

Nucleation and Growth of Diamond in High Pressure

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In diamond synthesis by metal film growth method under high pressure and high temperature, the nucleation and growth of diamond was observed dependent on the carbon source variation from graphite powder to the heat treated powders of lamp black carbon. At the low driving force condition near equilibrium pressure and temperature line, nucleation of diamond did not occur but growth of seed diamond appeared in the synthesis from lamp black carbon while both nucleation and growth of diamond took place in the synthesis from graphite. Growth morphology change of diamond occurred from cubo-octahedron to octahedron in the synthesis from graphite but very irregular growth of seed diamond occurred in the synthesis from lamp black carbon. Lamp black carbon transformed to recrystallized graphite first and very rare nucleation of diamond was observed on the recrystallized graphite surface. Growth morphology of diamond on the recrystallized graphite was clear cubo-octahedron even at higher pressure departure condition from equilibrium pressure and temperature line.

Key words : Diamond, HPHT, Nucleation, Growth, Morphology

I. Introduction

Industrial diamond granules are usually synthesized from graphite in a metal solvent under high pressure and high temperature (HPHT). Diamond is known to be synthesized through dissolution of graphite in the molten metal, diffusion across metal thin film and precipitation as diamond.¹⁻³⁾ The nucleation and growth of diamond has been investigated in many aspects in this metal film growth process since the first success of diamond synthesis. In the pressure-temperature phase diagram, diamond synthesis was found to be possible in the v-shaped valley located inside the two lines. One line is the eutectic melting line of the solvent metal and the other line is the equilibrium graphite-diamond transformation line.^{4,5)} The nucleation and growth rates have been examined to be very sensitive to the parameters such as pressure, temperature and interfacial energy between diamond and molten metal even inside the v-valley.^{6,7)} The rates increased significantly with pressure increase. Nucleation zone was also investigated depending on the solvent metal in the v-valley and more detailed nucleation area was observed.^{8,9)} The effect of carbon source material and seed diamond on nucleation was also investigated,^{2,8-13)} however, the nucleation and growth of diamond was not analysed on the morphological relations to the driving force. The nucleation and growth control at the low driving force condition is very important in order to improve diamond quality. In this investigation, the growth of seed diamond was observed firstly varying the carbon source material in ord-

er to understand the morphological change at low driving force condition. The diamond synthesis without seed crystals was also investigated varying the carbon source materials in order to observe the nucleation and growth and analyse the nucleation.

II. Experimental Procedure

The experiments were made firstly to study how seed diamond crystals can grow in the melt saturated with graphite and lamp black carbon respectively, and second to examine how the nucleation and growth of diamond can occur in the two different carbon sources. Graphite and lamp black carbon powders were from Fisher co. and heat treatment were done at the temperature of 1400°C for one hour at 0.1 Torr pressure in order to minimize adsorbed gas effect.¹⁴⁾ Scanning electron microscopy of graphite and lamp black carbon powders was shown in Fig. 1. Graphite powder has mean size of about 10 μm as shown in Fig. 1(a). Lamp black carbon showed typical very small mean size of 1100-1200 \AA as in Fig. 1(b). X ray diffraction pattern of graphite and lamp black carbon powder was shown in Fig. 2. Graphite powder showed typical narrow peak at $2\theta=26.5^\circ$. Lamp black carbon heat treated at the high temperature of 2450°C showed partly crystallized graphite pattern but those heat treated at the temperature of 1400°C or non-heat treated exhibited broad band around $2\theta=24-28^\circ$. Lamp black carbon had, therefore, so called turbostratic carbon structure.

