JOURNAL OF MATERIALS SCIENCE 20 (1985) 2477–2482

Effect of high-pressure pre-treatment of starting carbon on diamond formation

AKIHIRO TSUZUKI, SHIN-ICHI HIRANO, SHIGEHARU NAKA
Synthetic Crystal Research Laboratory, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Japan

Four starting carbons differing in crystallinity and grain size were pre-treated with or without nickel at 3 GPa and 1800° C or at 6 GPa and 1700° C. Diamond synthesis from carbons pre-treated and then further treated in vacuum was carried out at 8 GPa and 1700° C. Pre-treated carbons with or without nickel, which were fully or partly graphitized, changed a little or did not convert to diamond at 8 GPa and 1700° C. Diamond did form from the pre-treated carbons after treatment in a vacuum at 1000° C. Diamond formation, even from the graphitized carbons, was found to be inhibited mainly by gases adsorbed on the treated carbon during the pre-treatment under high pressure.

1. Introduction

Diamond is synthesized from graphite in the presence of transition metals as solvent–catalyst under static pressure [1]. Diamond formation is generally thought to be a dissolution–precipitation process. In the diamond stable region metastable graphite, which has a larger solubility in molten metal than stable diamond, dissolves into the melt to the point where the metal–carbon melt is supersaturated in diamond, and stable diamond precipitates from the melt. Elemental carbon exists not only as diamond or crystallized graphite, but also as various less crystallized states.

Kassatochkin *et al.* [2] investigated the rate of diamond formation from various starting carbons in the presence of solvent–catalyst metals. They claimed that amorphous carbons were first graphitized and then transformed to diamond, so that incubation time was required. On the other hand, Gankevich *et al.* [3] reported that amorphous carbons were mainly graphitized in the presence of solvent–catalyst metals even in the diamond stable region, and that the most important factor was not the crystallinity of graphite formed under high pressure but that of the starting carbon itself. The present authors [4] studied the behaviour of several starting carbons having different crystallinities in the presence of nickel under conditions of high pressure and temperature, and found that carbon composed of a non-graphitic component had a higher solubility in molten nickel than well-crystallized graphite; however, it only graphitized instead of transforming to stable diamond. They proposed [5] that diamond formation in the presence of solvent–catalyst metals was inhibited by gaseous species adsorbed on to the carbon, especially those containing hydrogen atoms.

The important question which still remained unsolved was whether graphite formed under high pressure could transform to diamond. In order to study this problem, four starting carbons which were used in previous work [4, 5] were pre-treated with or without nickel at high pressure and temperature.

2. Experimental procedure

The crystallinities of four starting carbons measured from (0 0 2) X-ray diffraction are shown in Table I. Graphitized pitch coke (GPC) was highly crystallized. Pitch coke (PC) was non-graphitic but graphitizable carbon. The grain size of these two carbons were about 5 μm. The glassy carbon treated at about 3000° C (GC-30) had both graphitic and non-graphitic components. The glassy carbon treated at about 2000° C (GC-20) was non-graphitic and non-graphitizable carbon. The grain size of these glassy carbons was about 100 μm.

0022–2461/85 $03.00 + .12

TABLE I Crystallinities of parent carbons*

Sample	$(c_0)_{002}$ (nm)		$(L_c)_{002}$ (nm)		P		Amount of G (%)
	NG	G	NG	G	NG	G	
GPC	–	0.6722	–	91	–	0.92	100
PC	0.6886	–	4.1	–	0	–	0
GC-30	0.6834	0.6728	5.4	38	0.27	0.88	19
GC-20	0.6927	–	2.6	–	0	–	0

*NG: non-graphitic, G: graphitic component, P: graphitization index.

Pre-treatment of starting carbon and diamond synthesis from treated carbons were carried out by a girdle-type high-pressure apparatus. Fig. 1 shows two high-pressure cell arrangements. One (Fig. 1a) has a small sample volume for the higher-pressure treatment, while the other (Fig. 1b) has a larger volume for relatively lower-pressure treatment. The powdered carbon samples were heated by a glassy carbon or graphite heater in both high-pressure cells. The pressures were calibrated at room temperature by the pressure-induced transitions of bismuth, thallium and barium in the smaller cell and bismuth and thallium in the larger cell [6]. The variation of temperature with applied electric power was determined by the melting points of silver, gold and nickel, the pressure-dependence of these being calibrated on the basis of earlier reports [7, 8].

