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Effect of ambient pretreatment of graphite and solvent-catalyst on diamond formation

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Diamond was formed from purified natural graphite under high pressure and temperature conditions (7 GPa, 1700° C) using a solvent-catalyst in the unary (Fe) or binary (Fe–Ti) system. The effect of an ambient pretreatment of the starting mixed powder (graphite and solvent-catalyst) was investigated in relation to the formation and grain growth of diamond. An initial desorption of adsorbed water vapour or harmful gases from the starting powder in vacuum (2×10^{-5} torr) at higher temperatures (>400° C) was required in order to increase the conversion ratio from graphite to diamond. The subsequent ambient pretreatment at 1000° C in different atmospheres was found to affect the grain growth process of diamond. The depression of grain growth was confirmed in both cases of pretreatments in vacuum (2×10^{-5} torr) and in an argon atmosphere (1×10^{-3} or 760 torr). The diamond grains were discrete in the vacuum pretreatment, while a particle joining between the diamond grains was promoted in the argon pretreatment. The pretreatment in an N_2 atmosphere (1×10^{-3} or 760 torr) tended to accelerate the grain growth of diamond.

1. Introduction

Diamond has been synthesized from various kinds of graphite by using 3d transition metals as solvent-catalyst [1–4]. The pretreatment of starting materials (graphite and metals) has been shown to be one of the major influencing factors on diamond formation [5–7]. Few papers have reported, however, on what kind of atmosphere in pretreatment is required to obtain a desired grain size or microstructure of diamond aggregate. In a previous paper [5], the importance of adsorbed gases or atmospheric gases which greatly affect the diamond formation yield, was manifested by using the starting carbons with additives (oxides, hydroxides, carbonates, etc.) or various intentionally adsorbed gases (N_2, O_2, CO_2, H_2 and CH_4). It was suggested that hydrogen gas and hydrogen-containing compounds in starting carbons have an inhibitory effect on diamond formation.

In the present work, the effect of an ambient pretreatment of the starting mixed powder (graphite and solvent-catalyst) in a high temperature range was investigated in relation to the formation and grain growth of diamond. Purified natural graphite with fully graphitized structure was chosen as a starting carbon, since the high conversion to diamond was expected by using highly crystalline graphite [8]. The binary system (Fe–Ti) as well as the unary system (Fe), was used as a solvent-catalyst in order to depress the grain growth of diamond by adding titanium to the catalytic active metal iron [9]. The conversion ratio from graphite to diamond and the grain size or grain growth of the diamond crystals were examined in detail.

2. Experimental procedure

Fig. 1 shows the experimental procedure for conversion from graphite to diamond. The starting carbon was natural graphite powder (285–325 mesh) which was highly purified at 2800° C in a Cl_2 atmosphere. Iron and titanium powders (purity > 99.8%, 300 mesh) were used as solvent-catalyst metals, the composition of which was 20 wt % (6.5 vol %) Fe, 14 wt % (4.5 vol %) Fe–6 wt % (3.4 vol %) Ti, or 10 wt % (3.2 vol %) Fe–10 wt % (5.6 vol %) Ti. These solvent-catalyst metals (20 wt % in total) were mixed with 80 wt % natural graphite for 30 min in a V-shaped rotary mixer. The mixed powder was pretreated first in vacuum (at 2×10^{-5} torr) at 400° C for 1 h, and subsequently in one of three kinds of atmosphere at 1000° C for 1–6 h; in N_2 (at 1×10^{-3} or 760 torr), in argon (1×10^{-3} or 760 torr) or in vacuum (2×10^{-5} torr). N_2 or argon gas ($100\,ml\,min^{-1}$) was streamed in the furnace during the pretreatment at 760 torr.

