

Nano-polycrystalline diamond synthesized from neutron-irradiated highly oriented pyrolytic graphite (HOPG)

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Abstract

Highly oriented pyrolytic graphite (HOPG) is a unique source material for the synthesis of new types of diamond. It can transform to layered nano-polycrystalline diamond (NPD) under static high pressure and high temperature (HPHT) and to “amorphous diamond” by introducing structural defects by neutron irradiation followed by shock compression. Here, we investigated the structural change of the neutron-irradiated HOPG through a HPHT treatment at 2300 °C and 15GPa by Raman, XRD, TEM and XANES analyses. The recovered sample consists of randomly oriented nanodiamonds (50-100 nm), showing clearly a different microtexture from those of the layered NPD and “amorphous diamond” reported by the previous studies. This is likely as a result of competing effects of the introduction of irradiation-induced defects, which provided the preferential nucleation sites for cubic diamond, and their partial recovery upon annealing during the HPHT treatment. The present result suggests that NPDs with various crystalline structures can potentially be synthesized from neutron-irradiated HOPG by controlling the density and distribution of the defects introduced.

Key Word: nano-polycrystalline diamond, graphite, high pressure high temperature, irradiation induced defects

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1. Introduction

The high-pressure synthesis of diamond from graphite and various other carbon sources has been extensively studied for several decades and widely applied for industrial and scientific purposes. Since a great breakthrough was made in the synthesis of pure binderless nano-polycrystalline diamond (NPD) from graphite [1], extensive studies have been conducted on conversion mechanisms and physical properties. Ultra-high hardness of NPD, surpassing that of single crystalline diamond [2], has drawn considerable attention for various industrial uses such as for cutting and wear-resistant tools and scientific applications such as for high pressure apparatuses [3-6].

Highly oriented pyrolytic graphite (HOPG) possesses good crystallinity, of which layered structure stacks along the c-axis. A new type of polycrystalline sintered diamond has been synthesized by direct conversion from HOPG at 15GPa and 2300 °C [7]. It is optically transparent and consists of layered nanocrystals (50–100nm thick) of cubic diamond, which are tightly bound to each other and have strong [111] preferred orientation along the stacking direction. This nanolayered diamond has excellent indentation hardness and is expected to have significantly high wear resistance on both ends of cylindrical sintered compact.

Shock compression, on the other hand, is another method to synthesize a novel diamond in a flash. By utilizing neutron-irradiated HOPG, “amorphous diamond”, which can be considered as a variety of the NPDs with an ultimately small crystalline size, has been synthesized by shock compression and rapid quenching (SCARQ) technique [8]. It is clear that irradiation-induced disordering affects the transformation to the “amorphous diamond” in the case of SCARQ. This indicates that the neutron-irradiated graphite is a unique starting material for the synthesis of diamond.

In the present study, we have tried high-pressure synthesis of diamond from highly oriented pyrolytic graphite (HOPG), which was neutron-irradiated in a nuclear reactor to a fluence up to 1.4×10^{24} n/m² ($E > 1$ MeV). The starting materials were heavily disordered by the irradiation. The purpose of this study is to investigate the effect of the irradiation-induced defects on the transformation process under a statically pressurized condition and to compare the result with those of the unirradiated and the shock compressed HOPGs.

2. Experimental

We utilized highly oriented pyrolytic graphite (HOPG-ZYA) from Union Carbide as a starting material. The material was neutron-irradiated in JAEA JRR-2 nuclear reactor at about 60 °C to a fluence of 1.4×10^{24} n/m² ($E > 1.0$ MeV). The

displacement per atom (dpa) is estimated to be about 0.2 dpa. [9]. High pressure and high temperature experiments were conducted using a 3000-ton Kawai-type multi-anvil apparatus (ORANGE-3000 at Ehime University). The graphite specimens were shaped to disks of ϕ 2.0 mm and 2.0 mm high and enclosed in a Ta capsule. A cylindrical rhenium heater (0.025 mm thickness), a thermal insulator (LaCrO₃) and a pressure medium made of Co-doped MgO were used for the high-pressure cell assembly. The furnace power was determined according to an independently established calibration of temperature against power for the same cell assembly. Tungsten carbide anvils with a truncated edge length (TEL) of 5 mm and a cell assembly were used.