The sample was compressed to the desired pressure at room temperature and the electric power was then applied and kept constant for a given time. After heat treatment the sample was quenched to room temperature under high pressure. Starting carbons were pre-treated for 10 min with or without nickel at pressures of 3 and 6 GPa and a temperature of up to 1800° C. Changes of crystallinity of carbons treated under high pressure were determined from the (0 0 2) X-ray diffraction of carbon with highly pure silicon as the internal standard, according to the procedure proposed by Noda *et al.* [9]. Diamond synthesis conditions were 8 GPa and 1700° C for 10 min, which are known to be favoured conditions for diamond formation. Diamond yields from pre-treated carbons were measured from the relative intensity of diamond (1 1 1) X-ray diffraction to that of graphite (0 0 2) X-ray diffraction, according to the calibration curve for the preferred orientation. In order to investigate the effects of adsorbed gases on pre-treated carbon, carbons treated under high pressure were re-treated at 2×10^{-5} torr and 1000° C for 3 h. The samples treated at 8 GPa and 1700° C for 10 min were observed by a scanning electron microscope (SEM).

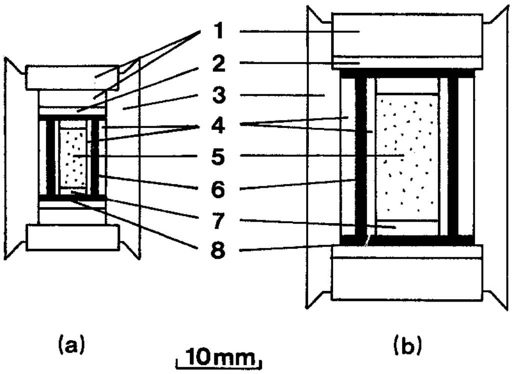

Figure 1 High-pressure cell arrangements for girdle-type high-pressure apparatus: (a) cell for higher pressure treatment, (b) cell for lower pressure treatment. 1. WC disc, 2. SKH–9 disc, 3. phrophyllite holder, 4. fired pyrophyllite sleeve, 5. sample, 6. GC or graphite heater, 7. fired pyrophyllite chip, 8. graphite plate.

3. Results and discussion

3.1. Diamond formation from carbons before pre-treatment

Four starting carbons containing 20 wt% Ni were treated at 8 GPa and 1700° C for 10 min. Table II shows the diamond yield from each carbon before pre-treatment. GPC transformed to diamond to the extent of about 95 wt% of carbon present; GC-30, which consisted of two components (graphitic and non-graphitic) converted to diamond to an extent of 75 wt%, which is less than that from

TABLE II Diamond yields from each starting carbon after treatment at 8 GPa and 1700° C for 10 min without pre-treatment

Starting carbon	Diamond yield (wt % of carbon present)
GPC	95
PC	0
GC-30	75
GC-20	0

TABLE III Effects on diamond formation* of pre-treatment of starting carbons at 3 GPa and 1800° C.

Sample	$(c_0)_{002}$ (nm)		$(L_c)_{002}$ (nm)		G/(NG + G) (%)	Diamond yield (%)
	NG	G	NG	G		
GPC	–	0.6720	–	49	100	26
PC	–	0.6726	–	28	100	0
GC-30	0.6794	0.6723	6.1	25	23	0
GC-20	0.6807	0.6721	4.8	31	56	0

*Treatment with 20 wt% Ni at 8 GPa and 1700° C for 10 min.

GPC. Both PC and GC-20 (composed of non-graphitic components) were graphitized and yielded no diamond. Prolonging the treatment time to 30 min did not influence the behaviour of any carbon at 8 GPa and 1700° C. Graphite formed from non-graphitic carbon at 8 GPa and 1700° C did not transform to diamond under these conditions.