Thus pretreated mixed powder (~50 mg) was packed into the specimen cell quickly in a globe box and set in the girdle-type high pressure apparatus. The cell assembly was the same as that in a previous paper [5] except that h-BN plates (2 mm in thickness) were arranged between the specimen powder and fired pyrophillite chip, and molybdenum plates (0.1 mm in thickness) were arranged between the graphite plate and SKH-9 disk. A constant high pressure and temperature treatment condition (7 GPa, 1700° C) was chosen so as to give an appropriate yield of diamond with reference to previous papers [4, 9]. The specimen was compressed to 7 GPa (accuracy: ±1.5%) and

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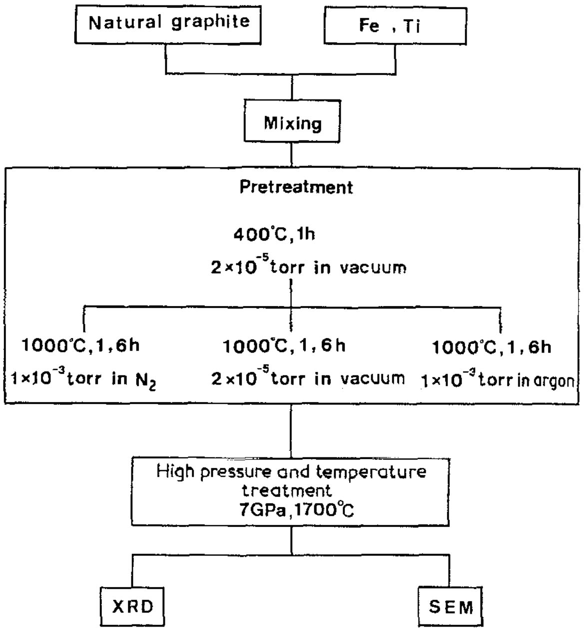


Figure 1 Experimental procedure for conversion from graphite to diamond.

then electric power was applied to the glassy carbon heater to heat the specimen up to 1700° C (accuracy: ± 20° C) in about 7 min. After the heat treatment for a desired reaction time, the specimen was quenched to room temperature under high pressure and then decompressed. The pressure was calibrated at room temperature by the pressure-induced phase transition of bismuth, thallium and barium [10]. The temperature was determined from the relation of the melting points of silver, gold and nickel under high pressure to the applied electric power, the pressure dependence of these being calibrated by earlier reports [11, 12].

The specimens were identified by X-ray powder diffraction. The conversion ratio from graphite to diamond was determined from the relative intensity of diamond 1 1 1 diffraction to that of graphite 0 0 2 diffraction by means of an established calibration curve. The microstructure of the specimen was examined by scanning electron microscope (SEM) after treatment in hot aqua regia for 1 h to eliminate residual graphite and metals.

3. Results and discussion

3.1. Effect of pretreatment on the conversion from graphite to diamond

Natural graphite powder which is exposed to the air would contain several kinds of adsorbed gases. Fig. 2 shows the pressure variation in the ambient pretreatment furnace as a function of pretreatment time, during which the furnace was kept evacuated by a diffusion pump. A heat treatment programme curve is also drawn in Fig. 2; the specimen was heated upto 400° C at the rate of 40° C min^{-1}, then held at 400° C for 1 h, followed by the temperature raised up to 1000° C for 35 min and held constant for further treatment time. The pressure in the furnace increased abruptly at the initial heating process from 6.5×10^{-5} torr to 2.8×10^{-4} torr and attained a maximum at $\sim 250°$ C. This peak would be attributed to the desorption of moisture which had been adsorbed on the graphite or metal surface. The pressure decreased gradually with time at the constant temperature of 400° C. The secondary maximum of pressure, although being a smaller one, appeared at the initial stage of the reheating process (the temperature would be 400–500° C). A small amount of the residually adsorbed gases would be outgassed by this heating, then the pressure decreased asymptotically to a constant pressure ($\sim 1 \times 10^{-5}$ torr) as pretreatment time elapsed.

