the melting line of the iron-cementite eutectic under pressure, and not by iron-graphite, which is confirmed by the calculation of the initial slopes of melting of these eutectics carried out in Ref. (10).

Fig. 2. Reaction zone of the direct-heating chamber

Fig. 3. Reaction zone of the chamber with independent heating

On the basis of the experiments we have carried out, the following conclusions may be drawn:

1. The carbide Fe_3C forms in the region of diamond stability.
2. The production of Fe_3C in the region of diamond growth indicates that its formation is a reaction accompanying diamond synthesis.
3. To obtain diamonds in the iron-graphite system, it is not sufficient that the pressure and temperature of the reaction correspond to the region of diamond synthesis; it is necessary that the amount of graphite exceed 25 at.% (relative to iron), corresponding to the stoichiometric composition of cementite. If the amount of graphite is equal to 25 at.%, then in the region of diamond growth only cementite is formed.
4. Since at high pressure cementite becomes a stable phase, the region of diamond synthesis in the Fe-C system is bounded on the left by the melting line of the iron-cementite eutectic under pressure (and not iron-graphite).

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Received
11 II 1970

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