3.2. Pre-treatment under 3 GPa without nickel

Four starting carbons were pre-treated in the absence of nickel at 3 GPa and 1800° C for 10 min, and were re-treated in the presence of 20 wt% Ni at 8 GPa and 1700° C for 10 min. The crystallinities of pre-treated carbons, and the diamond yield from these carbons, are shown in Table III. PC and GC-20 were substantially graphitized by pre-treatment at 3 GPa and 1800° C. PC had only a graphitic component after pre-treatment. The crystallinity of GC-30 did not change so much from the initial value, but that of GPC became much lower by pre-treatment. Non-graphitic carbons were graphitized. The crystallinity, measured as $(L_c)_{002}$, was lowered for graphitic carbon by the pre-treatment. Diamond formed from pre-treated GPC to about 25 wt% of carbon present, but did not form from the other three carbons treated at 8 GPa and 1700° C for 10 min. The diamond yields from GPC and GC-30 were greatly reduced, and no diamond formation was found in the case of PC and GC-20.

It has been found that adsorbed gases inhibit diamond formation in the presence of solvent–catalyst metals [5]. Each pre-heated carbon was therefore heat-treated at 2×10^{-5} torr and 1000° C for 3 h to remove adsorbed gases, and re-treated in the presence of 20 wt% Ni at 8 GPa and 1700° C. The crystallinities of carbons after treatment in vacuum, and diamond yields from these carbons, are shown in Table IV. Recovery of the crystallinity was found only in GPC, while no change in crystallinity was observed in other carbons after treatment in a vacuum. Diamond formation was detected in all carbons after treatment in a vacuum; however, the amounts of diamond formed from GPC and GC-30, which were less than those from GPC and GC-30 without pre-treatment, were larger than from PC and GC-20.

The changes in $(L_c)_{002}$ of GPC, and the variation of diamond yield with pre-treatment temperature at 3 GPa for 10 min, are shown in Fig. 2. $(L_c)_{002}$ became lower with increase of treatment temperature, and the diamond yield also changed in accordance with the change in $(L_c)_{002}$. Although the crystallinity of GPC pre-treated at 3 GPa and 1400° C was almost the same as that of GPC pre-treated at 3 GPa and 1800° C with subsequent treatment in a vacuum, the amounts of diamond formed were quite different. Carbon treated under high pressure is considered to be strained. Mizushima [10] suggested that the strain in carbon can be estimated from $(L_c)_{00l}$. In this work, the strain in treated carbon was

TABLE IV Effects on diamond formation heat treatment in a vacuum of pre-treated carbons*

Sample	$(c_0)_{002}$ (nm)		$(L_c)_{002}$ (nm)		G/(NG + G) (%)	Diamond yield (%)
	NG	G	NG	G		
GPC	–	0.6722	–	60	100	91
PC	–	0.6729	–	31	100	10
GC-30	0.6807	0.6726	6.3	28	20	49
GC-20	0.6778	0.6720	5.4	30	54	15

*Treatment at 2×10^{-5} torr and 1000° C for 3 h; then with 20 wt% Ni at 8 GPa and 1700° C for 10 min.

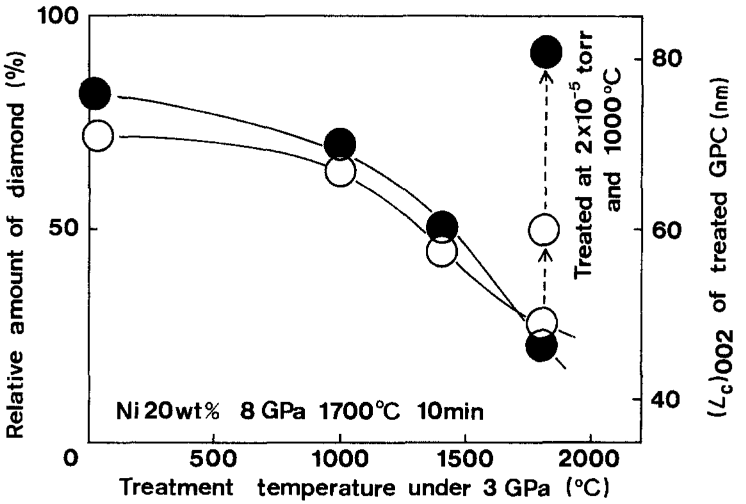

Figure 2 Changes of $(L_c)_{002}$ and diamond yield from GPC in the presence of 20 wt% Ni at 8 GPa and 1700° C for 10 min, with pre-treatment at temperature shown at 3 GPa for 10 min.