The coexisting species in the specimens after ambient pretreatment and after high pressure and temperature treatment (7 GPa, 1700° C, 15 min) are summarized in Table I, where the treated specimens which contain 20 wt % Fe and 14 wt % Fe–6 wt % Ti as solvent-catalyst, were identified by X-ray powder diffraction. In case of 20 wt % Fe solvent-catalyst, all the mixed powders that were pretreated in vacuum (1000° C, 1 h, 2×10^{-5} torr), in argon (1000° C, 1 h, 1×10^{-3} torr) and in N_2 (1000° C, 1 h, 1×10^{-3} torr), comprised graphite, iron and a small amount of Fe_3C. After the high pressure treatment of these powders, Fe_3C and unconverted graphite were detected together with the formed diamond. The behaviour of iron carbide in these treatments corresponds to earlier reports [4, 13], although Fe_7C_3 could not be detected in the present case. On the other hand, in the 14 wt %–6 wt % Ti system, Ti and TiC_x were identified together with graphite, iron and Fe_3C after pretreatments both in

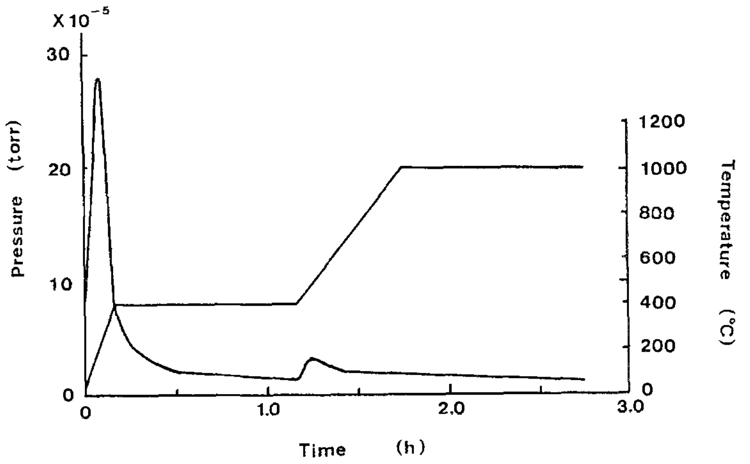


Figure 2 Pressure and temperature variation in the furnace as a function of pretreatment time.

TABLE I The coexisting species in specimen (a) after the ambient pretreatment (1000° C, 1 h) and (b) after the high pressure and temperature treatment (7 Gpa, 1700° C, 15 min). D, diamond; G, graphite.

Pretreatment	In vacuum		In argon		In N_2	
Solvent-catalyst composition	(a)	(b)	(a)	(b)	(a)	(b)
20 wt % Fe	G Fe_3C Fe	D, G Fe_3C	G Fe_3C Fe	D, G Fe_3C	G Fe_3C Fe	D, G Fe_3C
14 wt % Fe–6 wt % Ti	G Fe_3C Fe TiC_x Ti	D, G Fe_3C TiC_x	G Fe_3C Fe TiC_x Ti	D, G Fe_3C TiC_x	G Fe_3C Fe TiC_x Ti Ti_2N	D, G Fe_3C TiC_x Ti_2N

vacuum and in argon. TiC_x and Fe_3C still coexisted with diamond and unconverted graphite after the high pressure treatment. In case of the pretreatment in N_2 atmosphere at 1×10^{-3} torr, a small amount of Ti_2N was detected after both treatments, while TiN coexisted with other species in the N_2 flow pretreatment at 760 torr. In the solvent-catalyst system, 10 wt % Fe–10 wt % Ti, the detected species were the same as those in the system 14 wt % Fe–6 wt % Ti.

Table II shows the conversion ratio from graphite to diamond and the average grain size of the formed diamond, when the mixed powder containing three kinds of solvent-catalyst systems were pretreated in vacuum, argon and N_2 atmospheres, and treated at 7 GPa and 1700° C for 15 min. The catalytic power in the binary system is retained even with the addition of noncatalytic metal (titanium) in every pretreatment [2, 9, 14]. There is a tendency for the conversion ratio to decrease slightly with an increase in titanium content (i.e. with the decrease in iron content). The difference in the conversion ratio among the three pretreatments is minor, although the ratio is slightly high in vacuum pretreatment. The conversion ratio for no pretreatment (i.e. the powders were handled in air at room temperature), however, was about 60% in the iron solvent-catalyst system. It is confirmed, therefore, that the dehydration process especially in the first step (400° C, 1 h in vacuum) of pretreatment was greatly effective to obtain a high conversion ratio [5].