Two kinds of experiments for high pressure and high temperature treatments were performed. One was the experiment in which the specimen was compressed to 23 GPa at room temperature (RT). The other was the experiment in which the specimen was compressed to 15 GPa and gradually heated up to 2300 °C in 30 min. The high temperature was kept for 20 min and after quenching the sample was decompressed in several hours.

The recovered products were examined by Raman spectroscopy (Renishaw RS-SYS 1000) equipped with Ar⁺ laser ($\lambda = 514.5$ nm) for phase identification and a focused X-ray diffractometer (Rigaku RAPID II-V) with copper K α radiation ($\lambda = 1.55419$ Å) operated at 40 kV and 30 mA. Each product was then processed by FIB system in order to prepare thin foil sections for microstructure observation by transmission electron spectroscopy (TEM). The products were also examined by the XANES spectroscopy using the 1.5 GeV synchrotron radiation facility of NewSUBARU at University of Hyogo, [10,11] in order to investigate the electronic orbital structure of the recovered specimens.

3. Results

Figure 1 shows Raman spectra of neutron-irradiated and un-irradiated HOPG specimens. An intense E_{2g} stretching mode (G band) centered at 1580 cm⁻¹, and weak D band (centered at 1350 cm⁻¹) were observed before irradiation. After the neutron-irradiation, extremely broad and grown-up D band were observed together with broadened G band, which indicates the irradiation-induced disordering [12]. A bright field TEM image and a corresponding selected area electron diffraction (SAED) pattern of the neutron-irradiated HOPG specimen are shown in Fig. 2 (a) and (b). High resolution TEM (HRTEM) image is shown in Fig. 2 (c). The original structure of HOPG is found to be significantly damaged by the neutron-irradiation, though the layered crystal structure of the original HOPG is still observable with a wavy deformation feature of the basal plane. A bright field TEM image and a corresponding diffraction pattern of the un-irradiated

HOPG specimen, on the other hand, show similar characteristics but the 00l diffraction spots of graphite show clearly a smaller degree of misorientation [7].

Figure 3 shows the Raman spectra obtained for the products of the experimental conditions of 2300 °C/15 GPa and 1500 °C/15GPa [13], together with the spectra of neutron-irradiated HOPG. For the higher temperature (2300 °C) a prominent peak is seen at 1332 cm⁻¹ presenting the formation of cubic diamond, while the product from the lower temperature (1500 °C) showed no sharp peak, though G and D peaks of HOPG, and a small broad peak around 1332 cm⁻¹ were observed. For both spectra a significant increase in background due to photoluminescence of samples was observed.

Figure 4 shows X-ray diffraction patterns of the specimens recovered at the experimental condition of 2300 °C/15 GPa, 1500 °C/15 GPa and RT/23 GPa, together with the diffraction patterns for the specimens of neutron-irradiated HOPG and original HOPG (un-irradiated). In the experiment at 2300 °C/15 GPa, strong and sharp cubic diamond (C-dia) lines, D111, D220, and D311, are observed. In the experiment at 1500 °C /15 GPa, the G002 diffraction peak mostly returned to the original peak position of HOPG. Also, the formation of hexagonal diamond (H100) and cubic diamond (D111 and D220) is confirmed. In the experiment at RT/23 GPa, a broad graphite G002 peak was observed, indicating that the disordered graphite structure with neutron-irradiated defects has remained even after high pressure treatment at room temperature. One should note that there is a small discrepancy of the G002 peak position between RT/23 GPa and original HOPG. For the latter, the interlayer spacing of G002 is estimated to 0.34 nm, while for the former, the spacing is estimated to 0.37 nm. This increase of the interlayer spacing is attributed to the lattice expansion due to neutron irradiation [14,15].

Figure 5 shows a bright field TEM image (a) and a corresponding SAED pattern (b) of the foil obtained by FIB-cutting of the product recovered at 2300 °C/15 GPa. The TEM image shows the uniform distribution of small grains of cubic diamond with the grain size of 50-100 nm. The SAED pattern shows sharp diffraction rings of D111, D220 and D331 of cubic diamond, suggesting that the product consists purely of cubic diamond crystals that are randomly oriented.

Figure 6 shows the XANES spectra obtained for the recovered products of (1) RT/23 GPa and (2) 2300 °C/15 GPa, together with the reference data (3) for standard cubic diamond crystal. Typical diamond spectral feature of a dip around 302 eV is recognized in the XANES measurements for the case (2). This suggests that the main part of the product from 2300 °C/15 GPa has the typical diamond structure.