Two kinds of high pressure cell were prepared to observe nucleation and growth from the two different car-

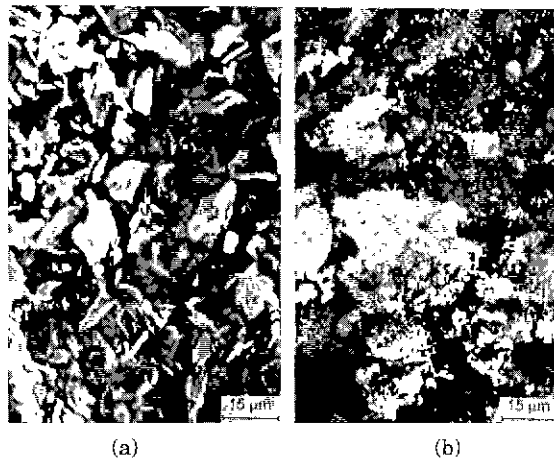


Fig. 1. SEM image of carbon source materials. (a) Graphite powder (b) Lamp black carbon.

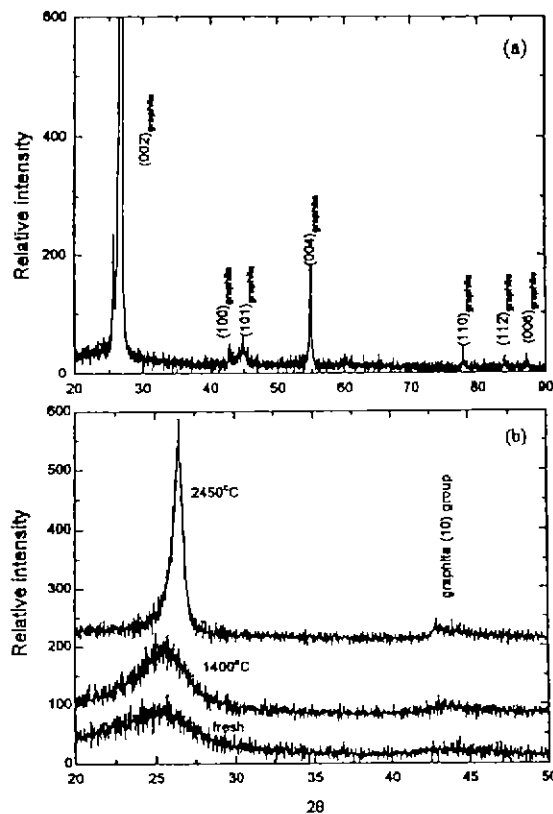


Fig. 2. X-ray diffraction patterns of carbon source materials. (a) Graphite powder (b) Lamp black carbon powders heat treated at 2450°C, 1400°C and room temperature.

bon sources clearly. One cell was constructed putting three layers, that is, carbon source layer, Fe-Ni (4:6) alloy disk layer and carbon source layer inside the salt pressure medium contained graphite heater tube as shown in Fig. 3. The other cell also had the same structure with three layers inside the heater tube except the three to five seed diamond cubo-octahedron crystals located just on and below the Fe-Ni (3:7) alloy disk. Thick-

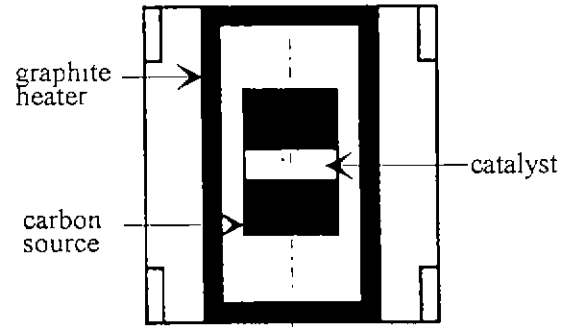


Fig. 3. The cross section of diamond synthesis cell inside the salt tube.

ness of Fe-Ni alloy disk was about 600 μm . Each constructed cell was treated at 4.3-4.7 Gpa and 1330-1450°C for 5-30 minutes with a belt-type high pressure apparatus. The pressure in the cell was calibrated at room temperature by the phase transition of Bi (2.55 Gpa), Tl (3.76 Gpa) and Ba (5.55 Gpa). The temperature was measured by inserting a (Pt-6 wt%Rh)-(Pt-30 wt%Rh) thermocouple in the cell center. The pressure effect on the electromotive force due to thermal expansion of the cell ingredients during heating were not compensated.