3.2. Effect of pretreatment on the grain growth of diamond

Table II shows that the grain size of diamond decreases remarkably by the addition of titanium in every pretreatment atmosphere. The grain growth of diamond is considered to be depressed in the presence of TiC_x particles, which will exist stably even under high temperature and pressure conditions [9]. The difference in the grain sizes among the three pretreatments can be seen also in Table II; the grain size by the pretreatment in N_2 atmosphere is not so depressed as those by the other two pretreatments. N_2 gas adsorbed on the graphite surface would have a positive effect on the grain growth of diamond. Fig. 3 shows the SEM photographs of the fractured surface of diamond, which formed at the reaction time of 15 min from 80 wt % natural graphite and 10 wt % Fe–10 wt % Ti solvent-catalyst with the pretreatment in one of three atmospheres (1000° C, 1 h) or with no pretreatment. The grain sizes with N_2 pretreatment (see Fig. 3c) and no pretreatment (see Fig. 3d) are similar to each other, although the developed facets in Fig. 3c are rarely seen in Fig. 3d. Large grains of diamond, however, with the grain sizes of 10–20 μm in diameter are observed in both cases. The adsorption of N_2 gas in air would have the same effect on the grain growth of diamond as the pretreatment in N_2 atmosphere. In contrast, the grain sizes by the pretreatment in vacuum and argon are 3–10 μm, which means a considerable depression of grain growth compared with that in N_2 atmosphere. It should be noted also that the grain morphology is a little different between the pretreatments in vacuum and argon atmosphere; the small grains are rather discrete in the case of pretreatment in vacuum, while the grains have a neck growth with the result of a densification process in sintering. The joining between the grains seems to be promoted in the presence of argon atmosphere. These effects of the difference in pretreatment atmospheres were observed typically in the binary solvent-catalyst system of Fe–Ti.

Fig. 4 shows the SEM photographs of the fractured surface of diamond which were obtained by a prolonged pretreatment time of 6 h (where the composition of the natural graphite and solvent-catalyst,

TABLE II The conversion ratio and grain size of diamond treated at 7 GPa and 1700° C for 15 min.

Solvent-catalyst composition	Pretreatment					
	In vacuum		In argon		In N_2	
	Conversion ratio (%)	Grain size (μm)	Conversion ratio (%)	Grain size (μm)	Conversion ratio (%)	Grain size (μm)
20 wt % Fe	90	20–50	85	20–50	85	20–100
14 wt % Fe–6 wt % Ti	80	5–20	80	5–20	80	10–40
10 wt % Fe–10 wt % Ti	75	5–10	75	3–10	70	10–20