4. Discussion

In the present study, we utilized HOPG which is characterized as crystalline with layers stacking along the c-axis. As the HOPG scarcely contains defects, we can elucidate the effect of the irradiation-induced defects on the transformation to diamond. Moreover, neutron irradiation is preferred over ion irradiation to investigate the effect of irradiation-induced defects, since no impurities are implanted during neutron irradiation and the irradiation-induced defects are uniformly formed in a wide range.

To reveal the effect of irradiation, we compared the present result with that of an earlier study using un-irradiated HOPG [7], which was treated under the same high pressure and high temperature condition as shown in Table 1. Both the HOPG specimens transformed to diamonds in the experimental condition of 2300 °C/15 GPa, but a remarkable difference appeared in the micro-structure: layered structure was formed for the un-irradiated HOPG, while granular to mosaic structure composed of randomly oriented diamond grain was observed for the irradiated one. Moreover, another difference is noted in the formation of hexagonal diamond: the product from the irradiated HOPG contains virtually no hexagonal diamond (Fig. 4) while that from un-irradiated HOPG contains a small amount [7]. In the experimental condition of 1500 °C/15 GPa, on the other hand, more complicated structure appeared compared to that of 2300 °C/15 GPa because at a such temperature the graphite-diamond transformation occurred more dominantly by the martensitic process than by diffusion process, as will be discussed in ref. [13].

A comparison of the present result to the product of the neutron-irradiated HOPG after shock compression and rapid quenching (SCARQ) shown in Table 1 should give some insights on the effect of irradiation-induced defects on the transformation. One should note that the neutron irradiated HOPG directly transformed to “amorphous diamond” whose grain size is extremely small so as not to detect the characteristic diamond vibration mode (T_{2g}) in Raman spectroscopy under the SCARQ. Defective sites relating to the irradiation-induced defects can be considered to produce a high density of diamond nucleation sites, leading to the synthesis of “amorphous diamond” [8]. In the present case, the nanocrystalline size of the diamond product is similar to that obtained using un-irradiated HOPG as shown in Table 1. We found that the defects introduced by the neutron irradiation were retained even after high pressure treatment at least up to 23 GPa at room temperature (Fig. 4). The recovery of the irradiation-induced defects during heating in the present (static compression) experiments is likely more remarkable than the case of shock compression due to the far slower heating rate, as discussed in the following.

The behavior of irradiation-induced defects in graphite has been investigated for

a long time [12,14-18], as it is important issues for the usage of graphite as a nuclear material. High energy particles passing through graphite lattice induce the displacement of atoms. If the energy transferred to an atom in the lattice by high energy particles is larger than the displacement threshold energy, the atom is displaced into the lattice to form an interstitial, leaving a vacancy behind, which is called Frenkel pair. Under prolonged irradiation, disordering occurs preferentially in the basal planes of graphite by the accumulation of dislocation dipoles [18], which would induce the buckling and rotation of basal planes as seen.

Frenkel pair is known to mutually annihilate on annealing above 300 °C [12-15]. However, the disordered structure is thermally stable on annealing at 600 °C [12] but a gradual recovering occurs between 800 °C and 2000 °C [13]. Then, the minor effect of neutron irradiation on the diamond transformation compared to the case of the shock compression may be derived from the annealing effect of irradiation-induced defects. On the other hand, the difference in microtexture between nanopolycrystalline diamonds synthesized from the neutron-irradiated and unirradiated HOPGs (showing granular-mosaic texture and layered texture, respectively) is probably related to their transformation mechanism. It seems that a large number of structural defects in the irradiated HOPG provide preferential nucleation sites for cubic diamond [8], and as a result, the diamond formation occurs dominantly by the nucleation and growth process rather than by the martensitic process, as discussed in detail by our earlier study [19].

5. Conclusion

Influence of the neutron irradiation to graphite (HOPG) starting material on the transformation to diamond under static high pressure and temperature (23 GPa, 2300 °C) was investigated. The XRD pattern of the recovered samples shows intense and sharp diffraction peaks of cubic diamond with no hexagonal diamond. The TEM observation indicated that the product consist of fine diamond grains (50-100 nm) with random orientations. The absence of hexagonal diamond and the formation of randomly oriented nano-polycrystalline-diamond (NPD) are distinct from the features of layered NPD synthesized from un-irradiated HOPG. This is probably due to the high density of defects introduced by neutron-irradiation in HOPG, which provides preferential nucleation sites for cubic diamond so that the diamond transformation occurs dominantly by the diffusion process rather than the martensitic process. Then, the control of the annealing should be a key issue to utilize the irradiation-induced defects on the synthesis of various crystallized structure of diamond from HOPG.