The cell were pressed and then heated indirectly with graphic heater to the synthesis temperature. After holding for determined time, the cell was cooled to room temperature and the pressure was released. After removal of the remained carbon layer, the solvent metal surface including diamond particles were observed by optical stereomicroscopy and scanning electron microscopy to identify the growth morphology of the diamond and re-crystallized graphite.

III. Results and Discussion

In the first series of experiment in order to investigate seed diamond growth in different carbon source, seed diamond with cubo-octahedron shape was inserted into the interface between solvent alloy and carbon source and growth test in HPHT was done for 5 minutes at the synthesis condition of low driving force, that is, 4.5 Gpa and 1450°C near the equilibrium line of graphite to diamond conversion in the pressure-temperature phase diagram. In this synthesis experiment growth of seed diamond was clearly observed. It is obvious that seed crystals with 600 μm size grew to bigger size (more than 800 μm) comparing the original crystal in Fig. 4(a) and other grown crystals in Fig. 4(b), Fig. 5 and Fig. 6. On the flat surface of grown crystal in Fig. 4 and 5, metal films were found to be covered. It explains that there was liquid metal film between the growing crystal and carbon source material and metal film growth process occurred naturally. Grown morphology of diamond crystal was completely different from original seed crystal and shape change occurred differently depending on the providing

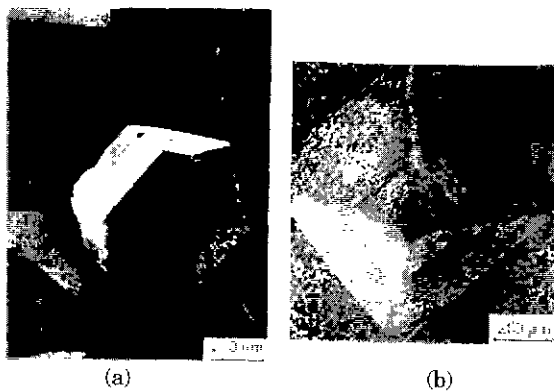


Fig. 4. SEM image of diamond crystals observed before and after growth. (a) Original seed crystal (b) Octahedral crystal grown from the graphite source at 4.5 GPa and 1450°C for 5 minutes.

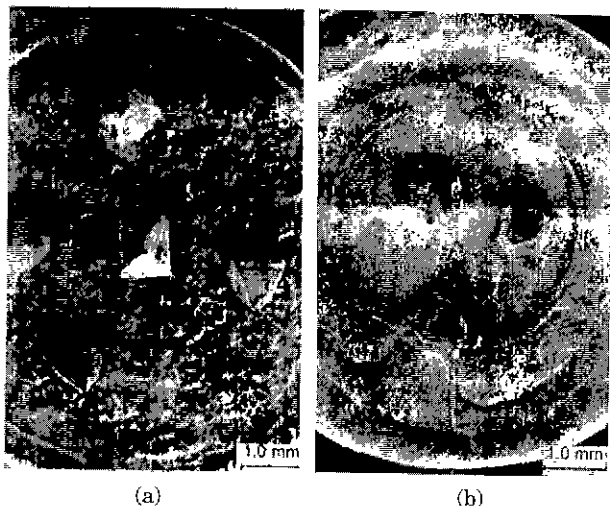


Fig. 5. SEM images of diamond crystals on solvent metals grown at 4.5 GPa and 1450°C for 5 minutes. (a) Grown crystals from the graphite source (b) Grown crystals from the heat treated lamp black carbon (partially graphitized).

carbon sources. Original cubo-octahedron seed crystals grew to octahedron shaped crystals in the diamond synthesis from graphite as shown in Fig. 4(b) and Fig. 5(a). This explains that growth rate of {100} plane was higher than that of {111} plane and lately grown {111} plane covered whole grown crystal surface. When the heat treated lamp back carbon powder (partially graphitized at 2450°C) was inserted instead of graphite powder, small irregular morphological change occurred as can be seen in Fig. 5(b). The faceted plane of {100} and {111} remained but some irregular crystals seemed to start to grow on the faceted planes. Completely different irregular morphology was obtained in case of the diamond synthesis from the lamp black carbon as shown in Fig. 6(a) and (b). Irregularly grown rate and the driving force of this growth were higher than those of the clearly faceted crystal growth. This morphological change from