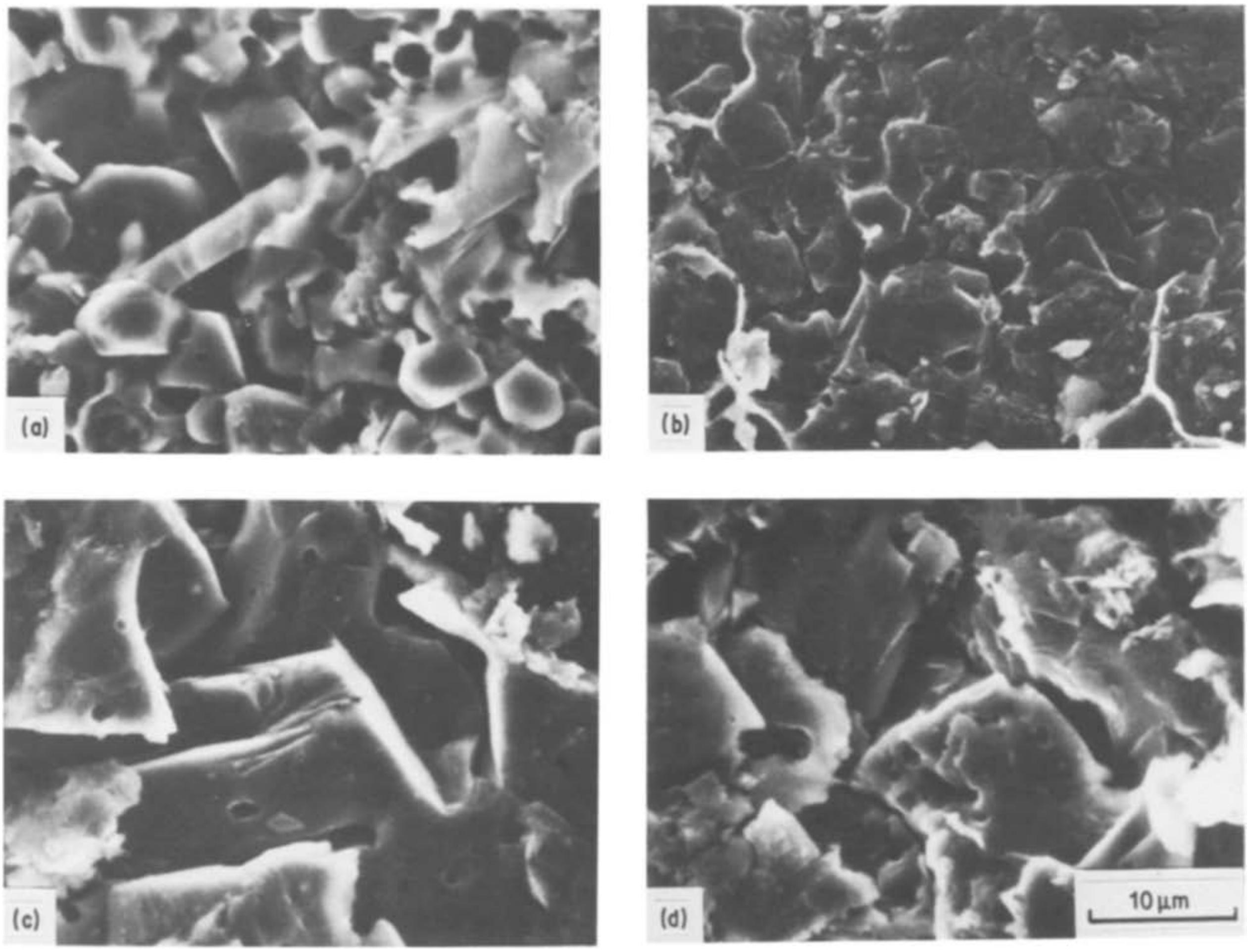


Figure 3 SEM photographs of the fractured surface of diamond treated at 7 GPa and 1700° C for 15 min in the presence of 10 wt % Fe–10 wt % Ti after the pretreatment at 1000° C for 1 h; (a) in vacuum (2×10^{-5} torr), (b) in argon (1×10^{-3} torr), (c) in N_2 (1×10^{-3} torr) and (d) with no pretreatment.

and the high pressure and temperature treatment conditions were the same as those in Fig. 3). The effect of an ambient pretreatment as seen in Fig. 3, seemed to be exaggerated, although the conversion ratios to diamond remained constant at those in Table I. In the vacuum pretreatment, a homogeneous texture with fine-grained particles of diamond (diameters ~ a few micrometres), can be seen in Fig. 4a, which would be accomplished by an outgassing of starting powder for 6 h (see Fig. 2). A densely packed microstructure, which appears to form strong interconnections between the growing diamond grains, is observed in argon pretreatment (see Fig. 4b). In the case of N_2 pretreatment, large grains of diamond with diameters of 40–50 μm, were formed by a grain growth promotion due to the higher concentration of adsorbed N_2 gas (compare Fig. 3c and Fig. 4c).

