

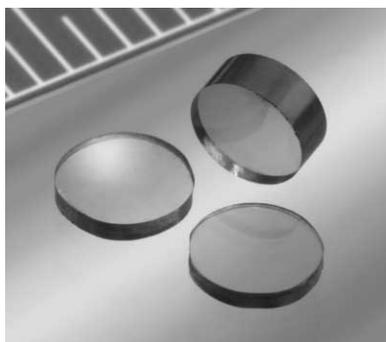
# Microstructure and Mechanical Properties of High-Hardness Nano-Polycrystalline Diamonds

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High-purity nano-polycrystalline diamonds synthesized by direct conversion of graphite under high pressure and high temperature have extremely high hardness, no cleavage and high thermal stability. Because of these features, they have an immeasurable potential for industrial uses in applications such as cutting tools and abrasion resistance materials. In order to clarify the factors contributing to their high hardness, the microstructures and mechanical properties of nano-polycrystalline diamonds synthesized by the direct conversion of various carbon materials were investigated. The results of indentation hardness tests revealed that polycrystalline diamonds synthesized from graphite under  $\geq 15$  GPa and at 2300°C to 2500°C (consisting of fine grains 10 to 30 nm in size and crystal layers) have very high Knoop hardness ( $H_k \geq 120$  GPa), whereas polycrystalline diamonds synthesized from non-graphitic carbons under  $\geq 15$  GPa and at 1800°C to 2000°C (consisting only of single nano-grains of 5 to 10 nm) have much lower hardness ( $H_k = 70$  to 90 GPa). The observation results of the microstructures of these nano-polycrystalline diamonds beneath the indents suggest that the existence of lamellar structure and the degree of grain bonding strength decisively influence the hardness and toughness of polycrystalline diamonds.

## 1. Introduction

Recently, the authors succeeded in synthesizing single-phase polycrystalline specimens of dense and super-hard diamond by direct conversion from graphite under ultrahigh pressure and high temperature<sup>(1), (2)</sup>. This polycrystalline diamond has an extremely fine texture consisting of diamond grains 10-30 nm in size<sup>(3)</sup>, and surpasses monocrystalline diamonds in terms of hardness<sup>(4)</sup>. It also has neither cleavability nor hardness anisotropy, and has excellent thermal stability. Consequently, it holds great promise as a new hard material for cutting tools and wear-resistant tools. Pursuing practical application of this nano-polycrystalline diamond, the authors are presently developing mass production technologies for increasing its size and yield. As shown in the previous report<sup>(2)</sup>, the size of the specimens obtained in the initial stage of development was about 1 mm, but as shown in **Fig. 1**, the authors have recently obtained high-quality polycrystalline diamond specimens of 4-5 mm in diameter that has no



**Fig. 1.** Nano-polycrystalline diamonds synthesized by direct conversion from graphite

cracks or contaminants. This nano-polycrystalline diamond consists of extremely fine grains, and is thought to exhibit extremely high hardness due to its lack of impurities and inclusions, but the specific mechanism by which it reaches high hardness has been unclear. Also, the hardness value can vary to a certain extent depending on the synthesis conditions, and the reasons for this are also not well understood<sup>(4)</sup>. It will be critically important to clarify these points in order to succeed in practical application of this material.