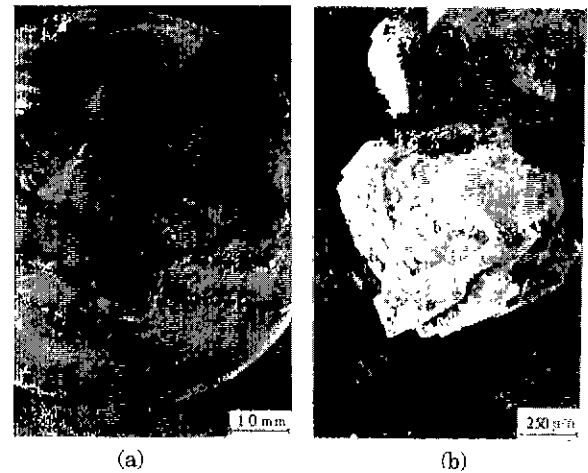


Fig. 6. SEM images of diamond crystals grown from the lamp black carbon source at 4.5 GPa and 1450°C for 5 minutes. (a) Irregular crystals on the solvent meta (b) Magnified view of the irregularly grown crystals.

well faceted to very irregular shape after growth relates very well with the structure difference of the carbon sources shown in Fig. 2. Higher the amorphous carbon content in the carbon source was, more irregular growth occurred and higher the graphite content in the carbon source was, more faceted growth took place. It is, therefore, clearly observed that seed diamond crystals grew through the metal film growth process, and that diamond crystals grew by the dissolution of lamp black carbon into the liquid solvent metal and the precipitation of carbon on the diamond surface without passing the recrystallized graphite. It is, however, observed that the growth and/or the nucleation and growth of recrystallized graphite also occurred in the diamond synthesis from graphite and/or lamp black carbon in the region where seed crystals were absent. Diamond growth and graphite recrystallization seemed to be independent parallel processes and not to be dependent connecting processes.

In order to examine the nucleation and growth of diamond during HPHT synthesis from graphite and lamp black carbon, experiments were done at a constant pressure of 4.5 Gpa varying temperature from 1330°C to 1450°C and at a constant temperature of 1390°C varying pressure from 4.3 Gpa to 4.7 Gpa for 5 minutes respectively. Diamond was not nucleated from graphite at the synthesis condition of 4.5 Gpa, 1450°C and 5 minutes as shown in Fig. 7(a). Very well faceted cubo-octahedron crystals were synthesized by just dropping the temperature to 1420°C and fixing other condition. Lowering the temperature more to 1390°C, many diamond crystals nucleated and grew as shown in Fig. 7(b). At much lower temperature of 1330°C, more diamond crystals appeared as can be seen in Fig. 9(a). In the diamond synthesis from the graphite with Ni-Fe(6:4) alloy solvent, diamond synthesizable zone in the pressure-temperature phase di-

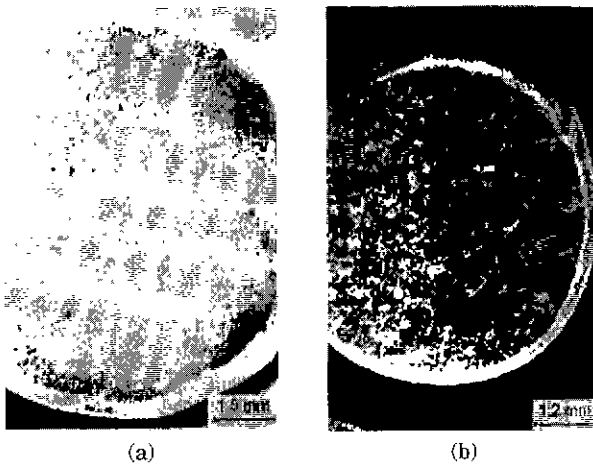


Fig. 7. Solvent metal surfaces after diamond synthesis from the graphite at 4.5 Gpa for 5 minutes varying the temperature. (a) 1450°C (b) 1390°C.

