

Pressure and Temperature Control and HPHT Diamond Synthesis Using FB25 Type Belt Apparatus

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Flat belt (FB) type high pressure apparatus has been successfully utilized in various high pressure experimental stations in Korea and Japan to conduct HPHT (high pressure and high temperature) diamond synthesis. Present paper discusses pressure calibration of FB apparatus at high temperature to establish P-T condition of diamond synthesis. We also present some examples of controlling P-T condition through careful experimental set-up of the high pressure sample cells. Finally we discuss reproducibility of pressure and temperature condition of the HPHT diamond synthesis.

Key Words : High pressure and high temperature, Diamond synthesis, Morphology control

I. Introduction

In the synthesis of diamond at HPHT, pressure and temperature condition is a key factor controlling nucleation and growth of diamond.¹⁾ Previously, few experimental results were presented on the P-T region of diamond synthesis evaluating P-T values.²⁾ Among them, the phase boundary curve presented by Kennedy and Kennedy³⁾ and minimum P-T condition of diamond synthesis in Ni-C⁴⁾ provide a standard condition to evaluate pressure and temperature.

In this study, we conducted diamond synthesis in the system Ni-C, Co-C, Fe-Co-C, Fe-Ni-C using Flat Belt (FB) apparatus⁵⁾ and salt pressure cell⁶⁾ to evaluate pressure and temperature values. We also present experimental examples how diamond morphology and impurity play with controlling P-T conditions.

II. Experiments

As shown in Fig. 1, NaCl cell and indirect heating graphite furnace are used for a pyrophyllite-paper gasket combination of a standard FB25H type cell assembly. Normally, we increase pressure first and then increased temperature with controlling input power to the heater. During the operation, we measure (1) oil pressure of the hydraulic ram/anvil displacement and (2) in-put power/current and voltage. Both anvil displacement and current-voltage measurements can be monitor reproducibility of pressure and temperature for different cells and HPHT excursions.

The sample cell and gasket assembly was inserted into tungsten carbide bore of high pressure cylinder. The lower part of the assembly was placed on the lower tung-

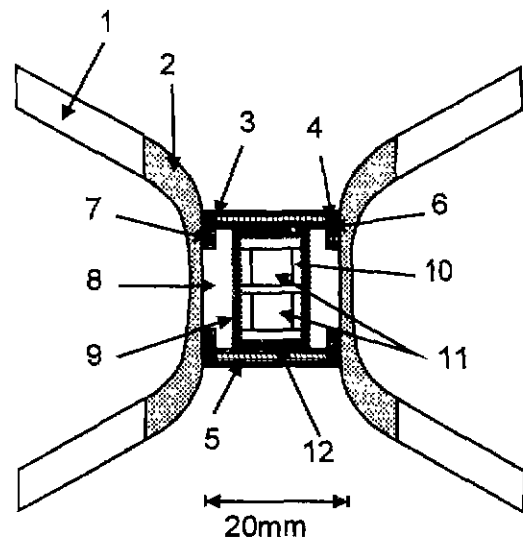


Fig. 1. Schematic drawing of the FB25H high pressure sample cell and gasket.

1. Laminated paper gasket, 2. pyrophyllite gasket, 3. SUS plate, 4. steel current ring, 5. sintered stabilized zirconia, 6. Mo plate, 7. Steel ring for prevent deformation of NaCl part, 8. outer NaCl sleeve (NaCl+10 wt% stabilized airconia powder), 9. graphite heater, 10. inner NaCl sleeve contained 10 wt% zirconia, 11. sample space.

ten carbide anvil.

III. Results and Discussion

1. Diamond synthesis in various metal-carbon systems

Strong⁴⁾ has determined a Ni-C eutectic point at 1390°C at 5.5 GPa. The eutectic point was almost con-

stant at this pressure range. Combining, graphite/diamond boundary by Kennedy and Kennedy, P (GPa) = T (C)/400 + 1.94,³⁾ and Ni-C eutectic point, we can estimate 5.4 GPa and 1384°C for a minimum P-T condition of diamond formation in the Ni-C system. Based on this standard, we can determine minimum P-T condition of diamond formation as shown in Fig. 2.