obtained from $(L_c)_{002}$ and $(L_c)_{004}$. The strain in treated carbon was relieved to only a little extent by treatment in a vacuum. The strain of GPC treated at 3 GPa and 1800° C and subsequently in a vacuum was larger than that of material treated at 3 GPa and 1400° C. However, the amounts of diamond formed from these two carbons were quite different.

The pre-treatment of starting carbon without nickel under 3 GPa changed the crystallinity of each carbon, but at the same time carbon formed under high pressure adsorbed various gaseous species which inhibited diamond formation; the high-pressure cell provided a closed system around the sample carbon, and only partly removed the adsorbed gases during heating. These gases adsorbed during treatment under high pressure were partially removed by treatment in a vacuum, and diamond formation then took place. Adsorbed gases can be taken to be the main factor determining whether diamond formed from pre-treated carbon only a little or not at all. The strain of carbon treated under high pressure may also influence diamond formation but is thought to be less important than adsorbed gases, since the crystallinity was not changed before and after treatment in a vacuum; on the other hand the desorption of gases affected diamond formation.

3.3. Pre-treatment under 3 GPa with nickel

Starting carbons were pre-treated in the presence of 20 wt% Ni at 3 GPa and 1800° C for 10 min, and treated carbons were re-treated at 8 GPa and 1700° C for 10 min. The crystallinities of pre-treated carbon and the diamond yields are shown in Table V. Nickel is known to act as a solvent–catalyst not only for diamond formation, but also for graphitization. All carbons formed by pre-treatment were composed only of a graphitic component. Except for GPC, which decreased its crystallinity, three other starting carbons were highly graphitized. The amounts of diamond formed from pre-treated carbons were very small or zero in amounts as in the case of pre-treatment without nickel even though all carbons had a graphitic structure. The subsequent treatment of pre-heated carbon at 2 x 10^{-5} torr and 1000° C for 3 h was carried out and diamond formation at 8 GPa and 1700° C were tested. Table VI shows the changes in crystallinity and diamond yield by

TABLE V Effects on diamond formation of pre-treatment of starting carbons, in the presence of 20 wt% Ni*

Sample	$(c_0)_{002}$ (nm)	$(L_c)_{002}$ (nm)	Diamond yield (%)
GPC	0.6721	61	22
PC	0.6714	55	0
GC-30	0.6711	49	15
GC-20	0.6714	46	0

*Treatment of 3 GPa and 1800° C for 10 min; then at 8 GPa and 1700° C for 10 min.

TABLE VI Effects on diamond formation of heat treatment in a vacuum* of pre-treated carbons

Sample	$(c_0)_{002}$ (nm)	$(L_c)_{002}$ (nm)	Diamond yield (%)
GPC	0.6720	71	85
PC	0.6716	55	50
GC-30	0.6717	49	92
GC-20	0.6716	46	70

*Treatment at 2 × 10^{-5} torr and 1000° C for 3 h; then at 8 GPa and 1700° C for 10 min.