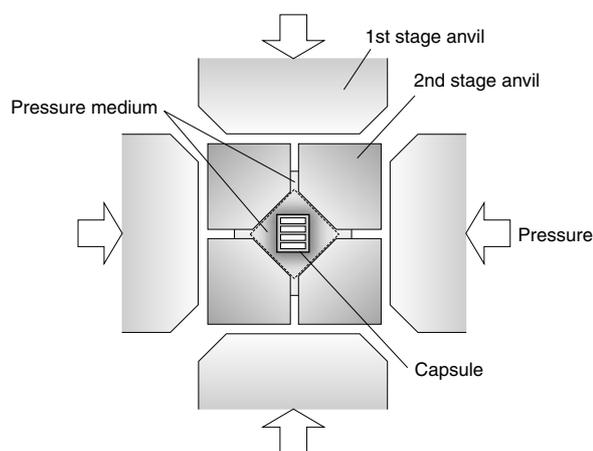
On the other hand, diamonds can be synthesized by direct conversion even if non-graphitic carbons such as amorphous carbon (a-G), glassy carbon (GC), carbon nanotube (CNT), or C<sub>60</sub> are used as starting materials<sup>(5), (6), (7), (8), (9)</sup>. The authors demonstrated that the textures of polycrystalline diamonds obtained from these non-graphitic carbons consist only of a homogeneous fine structure formed in a process of diffusion phase transition, and that polycrystalline diamonds consisting of extremely fine single nanoscale grains (less than 10 nm) of diamond<sup>(10)</sup> can be obtained by direct conversion at low temperatures between 1600°C and 2000°C. The microstructure and mechanical behavior of nano-polycrystalline diamonds created using these starting materials are very interesting. Through systematical study, the mechanism behind the high hardness of polycrystalline diamonds obtained by direct conversion can be clarified, and the practical understanding essential to further improve and stabilize their characteristics can be gained.

Using graphite as well as various non-graphitic carbons as starting materials, the authors synthesized polycrystalline diamonds under a variety of synthesis conditions, and systematically studied their microstructural features, hardness, and microscopic deformation/fracture processes<sup>(11), (12)</sup>. This paper summarizes the relationship between microstructural features and mechani-

cal properties, as well as the influences of starting materials and synthesis conditions as revealed in the results of the authors' studies.

## 2. Synthesis of Nano-Polycrystalline Diamonds Made from Various Carbon Materials

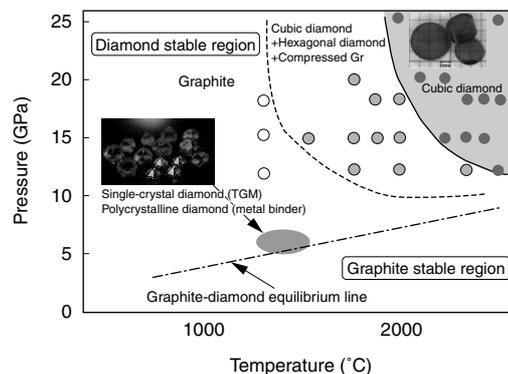
A compact of high-purity isotropic graphite (Gr), amorphous carbon made from mechanically pulverized high-purity graphite powder (hereinafter referred to as a-C), glassy carbon (GC), carbon nanotube (CNT), and fullerene ( $C_{60}$ ) were used as starting materials. As shown in **Fig. 2**, these were processed at high pressure (15 to 21 GPa), high temperature (1200°C to 2500°C), and holding time of 10s to 10000s with a Kawai-type (6-8 type) double-stage multianvil apparatus<sup>(13)</sup> using indirect heating from a rhenium or  $LaCrO_3$  heater.



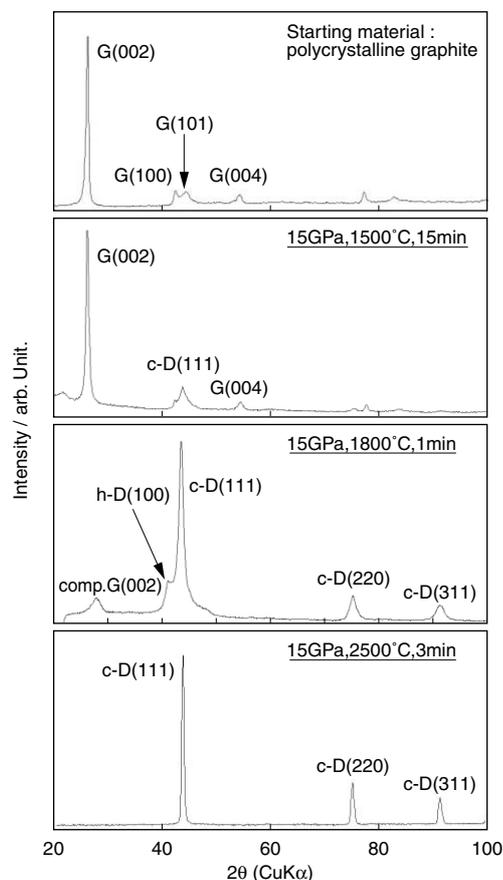
**Fig. 2.** Kawai-type (6-8 type) double-stage multianvil apparatus