We estimated minimum P-T condition of diamond formation in the Co-C system as 5.24 GPa and 1320°C and in the system invar (Fe66Ni34)-C as 4.85 GPa and 1164°C based on the minimum P-T condition for di-

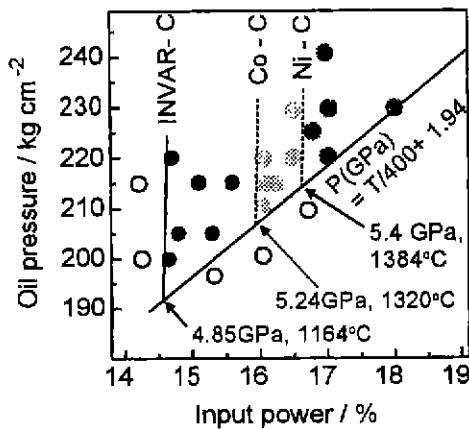


Fig. 2. Pressure and temperature condition of diamond formation in the system invar-C, Co-C and Ni-C. Minimum P-T conditions were estimated an intersect of minimum temperature curve and graphite diamond boundary. The percent of input power corresponds temperature while oil pressure of the ram corresponds to press load and sample pressure. The run area of the hydraulic press used was 2205.1 cm².

amond formation in Ni-C system. Based on the minimum P-T conditions estimated in Fig. 2, we can determine the relation between input power versus temperature of the sample. Independent temperature calibration using Pt/Pt 13% Rh thermocouple showed about 15°C difference between measured and estimated temperature.

We determined press load versus sample pressure based on the results shown in Fig. 2. Independently, we determined pressure of the phase transformation of CaGeO₃ (garnet/perovskite phase). The boundary curve of this transformation was determined by Suskin *et al.*⁷⁾ as P (GPa) = $6.9 - 0.0008T$ (°C). Difference of the transformation pressure is very small if temperature measurement varied for 100°C, because temperature coefficient of the transition was very small if temperature measurement was very small.

The results on the pressure calibrations based on the diamond synthesis and CaGeO₃ phase transition at high temperature were agreed within 0.05 GPa at about 6 GPa range. Estimated pressure was determined to be increased 20% from room temperature calibration due to the thermal expansion of salt cell. The result on the pressure increase at about 1400°C in salt cell of the belt apparatus was agreed with the calibration by Strong and Bundy.⁸⁾

2. Morphology and Impurity in the Diamond Crystal for the Evaluation of Temperature Control Technique

We examined morphology of diamond single crystal grown in Ni-5% Ti alloy at 5.7 GPa and between 1300 and 1500°C. The growth run was carried out for 3 h in a solvent bath of 7 mm in diameter and 3 mm thickness

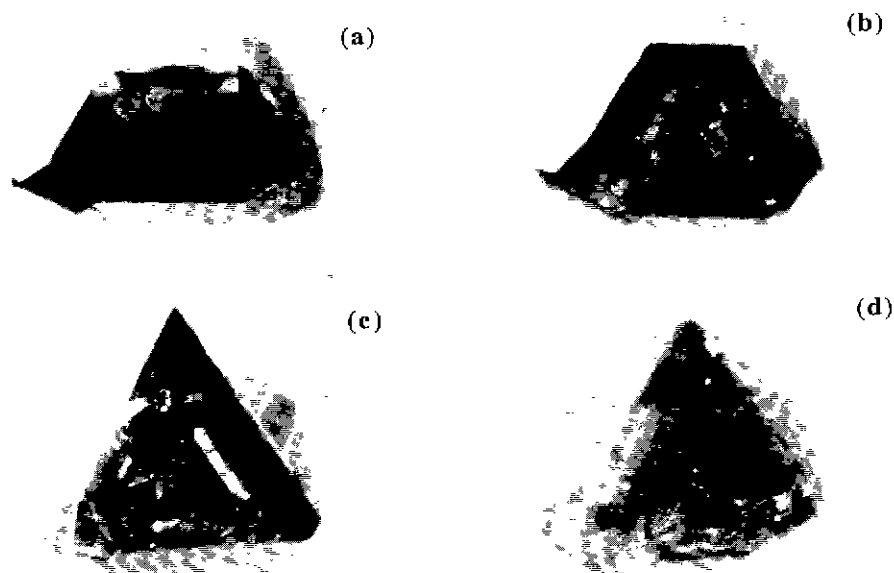


Fig. 3. Morphological change of diamond single crystals grown in Ni-5 wt% Ti solvent at (a) 1310°C, (b) 1340°C, (c) 1450°C and (d) 1500°C for 3 h. Pressure of the growth conditions were all at 5.7 GPa.

using a FB25H type apparatus. As shown in Fig. 3, when we increase growth temperature, the morphology of diamond crystals was changed from cubo-octahedral to octahedral one with decreasing relative area of (100) surface. This trend was agreed with general scheme of the morphological change of diamond by growth temperature. But it is noteworthy that present data are very systematic to show the morphological change of diamond crystals. Furthermore, semiquantitative analysis of nitrogen content by IR method distinctly showed a reasonable change of nitrogen content at C-center (Nc) as shown in Fig. 4.