Acknowledgments

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Figures

Fig. 1. Raman spectra of the original HOPG and neutron-irradiated HOPG.

Fig. 2. A bright field TEM image and corresponding SAED pattern of the neutron-irradiated HOPG specimen are shown in (a) and (b). The HRTEM image of the same specimen is shown in enlarged scale in (c)

Fig. 3. Raman spectra for the products obtained at 2300 °C/15 GPa and 1500 °C/15 GPa. As a reference, Raman spectrum of neutron-irradiated HOPG is shown.

Fig. 4. X-ray diffraction patterns are shown for 2300 °C/15 GPa, 1500 °C/15 GPa and for RT/23 GPa. For reference, the diffraction pattern of neutron-irradiated HOPG and original HOPG are shown.

Fig. 5. (a) TEM image and (b) corresponding SAED pattern of the products obtained synthesized at 2300 °C/15 GPa experiment.

Fig. 6. XANES spectra for the products of RT/23 GPa and 2300 °C/15 GPa. For reference, the XANES spectrum of crystalline cubic diamond is shown.

Table 1. Synthesis conditions and experimental results.

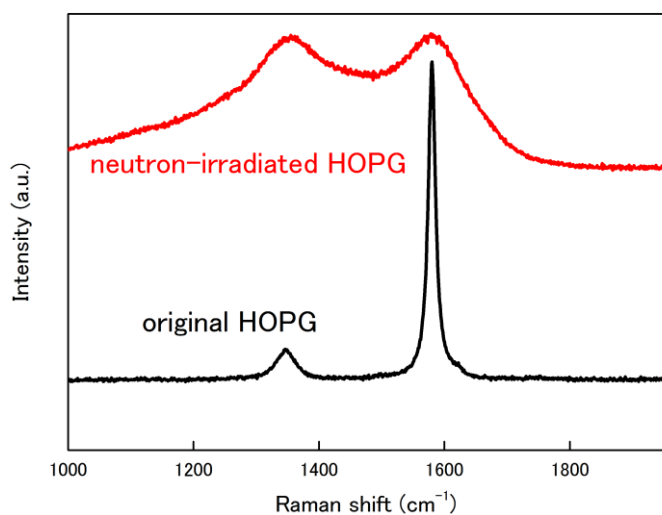


Fig. 1. Raman spectra of the original HOPG and neutron-irradiated HOPG.

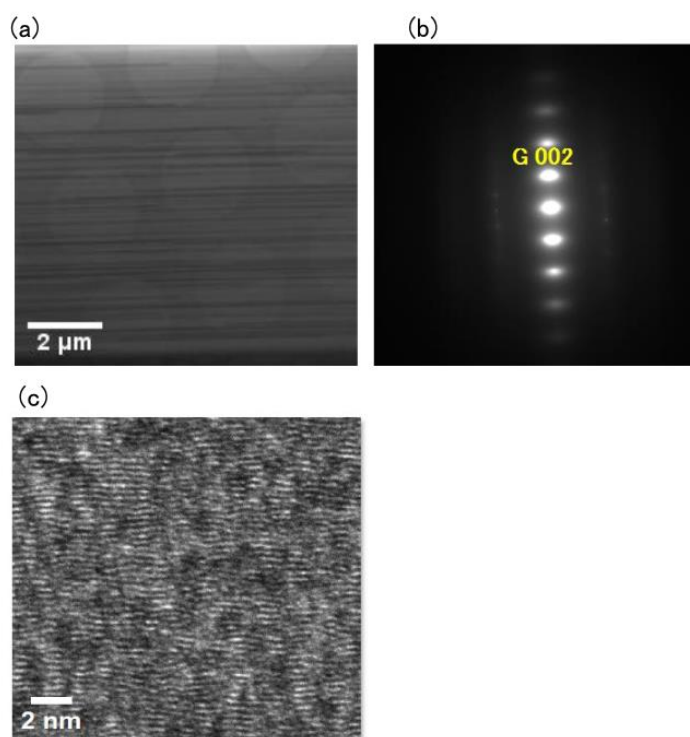


Fig. 2. A bright field TEM image and corresponding SAED pattern of the neutron-irradiated HOPG specimen are shown in (a) and (b). The HRTEM image of the same specimen is shown in enlarged scale in (c)