When the starting material was graphite, it was converted into cubic diamonds (c-Dia) in the region shown in **Fig. 3**. **Figure 4** shows the X-ray diffraction pattern of such a case. At a pressure of 15 GPa, graphite begins to convert partially into c-Dia and hexagonal diamonds (h-Dia) at approximately 1500°C, and converts completely into c-Dia at 2300°C or higher. This conversion is accompanied simultaneously by sintering, resulting in a solid single-phase polycrystalline diamond. Unconverted graphite remains as compressed graphite (comp. Gr). Unconverted graphite remains at temperatures lower than 2000°C, and solid agglomerates cannot be obtained.

To the contrary, when the starting material is non-graphitic carbon, it is converted into c-Dia at 1500°C to 1600°C or higher, and h-Dia and comp. Gr are not detected<sup>(10)</sup>. **Figure 5** shows the X-ray diffraction pattern of a specimen observed in the case where the starting material was GC and it was sintered under different temperatures at 15 GPa. The results were the same with other non-graphitic carbon starting materials such as a-C,  $C_{60}$ , and CNT. It was also found that the previously



**Fig. 3.** Experimental results of high-pressure and high-temperature tests of direct conversion from graphite to diamond

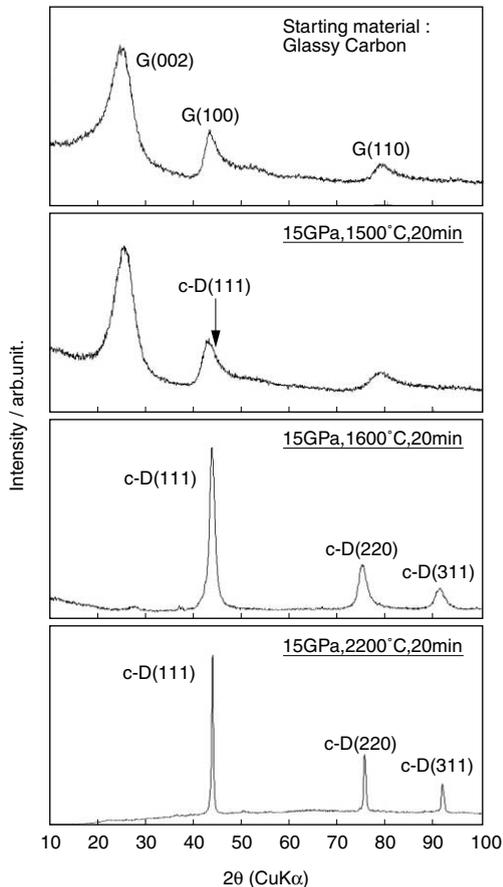


**Fig. 4.** X-ray diffraction patterns of specimens obtained from graphite after high-pressure high-temperature treatment

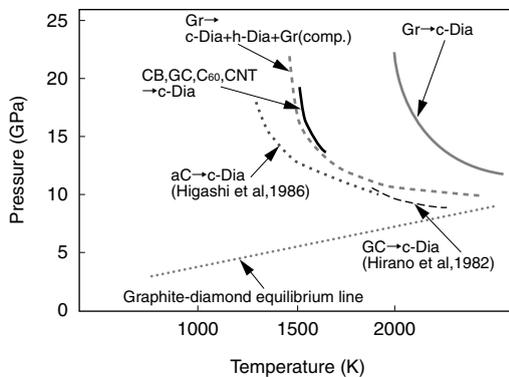
reported phenomenon in which non-graphitic carbon converts into graphite under pressures of about 10 GPa (the Ostwald's step rule)<sup>(14)</sup> was not observed at 12 GPa or higher.