The isolated nitrogen impurity namely C-center nitrogen decreased with increasing Ti content in the solvent and increasing growth temperature. The amount of incorporated nitrogen as C-center in the diamond grown in Ni solvent was relatively higher level than that of grown in Fe-Co. It is interesting to investigate/temperature/pressure conditions. As indicated in the present results, FB25 apparatus can be used for such experiments with control pressure and temperature precisely. In a practical operation of the experiments measurements of anvil displacement and heating voltage/current are essential to check unexpected pressure change or unusual cell deformation. Heating voltage/current measurements also sensitive to the cell deformation and unexpected fluctuation of pressure and temperature. In our experience, nucleation density and size of diamond can be controlled by monitoring two of these parameters in each run.

Quality and accuracy of the size of the graphite heater are important factors to maintain reversibility of input power and temperature relationship. We used homogeneous textured graphite (Toyo Tanso ISO-63). Direction of the cutting graphite block was maintained as same direction. Precision of the dimension of the graphite tube was kept within ± 0.02 mm. The monitored resistance of the heater at about 1300°C was within $\pm 3\%$. If accuracy of the resistance measurements was improved, more precise temperature control can be realized. At present, we can control temperature within $\pm 10^\circ\text{C}$.

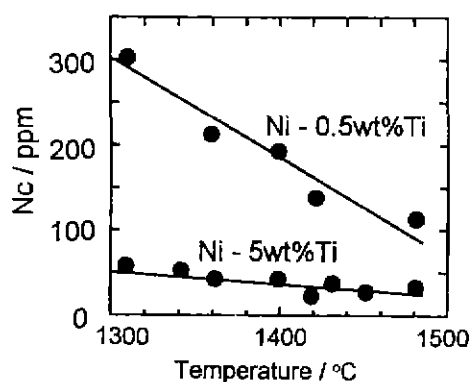


Fig. 4. Concentration of isolated nitrogen impurity (C-center nitrogen) versus growth temperature. The concentration was semiquantitatively measured by IR spectroscopy.

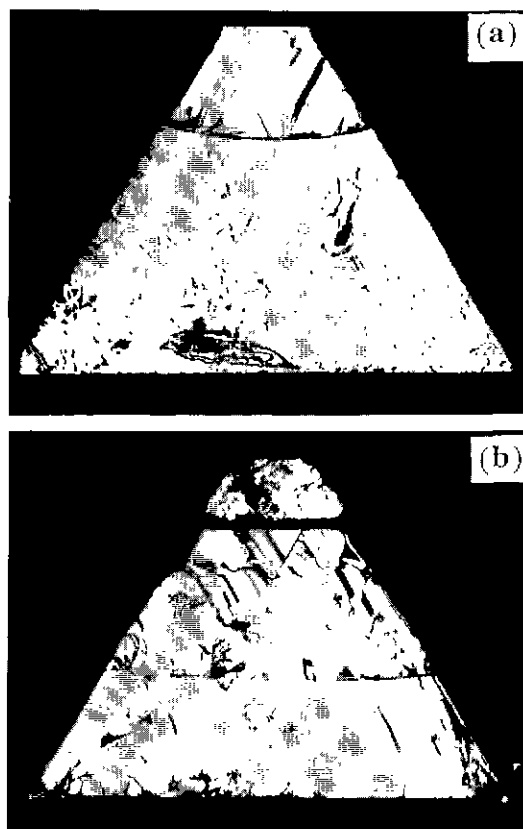


Fig. 5. Recrystallized seed crystal treated in Fe-Co solvent at 5.9 GPa for 3 h. (a) 1315°C and (b) 1335°C.

3. Seed Recrystallization in Fe-Co Solvent

We conducted diamond growth experiments using Fe-Co solvent. The growth P-T condition of diamond in this system was separated into three regions. At about 5.9 GPa, distinct nucleation boundary was observed at about 1300°C. At lower temperature than 1300°C, nucleation density of diamond was very small and only very small amount of tiny diamond crystals were observed. We deduced the boundary temperature correspond to decomposition temperature of cementite phase.⁹⁾

Above 1300°C, the diamond seed crystal dissolved into Fe-Co solvent partly and recrystallized on the residual seed crystal as shown in Fig. 5. The figure shows (111) surfaces of the seed and recrystallized diamond. The surface showing growth step parallel to the (111) edge was recrystallized zone. The temperature difference between (a) and (b) was estimated to be about 20°C, because we estimated temperature for the sample (a) was 1315°C and 1335°C for sample (b). As shown in the figure, recrystallized zone was developed with increase of solvent temperature. This trend maintained to 1420°C. This is a good example to show precise control of temperature in FB25H apparatus.

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