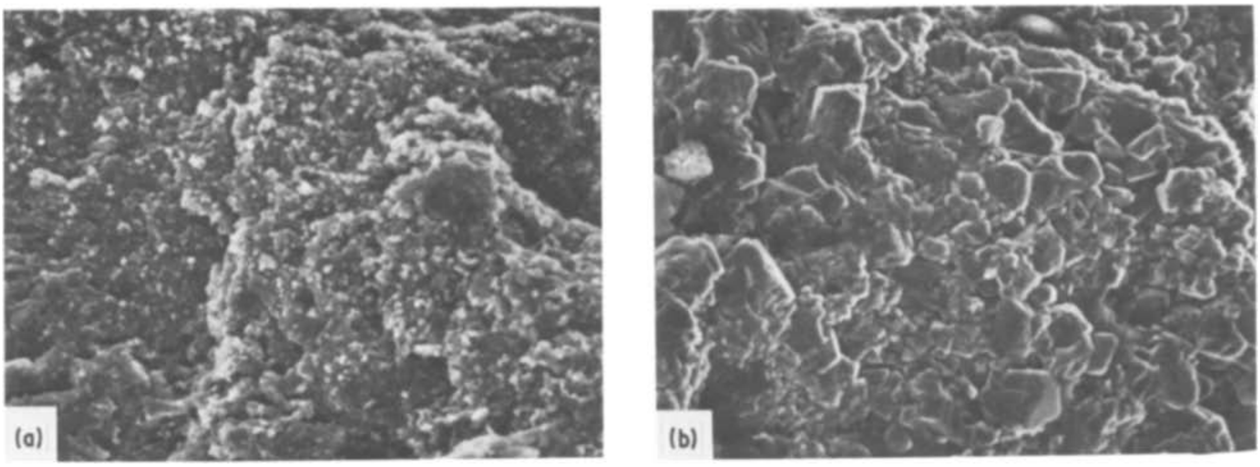
The grain growth process was examined as a function of high pressure and temperature treatment time. Fig. 5 shows the SEM photographs of the fractured surface of diamond which were obtained by the pretreatment time for 1 h in three different atmospheres and by the high pressure and temperature treatment time for 1 min. The conversion ratio from graphite to diamond for this initial stage of treatment, was about 50% in each ambient pretreatment. Fine grains with diameters of 2–3 μm can be seen in every case, suggesting that the initial nucleation process of diamond occurs during a short reaction time of 1 min. The grain growth by sintering might not be a major process at this stage of short reaction time. The conversion ratio at the high pressure and temperature treatment time of 5 min was 70–75%, however, after which the conversion ratio was kept constant for a further reaction time of 5–60 min.

Comparing this result with the microstructures in Fig. 3 (the high pressure and temperature treatment time was 15 min, other treatment conditions were the same), one can notice that the grain growth velocities are different among the three pretreatment atmospheres, indicating that the grain growth would be depressed in the inert atmospheres such as in vacuum or in argon.

It was found by the pretreatment at 760 torr (in N_2 or argon flow) that the remarkable difference in microstructures could not be observed in case of argon flow pretreatment. However, the grain growth was further promoted in N_2 flow pretreatment, ocasionally exhibiting exaggerated grain growth of diamond with diameters above 50 μm.

4. Conclusions

The effect of an ambient pretreatment of starting powder (natural graphite and solvent-catalyst) on the formation and grain growth of diamond was investigated under constant high pressure and temperature



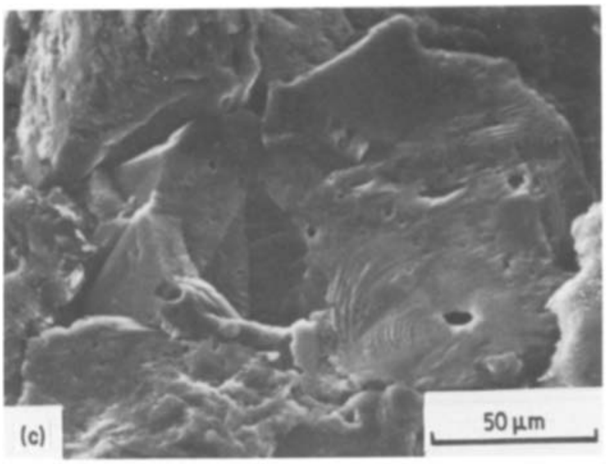


Figure 4 SEM photographs of the fractured surface of diamond treated at 7 GPa and 1700° C for 15 min in the presence of 10 wt % Fe–10 wt % Ti after the pretreatment at 1000° C for 6 h; (a) in vacuum, (b) in argon and (c) in N_2.

treatment conditions (7 GPa, 1700° C). The following results were obtained in cases of the initial degassing pretreatment (400° C, 2×10^{-5} torr, 1 h) and the subsequent ambient pretreatment (at 1000° C in N_2 at 1×10^{-3} or 760 torr, in argon at 1×10^{-3} or 760 torr, or in vacuum at 2×10^{-5} torr).