As the results in **Fig. 4** and **Fig. 5** show, the temperature at which non-graphitic carbon starts to convert to diamond is almost the same as that in the case where graphite is used as the starting material. However, in the case of graphite, for example, at 15 GPa, h-Dia and residual comp. Gr are confirmed to exist at 2200°C or

lower. But when non-graphitic carbon is used as the starting material (regardless of the type), the complete conversion to c-Dia takes place at 1600°C or higher without intermediate phases of h-Dia and comp. Gr, and a single-phase polycrystalline diamond is obtained. Conditions for conversion of non-graphitic carbon into diamonds and graphite into diamonds were compared, and the comparison results are shown in **Fig. 6**.



**Fig. 5.** X-ray diffraction patterns of specimens obtained from glassy carbon after high-pressure high-temperature treatment

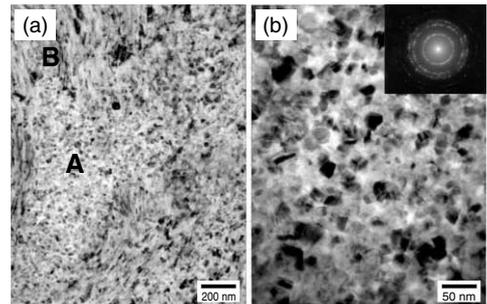


**Fig. 6.** Results of high-pressure and high-temperature experiments of direct conversion to diamond from graphite and from non-graphitic carbon

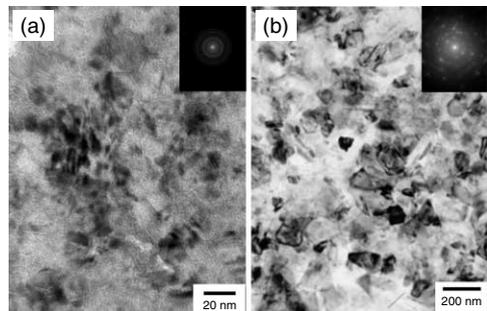
### 3. Microstructural Features

The surface of each of the various nano-polycrystalline diamond specimens obtained above was polished with a metal-bonded diamond wheel, and then a thin plate was prepared by slicing using an FIB device. The microstructure of a sliced specimen was observed under a high resolution transmission electron microscope (TEM). The TEM images of polycrystalline diamonds obtained from Gr, GC, and C<sub>60</sub> were shown in **Figs. 7, 8, and 9**, respectively.

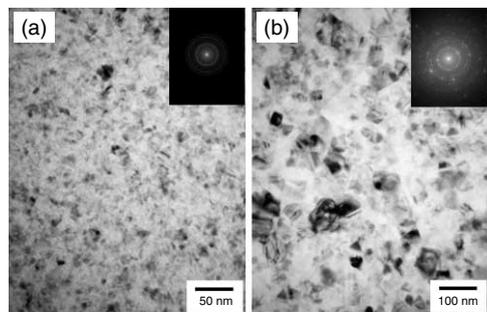
Using graphite as the starting material produced a mixed texture of a homogeneous structure consisting of



**Fig. 7.** TEM and electron diffraction images of polycrystalline diamond synthesized directly from graphite at 18 GPa, 2500°C, 10 sec. (a) X50000: Region A is homogeneous fine structure and region B is lamellar structure, (b) X200000: Enlarged view of region A (homogeneous fine structure)



**Fig. 8.** TEM and electron diffraction images of polycrystalline diamonds synthesized directly from glassy carbon at (a) 18 GPa, 2000°C, 20 min. and (b) 21 GPa, 2250°C, 6 min.



**Fig. 9.** TEM and electron diffraction images of polycrystalline diamonds synthesized directly from C<sub>60</sub> at (a) 18 GPa, 1800°C, 30 min. and (b) 18 GPa, 2000°C, 35 min.

fine-grained diamond particles (**Fig. 7**, region A) and a lamellar structure consisting of layered diamonds (**Fig. 7**, region B). The homogeneous structure was formed through a diffusion process (from Gr to c-Dia), and the lamellar structure was formed in a two-step martensitic process (from Gr to h-Dia to c-Dia) <sup>(2), (3)</sup>. All grain sizes in the homogeneous structure were within the range of 10 to 30 nm, and no conspicuous growth of grains was observed even at a synthesis temperature of 2500°C.

