Lowering P, T boundary for synthesis of pure nano-polycrystalline diamond

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Abstract. Attempts have been made to synthesize nano-polycrystalline diamond (NPD) from graphite at pressures of 12, 13 and 14 GPa at temperatures 2200-2600°C using multi-anvil apparatus. The lower temperature limit for NPD formation increased with decreasing pressure, and we found that pure NPD can be synthesized even at the lowest pressure of 12 GPa, although quite high temperatures of exceeding 2600°C are required. This result demonstrates that NPD can be formed at significantly lower pressures than ever synthesized, which should provide an important constraint in synthesizing larger NPD samples under limited press loads.

1. Introduction

Well sintered polycrystalline diamond aggregate without any extraneous substances is an ideal hard material in terms of both mechanical durability and thermal stability. We previously reported synthesis of pure polycrystalline diamond (nano-polycrystalline diamond, NPD) from graphite by a direct conversion method under high pressure and high temperature using a Kawai-type multi-anvil apparatus [1]. This NPD consists of fine diamond grains of several tens of nanometers and has extremely high hardness, equivalent to or even higher than the hardest plane of single crystal diamonds [2, 4]. Because of these features, NPD has immeasurable potential for applications to high pressure anvils, as well as for industrial applications. The dimensions of NPD samples were limited to less than 1 mm and exhibited some major cracks in these earlier studies. For applying this material to these applications, synthesis of NPD with larger dimensions is strongly desired. However, the sample volume is limited by the pressure that is needed for synthesis. As the lower limits of pressure/temperature conditions for NPD formation have not been well known to date, we have investigated these lower limits for NPD synthesis.

2. Experimental

The starting material was high purity polycrystalline graphite (99.99%; Nilaco Co. Ltd.) with a rod shape of 4.6 mm in diameter and 3.0 mm in thickness, which was enclosed in a Ta capsule, surrounded by a semi-sintered MgO sleeve. A Re foil was used as a heater and inserted into a LaCrO$_3$ sleeve. The temperature was measured using a $W_{97}\text{Re}_{3}-W_{75}\text{Re}_{25}$ thermocouple. In order to avoid the thermocouple reacting with the LaCrO$_3$ thermal insulator at high temperature, the thermocouple wire was completely covered with Al$_2$O$_3$ or MgO sleeves. In this manner, temperatures of about 2500°C could be measured.
accurately on a routine basis. Pressures were estimated on the basis of phase transitions in several reference materials at room temperature (ZnTe, 12.0 GPa; ZnS, 15.6 GPa).

A DIA type 3000-ton multi-anvil apparatus (ORANGE-3000, GRC, Ehime Univ.) was used, and experiments were carried out under high pressure and high temperature conditions of 12-14 GPa and 2200-2600°C. Pressure was increased first and released slowly, after the sample was kept at the target pressure and temperature for 5-30 min. The recovered samples were inspected by an optical microscope, and they were further examined by a micro-focus X-ray diffractometer and Raman spectroscopy for phase identification. The knoop hardness of some of the samples was also measured as described in [4].

![Graph showing phase transition and synthesis conditions](image)

**Fig 1.** The lower boundary for synthesis of pure transparent NPD compared with the results at higher pressures [3]. Squares are the present runs, while circles correspond to those of the earlier study [3]. Open symbols represent the P, T conditions where pure NPD were obtained.

| Run no | P (GPa) | T (°C) | Time (min) | Optical appearance | Phases present |
|--------|---------|--------|------------|--------------------|----------------|
| OT459  | 14.0    | 2200   | 30         | black              | c-dia, h-dia, gr |
| OT468  | 14.0    | 2400   | 30         | transparent        | c-dia          |
| OT501  | 13.0    | 2400   | 25         | black              | c-dia, h-dia, gr |
| OT469  | 13.0    | 2500   | 30         | transparent        | c-dia          |
| OT460  | 13.0    | 2500   | 30         | transparent        | c-dia          |
| OT537  | 12.5    | 2500   | 24         | transparent\*      | c-dia          |
| OT465  | 12.0    | 2400   | 30         | black              | c-dia, h-dia, gr |
| OT461  | 12.0    | 2500   | 20         | black              | c-dia, h-dia, gr |
| OT597  | 12.0    | 2600   | 5          | transparent        | c-dia          |

\* trace dark spots were observed; c-dia = cubic diamond, h-dia = hexagonal diamond, gr = compressed graphite.