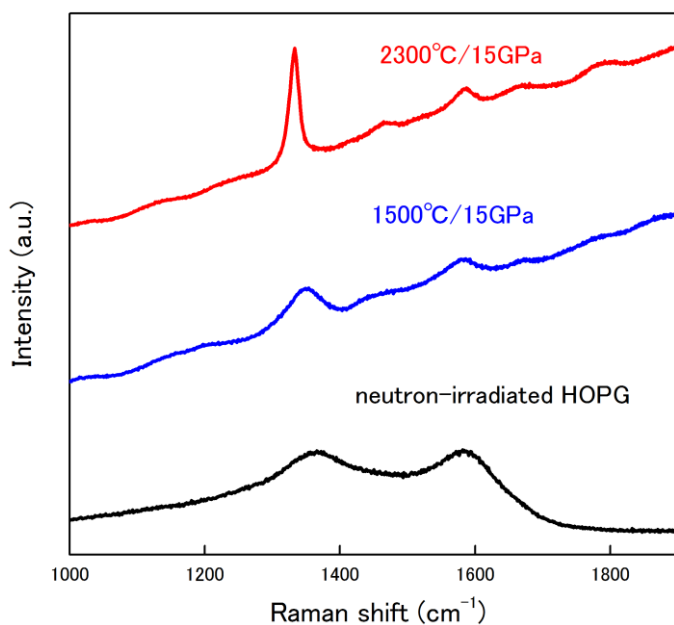


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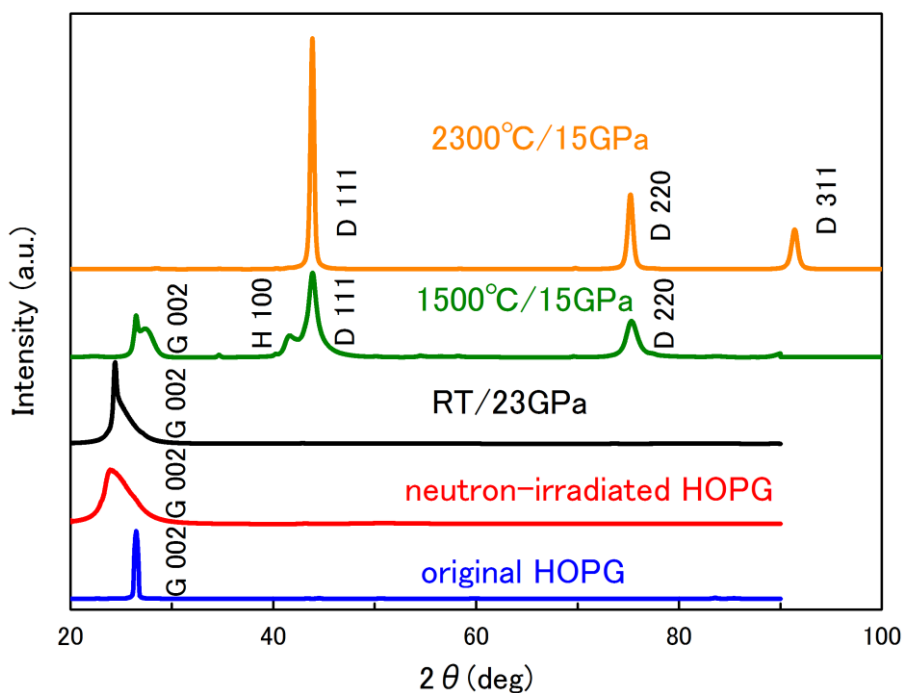