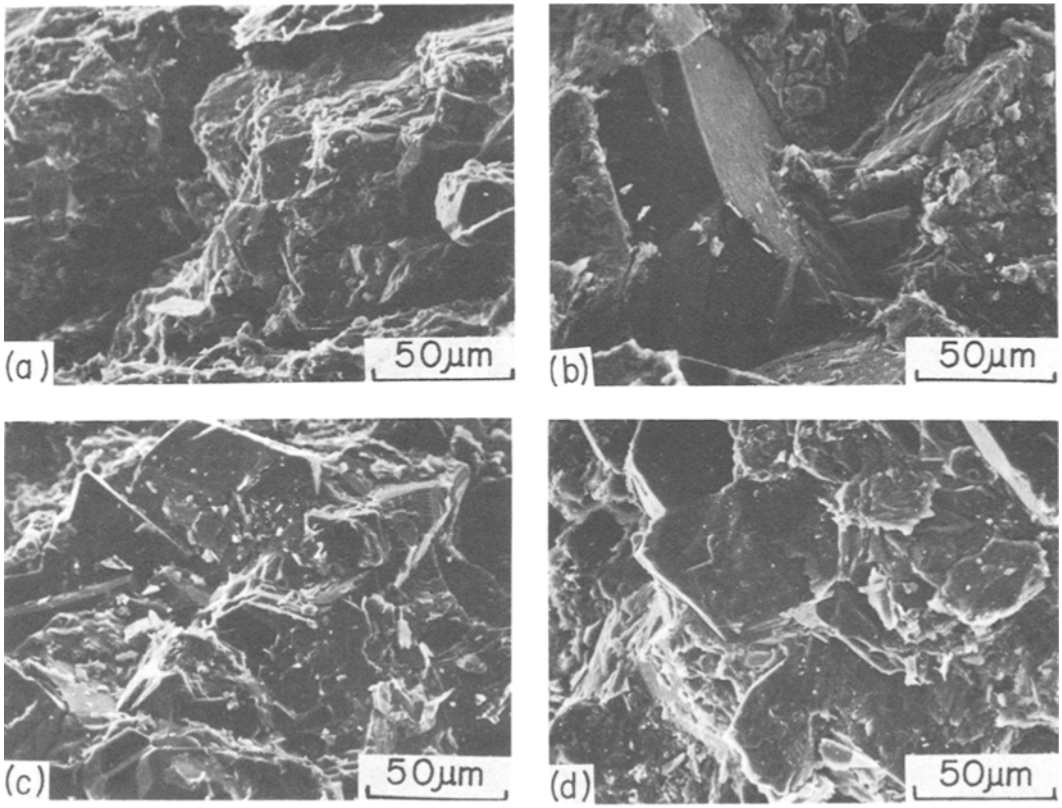

Figure 3 SEM photographs of specimens from each starting carbon treated at 8 GPa and 1700° C for 10 min, after pre-treatment in the presence of 20 wt % Ni at 3 GPa and 1800° C for 10 min, and then at 2×10^{-5} torr and 1000° C for 3 h. (a) GPC, (b) PC, (c) GC-30, (d) GC-20.

treatment in a vacuum. A recovery of crystallinity in GPC was found, but no changes were seen in the other three carbons. The amount of diamond formed was substantial, being 50 wt % of carbon present from PC and 91 wt % from GC-30.

The order of the amounts of diamond formed did not correspond with that of the crystallinities of carbons treated in a vacuum. Diamond formation was affected greatly by gases adsorbed on treated carbon in the case of pre-treatment with or without nickel, though the crystallinities of carbons treated with nickel were higher than for those without nickel. The order of ease of diamond formation may be determined by both the crystallinity and the grain size of the starting carbon.

Fig. 3 shows the diamond formed from each carbon after treatment in a vacuum. Diamond grains formed from GPC (Fig. 3a) and GC-20 (Fig. 3d) were partially inter-grown by self-bonding and had grain sizes ranging from 50 to 100 μm. The diamond formed from PC (Fig. 3b) was relatively isolated and had a larger grain size than the others.

3.4. Pre-treatment under 6 GPa with nickel

In order to study the effect of pre-treatment pressure, starting carbons were pre-treated in the presence of 20 wt % Ni at 6 GPa and 1700° C for 10 min, and were re-treated at 8 GPa and 1700° C for 10 min as in the case of pre-treatment under 3 GPa. They were further treated at 2×10^{-5} torr and 1000° C for 3 h, and the diamond yields after treatment in a vacuum were obtained. Table VII shows the crystallinities of pre-treated carbons and

TABLE VII Effects on diamond formation of pre-treatment of starting carbons in the presence of 20 wt % Ni*

Sample	$(c_0)_{002}$ (nm)	$(L_c)_{002}$ (nm)	Diamond yield (%)
GPC	0.6723	59	12
PC	0.6717	40	0
GC-30	0.6716	44	20
GC-20	0.6718	45	0

*Treatment at 6 GPa and 1700° C for 10 min; then at 8 GPa and 1700° C for 10 min.