**3. Results and discussion**

Experimental conditions and the results of the present runs are shown in Fig 1. Single phase of NPD was formed at temperatures above 2400°C at 14 GPa, while the minimum temperature for synthesis of
NPD increased with decreasing pressure; \( T \geq 2500^\circ \text{C} \) at 13 GPa and \( T \geq 2600^\circ \text{C} \) at 12 GPa. Thus obtained pure NPD samples were optically transparent as shown in Fig 2 (a), and the X-ray diffraction measurement demonstrated that these samples are composed of only cubic diamond (Fig 3). On the other hand, the samples contained small amounts of graphite and hexagonal diamond below the reaction boundary shown in Fig 1, and were dark grey in color and opaque (Fig 2 (b)).

**Figure 2.** Optical microscope images of pure NPD (a, OT461, 12 GPa, 2600\(^\circ\)C) and that of the opaque sample with a small amount of hexagonal diamond and graphite (b, OT461, 12 GPa, 2500\(^\circ\)C). Both samples have dimensions of \( \sim 3.8 \text{ mm} \) in diameter and \( \sim 2.5 \text{ mm} \) in thickness.

**Figure 3.** An X-ray diffraction profile of the NPD sample synthesized at 12 GPa, 2600\(^\circ\)C (OT597). All diffraction peaks correspond to those of cubic diamond.

Raman spectroscopic measurement on the transparent NPD samples yielded a diamond band around \( 1332 \text{cm}^{-1} \), with a relatively broad full width at the half maximum of the peak (FWHM of 8-11 cm\(^{-1}\)), consistent with the small size of the diamond particles thus synthesized by direct conversion from graphite [3]. However, the FWHMs of the Raman peaks for the present samples that were synthesized at relatively low pressures and high temperatures are significantly smaller than those of the NPD synthesized at higher pressures (FWHM=11-20 cm\(^{-1}\), [3]), suggesting that the grain size of the present NPD samples should be significantly larger than those reported earlier [4]. Knoop hardness of two such NPD samples (Run OT537 and OT 460) was measured according to the method described earlier [4], yielding values of \( H_k = 116 \text{ GPa} \) and 125 GPa, respectively, which are slightly lower than those of the hardest NPDs reported in our earlier study (130-145 GPa; [4]). This may be attributed to the
difference in grain sizes in the samples of these two studies, although further systematic studies are needed to confirm this idea.

The lower P, T boundary, above which the pure NPD was formed, is consistent with the boundary determined at higher pressures of 15-25 GPa [3], which demonstrated that the pure NPD can be synthesized at a pressure as low as 12 GPa, although quite high temperatures of above 2600°C are required at this pressure. Moreover, the hardness of such NPDs synthesized in the lower pressure region tends to be lower than those NPDs obtained at higher pressures presumably due to the grain growth at high temperatures and also because the P, T conditions are closer to the graphite-diamond equilibrium boundary, where the nucleation rate of diamond should be smaller than those at higher pressures and accordingly would enhance the crystal growth. Thus the hardness of the NPD may be controlled by controlling the P, T conditions of its synthesis.

The size of the NPD rod thus synthesized shrank by about 20% in both diameter and length, but otherwise maintained its original shape, although some cracks were observed particularly at the peripheral parts of the top and bottom surfaces of the sample (Fig 2 (a), (b)). However, the occurrence of such cracks could be suppressed by controlling the unloading processes and by optimizing the cell design to realize hydrostatic environments around the sample. In this manner, we are now able to synthesize flawless NPD rods of 6-7 millimeters in both diameter and length, which could be used for industrial and scientific applications utilizing its peculiar nature of super hardness, high optical transparency, large and isotropic stiffness, and superior endurance at high temperature. In fact, some recent studies demonstrated the potential importance of this novel hard material in pressure generation using both the diamond anvil cell [5] and the multi-anvil apparatus [6].

5. References

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