1. Desorption of adsorbed water or harmful gases from the starting powder in vacuum (2×10^{-5} torr) at higher temperatures (> 400° C) was effective to increase the conversion ratio from graphite to diamond.
2. The difference in conversion ratios from graphite to diamond by pretreatments in three atmospheres (in vacuum, argon and N_2) were minor in both unary (Fe) and binary (Fe–Ti) solvent-catalyst systems.
3. The grain growth of the formed diamond can be depressed by the pretreatment in vacuum or in argon atmosphere. This effect was observed typically in the binary solvent-catalyst system of Fe–Ti.
4. The diamond grains formed by the pretreatment in vacuum were discrete, while the formation of the particles joining the diamond grains was promoted by the pretreatment in argon atmosphere.

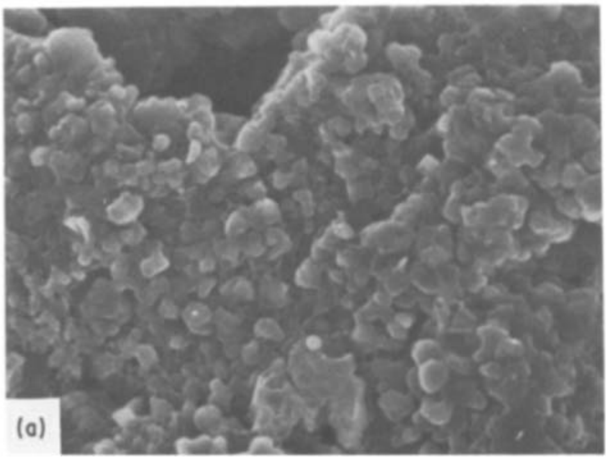
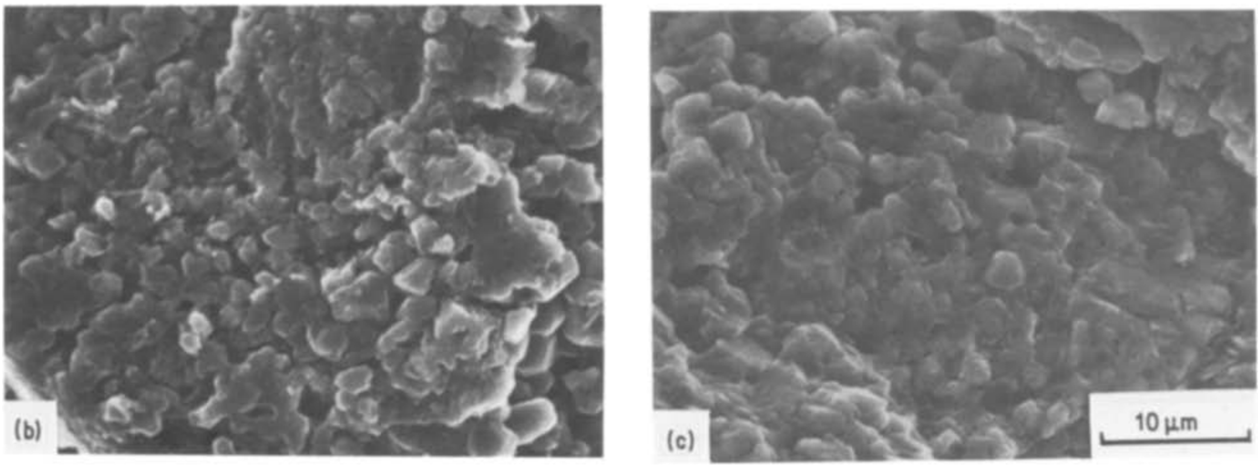


Figure 5 SEM photographs of the fractured surface of diamond treated at 7 GPa and 1700° C for 1 min in the presence of 10 wt % Fe–10 wt % Ti after the pretreatment at 1000° C for 1 h; (a) in vacuum, (b) in argon and (c) in N_2.



5. The pretreatment in N_2 atmosphere was found to accelerate the grain growth of diamond in both unary and binary solvent-catalyst systems.

The reaction sintering of diamond with the help of these ambient pretreatments of starting powder, will be described in a subsequent paper.

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