TABLE VIII Effects on diamond formation heat treatment in a vacuum* of pre-treated carbons

Sample	$(c_0)_{002}$ (nm)	$(L_c)_{002}$ (nm)	Diamond yield (%)
GPC	0.6726	60	34
PC	0.6723	43	25
GC-30	0.6720	46	80
GC-20	0.6719	45	65

*Treatment at 2×10^{-5} torr and 1000° C for 3 h; then at 8 GPa and 1700° C for 10 min.

the amounts of diamond formed, and Table VIII shows those of carbons after treatment in a vacuum. All carbons were graphitized by pre-treatment with nickel, and the behaviour of diamond formation before treatment in a vacuum was similar to that following pre-treatment under 3 GPa. Treatment in a vacuum influenced the yield of diamond. The amount of diamond formed was on the whole not as much as in the case of pre-treatment under 3 GPa. The diamond yield from treated GPC was not recovered even by treatment in a vacuum. The effects of pre-treatment pressure were obvious for GPC, which was highly crystallized and consisted of a fine powder.

These results indicate that gases adsorbed on treated carbon are most harmful for diamond formation; and there can be also an effect of strain in graphite formed under high pressure, especially in the case of GPC.

4. Conclusions

Four starting carbons (GPC, PC, GC-30 and GC-20) which differed in crystallinity and grain size were pre-treated with or without nickel at 3 and 6 GPa. The non-graphitic carbons of PC and GC-20 were partially graphitized even in the absence of nickel at 3 GPa and 1800° C. GPC and GC-30 showed decreased or unchanged crystallinity. Diamond formation after pre-treatment was found to decrease or not to take place. The treatment of these carbons in a vacuum was effective in recovering the diamond yield. All four carbons were changed to graphitic carbon by treatment in the presence of nickel under 3 and 6 GPa. It was necessary for diamond formation to treat in a vacuum the graphite formed under high pressure, in order to remove adsorbed gases. The amount of diamond formed did not correspond with the crystallinity of the graphite. Pre-treatment under higher pressured tended to reduce the diamond yield.

Diamond formation from graphite formed under high pressure did not take place so readily. The adsorption of harmful gases on graphite during graphitization under high pressure was considered to be responsible for the inhibition of diamond formation. The adsorbed gases could be removed to a considerable extent by treatment at 2×10^{-5} torr and 1000° C. There may be an influence of strain induced in graphite formed under high pressure. This work reveals that the starting carbon for diamond synthesis should have a high crystallinity, and that adsorbed gases should be removed before synthesis.

Acknowledgement

The authors would like to thank Associate Proffessor A. Senoo, Nagoya University, for his kind help in the vacuum treatment of carbon.

References

1. F. P. BUNDY, H. T. HALL, H. M. STRONG and R. H. WENTORF Jr, *Nature* **176** (1955) 51.
2. V. I. KASATOCHKIN, L. E. SHTERENBERG, V. N. SLESAREV and Y. N. NEDOSHIVIN, *Dokl. Akad. Nauk SSSR*, **194** (1970) 801.
3. L. T. GANKEVICH, V. G. NAGORNYI and N. N. SHIPKOV, *Sint. Almazy* **3** (1977) 6.
4. A. TSUZUKI, S. HIRANO and S. NAKA, *J. Mater. Sci.* **19** (1984) 1153.
5. *Idem, ibid.* **20** (1985) 2260.
6. H. T. HALL, US National Bureau of Standards Special Publication No. 326 (1971) p. 313.
7. L. H. COKEN, W. KLEMEN Jr and G. C. KEN NEDY, *Phys. Rev.* **145** (1966) 519.
8. H. M. STRONG and F. P. BUNDY, *ibid.* **115** (1959) 278.
9. T. NODA, M. INAGAKI, S. HIRANO and K. AMANUMA, *Bull. Chem. Soc. Jpn.* **41** (1968) 1245.
10. M. MIZUSHIMA, *Tanso* **52** (1968) 9.

Received 30 July
and accepted 10 September 1984