

EFFECT OF GASES ADSORBED ON RAW MATERIAL ON THE CONDITIONS OF DIAMOND FORMATION

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Variations of the P-T conditions of diamond formation by hydrogen adsorbed on the raw carbon were studied. Various raw carbons which differed in pretreatment were prepared. The experimental results attest that the catalyst-graphite eutectic line shifts to a higher temperature by the adsorption of hydrogen on the raw carbon.

1. Introduction

The surface of the raw carbon used in diamond synthesis actively adsorbs many kinds of gases, including hydrogen, oxygen, nitrogen and so on.

Tsuzuki, Hirano and Naka¹⁾ have reported that hydrogen and compounds containing hydrogen atoms impede the conversion of graphite to diamond, and that oxygen does so to a lesser degree, but that CO and CO₂ have no effect. The results of Wakatsuki²⁾ also show that the amount of diamond formation increases by preheating the raw carbon in a vacuum. However, the conditions of diamond formation that might vary with differences in the quantity of adsorbed gases have not been reported.

In this paper, several kinds of raw carbons which differed in pretreatment were prepared and their conditions of diamond formation were studied.

2. Experiments

A belt-type high pressure and temperature apparatus was applied. Pressure at room temperature was calibrated using the transition points of Bi and Tl, and that at high temperature by the change of Ag melting point³⁾. The relation between heating-power and temperature was confirmed by a Pt30% Rh-Pt6%Rh thermocouple at high pressure.

Three types of artificial graphitic carbons for the raw materials of diamond synthesis were prepared as follows; dried at 150°C (A), degasified at 1000°C

and 10⁻⁴ Torr (B) and heated at 300°C in hydrogen gas after degasification (C). The results of the gas analysis and graphitization ratio are shown in Table 1.

55Fe-29Ni-16Co alloy was used as a catalyst for diamond synthesis. The synthesizing experiments were carried out at pressures of 48-56 kbar and temperatures of 1000-1600°.

3. Results and discussions

The experimental results show sharp boundaries of diamond formation, as shown in Figs. 1 and 2. The bottoms of the diamond formation fields are nearly equal at 50.5 kbar. In the case of A, B and C, the graphite-diamond equilibrium line determined by the high-temperature end of the diamond formation field appears to be parallel to the extrapolated line of Berman and Simon⁴⁾, i.e.,

$$P \text{ (kbar)} = 7.1 + 0.027T \text{ (°K)}.$$

Table 1. Characterization of the raw materials—results of gas analysis and graphitization ratio

| | A | B | C |
|----------------------------|-------|-------|------|
| H | 7.4 | 1.6 | 2.9 |
| O | 201.0 | 36.2 | 36.1 |
| N | 18.9 | 0 | 0 |
| <i>L_c</i> (002) | | 610 | |
| <i>d</i> (002) | | 3.366 | |
| Franklin's <i>p</i> value | | 0.374 | |

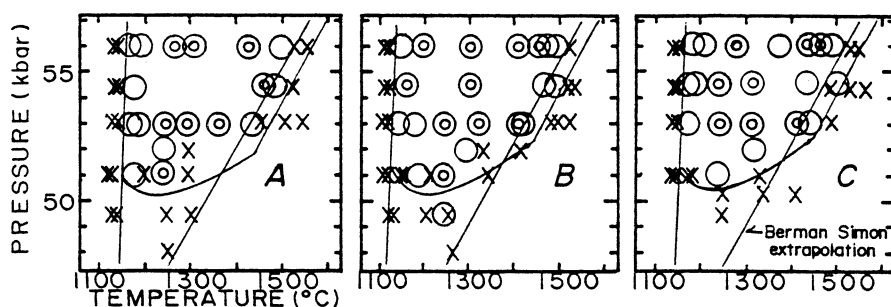


Fig. 1. Diamond synthesis conditions. ⊙, many diamonds formed; ○, a few diamonds formed; ×, diamond not formed, high temp; ※, diamond not formed, low temp.

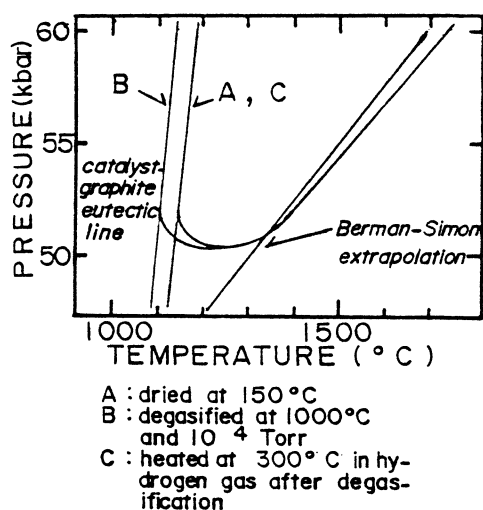


Fig. 2. Boundaries of the P, T zone for diamond formation. A, dried at 150°C; B, degasified at 1000°C and 10^4 Torr; C, heated at 300°C in hydrogen gas after degasification.

However, the catalyst-graphite eutectic line of B determined by the low-temperature end of the diamond formation field shifts to a lower temperature (by 50°C) than that of A or C.

In comparing B and C in Table 1, the difference of eutectic line is considered to be due to the

difference in the quantity of hydrogen. On the other hand, considering A, the conditions of diamond formation are the same as those of C in spite of differences in the quantity of hydrogen, oxygen and nitrogen. The result may have two explanations: either (a) the shift of the eutectic line does not change by the increase of hydrogen, or (b) the effect of the increase of hydrogen balances with an effect of nitrogen which may advance the conversion; therefore the eutectic line does not change.

Thus it was confirmed that the catalyst-graphite eutectic line shifts to higher temperatures by the increase of hydrogen adsorbed on the raw carbon. Hence, it is considered that hydrogen may act as an impeder on the stage of dissolving the raw carbon in catalyst rather than on that of crystallization of diamond from catalyst.

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