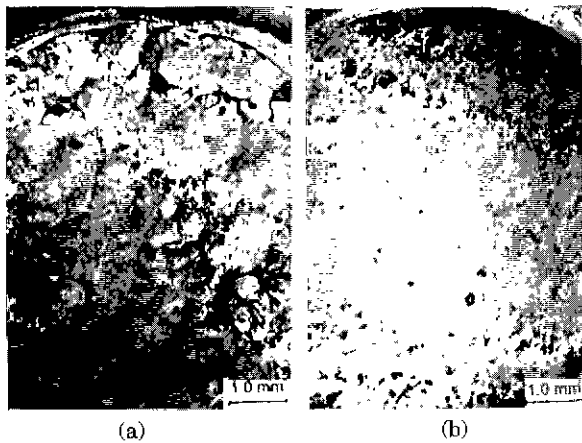


Fig. 8. Solvent metal surfaces after diamond synthesis from the graphite at 1390°C for 5 minutes varying the pressure. (a) 4.7 Gpa (b) 4.3 Gpa.

agram seemed to be located between two temperatures of 1320°C and 1430°C at 4.5 Gpa. Lowering the synthesis temperature at constant pressure, the distance from the Berman-Simon equilibrium line becomes longer in the phase diagram and the driving force increases higher. Higher nucleation rate observed in this experiment by lowering the temperature was naturally due to the higher driving force effect. At a constant temperature of 1390°C pressure effect was investigated by changing the pressure 4.3, 4.5 and 4.7 Gpa respectively. Increasing the pressure, number of nucleated and grown crystals increased as shown in Fig. 7(a) and Fig. 8(a) and (b). Growth morphology also changed from the flatly faceted crystal surface to the defected crystal with central dug spot where Berg effect was appeared as shown in Fig. 10(a). Larger number of nucleated crystals and more defected morphology change were also due to the higher driving force according to the pressure increase. Replacing the carbon source material from graphite to

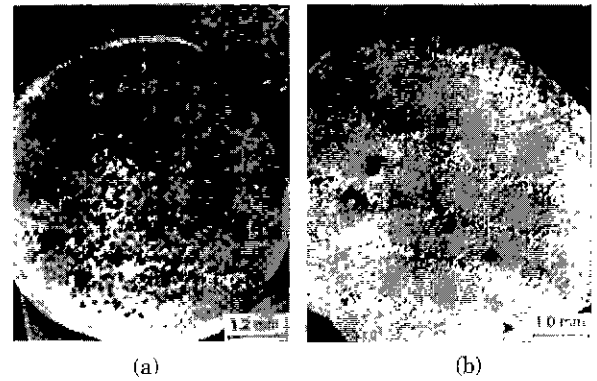


Fig. 9. Solvent metal surfaces after diamond synthesis for 5 minutes. (a) Diamond synthesis from the graphite source at 4.5 Gpa and 1330°C (b) Diamond synthesis from the lamp black carbon source at 4.7 Gpa and 1450°C.

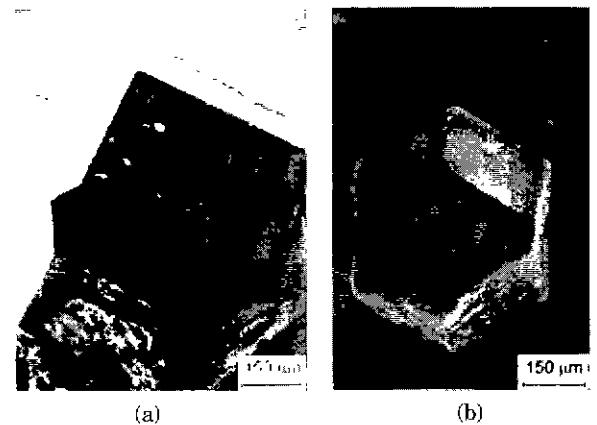


Fig. 10. SEM images of diamond crystals synthesized at 4.7 Gpa and 1450°C for 5 minutes varying carbon sources. (a) Diamond crystals synthesized from the graphite source. (b) Diamond crystals synthesized from the lamp black carbon source