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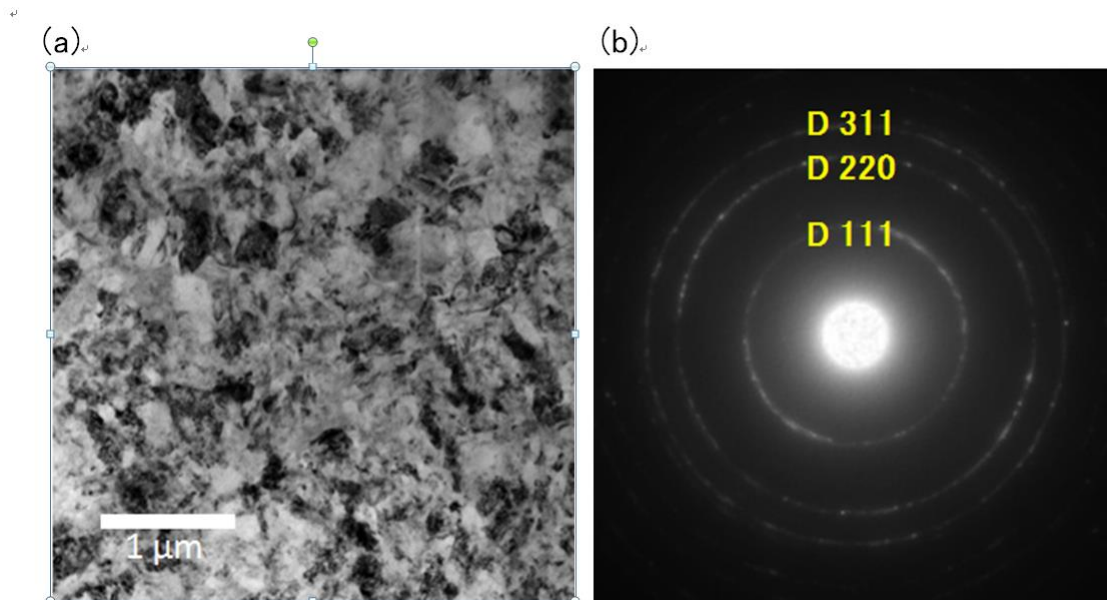


Fig. 5. (a) TEM image and (b) corresponding SAED pattern of the products obtained synthesized at 2300 °C/15 GPa experiment.

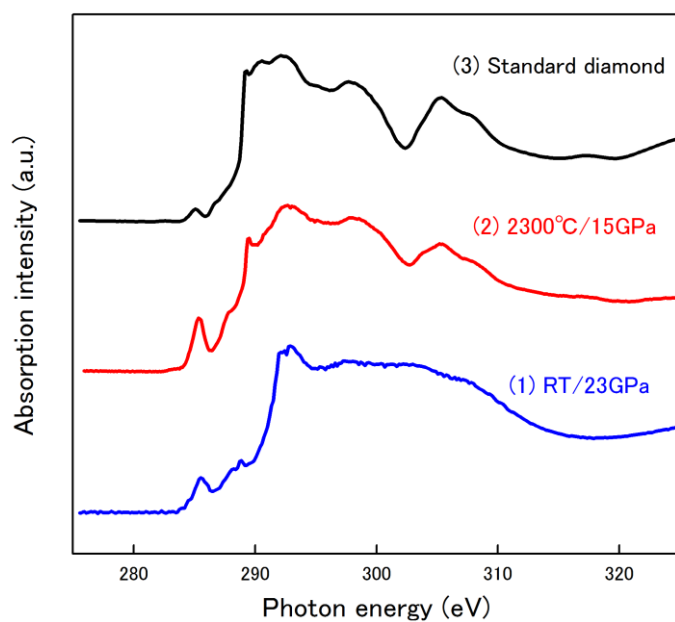


Fig. 6. XANES spectra for the products of RT/23 GPa and 2300 °C/15 GPa. For reference, the XANES spectrum of crystalline cubic diamond is shown.

Table 1: Synthesis conditions and experimental results.

Starting materials	Method of compression	T(°C)/ P(GPa)	Duration of compression	phases	Nanocrystal shape	Nanocrystal size (nm)
Neutron-irradiated HOPG	Static pressure	2300°C/ 15 GPa	20 min	C-dia	Randomly oriented nano-diamond	50-100 nm (Diamond)
Un-irradiated HOPG	Static pressure	2300°C/ 15 GPa	20 min	C-dia, H-dia	Layered nanocrystal	50-100 nm
Neutron-irradiated HOPG	Static pressure	1500°C/ 15 GPa	20 min	C-dia, H-dia, Gr	Randomly oriented nano-diamond, Broken graphite	<< 50 nm (Diamond) 1-2 μ m (Graphite)
Neutron-irradiated HOPG	Shock compression and rapid quenching (SCARQ)	4100°C (estimated) / 51GPa	540 nsec (estimated)	Amorphous dia	Randomly oriented nanocrystal	extremely small