lamp black carbon, the same HPHT synthesis experiment were done. Below the pressure of 4.5 Gpa diamond was not synthesized at any temperature and mor longer time from the lamp black carbon. In this condition only graphite recrystallization was observed as nearly hexagonal grain prints on the solvent metal surface instead of diamond appearance. As a synthesizing condition of 4.7 Gpa, 1450°C and 5 minutes, several diamond crystals appeared as shown in Fig. 9(b). A clear cubo-octahedron diamond crystal was observed as shown in Fig. 10(b) magnifying the grown crystal by SEM. From this synthesis result it was found that diamond synthesizable zone moved to higher pressure and lower driving force was exerted to grow the diamond. Comparing Fig. 10(a) and (b), the difference of driving force is obvious. It was, here, clearly found that lamp black carbon transformed primarily to recrystallized graphite and diamond could not nucleate from the lamp black carbon, however, diamond crystals nucleated from the recrystallized graphite after transformation and grow to

clean cubo-octahedron shape with lower driving force condition even at higher pressure. In the diamond synthesis from amorphous carbon like lamp black carbon, Ostwald step rule seemed to be applied here, that is, the transformation of lamp black carbon with higher free energy to the stable diamond with lowest free energy could not directly occur without passing the metastable recrystallized graphite with intermediate free energy.¹³⁾ Considering the growth experiment results and the nucleation and growth experiment results simultaneously, the nucleation of diamond could be explained as follows. Diamond nucleation seemed to occur on the stable graphite surface which did not move by surface reactions such as dissolution and precipitation. Diamond seemed to nucleate just on the graphite surface. Graphite structure, that is, whether it was recrystallized or not, influenced the driving force. Even at the stable diamond conversion region of the phase diagram, recrystallization of graphite could take place and diamond could not nucleate on the graphite surface where recrystallization reaction occurred. Diamond nucleation could occur on the graphite-solvent metal interface where graphite did not start to recrystallize or graphite finished to recrystallize. The driving force of diamond nucleation from the graphite is naturally higher than that from the recrystallized graphite since recrystallized graphite has lower free energy than the graphite.^{13,15)}

IV. Conclusion

The growth of seed diamond and the nucleation and growth of diamond were investigated depending on the carbon source materials at HPHT experiment. In the diamond growth experiment of 4.5 Gpa, 1450°C and 5 minutes, cubo-octahedral seed diamond grew to octahedron shape from graphite source, to slightly irregular cubo-octahedron morphology from heat treated (partially graphitized) lamp black carbon source and to very irregular shape from lamp black carbon. At this low driving force condition which diamond did not nucleate, the growth of seed diamond occurred showing different morphology dependent on the carbon source material. The morphology change related to the driving force of diamond transformation, that is, graphite source had lower driving force and lamp black carbon source had higher driving force due to higher carbon solubility of amor-

phous carbon in the solvent metal.

In the nucleation and growth of diamond experiment, graphite source exhibited diamond nucleation below 1420°C at 4.5 Gpa for 5 minutes while lamp black carbon source showed nucleation at the condition of 1450°C, 4.7 Gpa and 5 minutes but did not show any nucleation below 4.5 Gpa at any temperature. Before diamond nucleation, lamp black carbon transformed to recrystallized graphite. The growth morphology of clean cubo-octahedron diamond from lamp black carbon source exhibited lower driving force even though the applied synthesis pressure was higher than the graphite source. Diamond nucleation seemed to occur on the stable graphite surface which did not move by the dissolution or precipitation reaction.

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