In contrast, the polycrystalline diamonds obtained from non-graphitic carbon, as shown in **Fig. 8** (GC) and **Fig. 9** (C<sub>60</sub>) had only a homogeneous structure consisting of fine grains, and no lamellar structure of any kind was found. This was also true in the cases where either a-C or CNT was used as the starting material. These diamond grains comprising the homogenous structure had polyhedral shapes and exhibited a random orientation. The morphology of these diamond grains suggests that they were formed in a diffusion transition process. There is a report <sup>(15)</sup> of rod-like diamond structures having been obtained using C<sub>60</sub> as the starting material, but no such structures could be found at all in the experiments conducted by the authors.

Also, polycrystalline diamonds obtained from non-graphitic carbon in a low temperature range (1600°C to 2000°C) were made up of extremely fine grains of less than 10 nm (single nanoscale). However, rapid grain growth occurred at 2000°C or higher, with grains being as large as about 50-100 nm (**Fig. 8 (b)** and **Fig. 9 (b)**). This was the opposite of the case of graphite as a starting material where almost no grain growth was observed at up to 2500°C <sup>(2), (3)</sup>.

As mentioned above, when non-graphitic carbon was used as the starting material, complete conversion to c-Dia with no remaining h-Dia or comp. Gr was observed even in a temperature range of 1600°C to 2000°C. Therefore, it is possible to manufacture extremely fine, homogeneous nano-polycrystalline diamonds consisting of single nanosize (less than 10 nm) diamond grains. However, at temperatures exceeding 2000°C, there is a greater tendency for grain growth than the case of graphite as the starting material. A number of differences are found among the non-graphitic carbons in their proclivity for grain growth after conversion to diamonds and in the temperature at which grain growth begins. The non-graphitic carbon's crystallized state and inclusions of minute amounts of volatile impurities like H and OH may affect atomic diffusion, and may also influence the starting temperature for direct conversion and extent of grain growth.

#### 4. Mechanical Properties

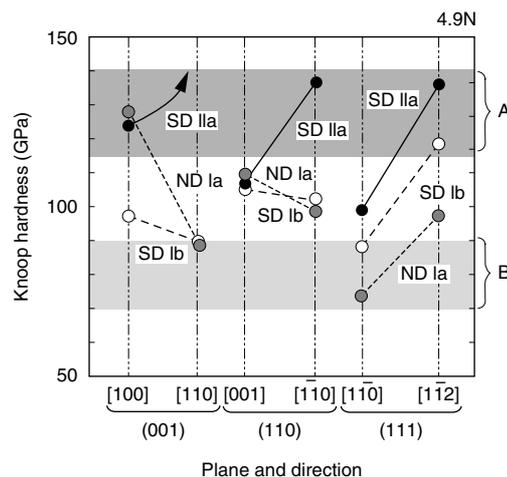
Next, the authors evaluated the micro-indentation hardness of each of the nano-polycrystalline diamond specimens. Surfaces were mirror-polished with a diamond wheel and indented with a load of 4.9 N, and the hardness was evaluated from the size of indentation. The indenter mainly used for this evaluation was a

super-hard Knoop indenter (indenter tip orientation: (001)<110>) <sup>(16)</sup> prepared by taking the tip orientation to the direction of high hardness of synthetic type IIa diamond monocrystals. Using this indenter allowed normal indentations to be left on the surfaces of polycrystalline diamonds without destroying the indenter tip, and thus to perform accurate hardness evaluations. Also, the hardness value was derived through comparison testing using the Knoop hardness in (001)<100> of synthetic type IIa single crystal diamonds as a reference.

**Table 1** shows the measured Knoop hardness of the polycrystalline diamond obtained from each of the different starting materials. Single-phase polycrystalline diamonds synthesized from graphite (specimens No. 1 to No. 3) all have hardness values exceeding 120 GPa. These values are about the same as the hardness values in the (001)<100> direction of high-purity synthetic type IIa single crystal diamonds, which are obviously higher than those of type I single crystal diamonds (indicated as region A in **Fig. 10**). On the contrary, when obtained

**Table 1.** Specimens and experimental results

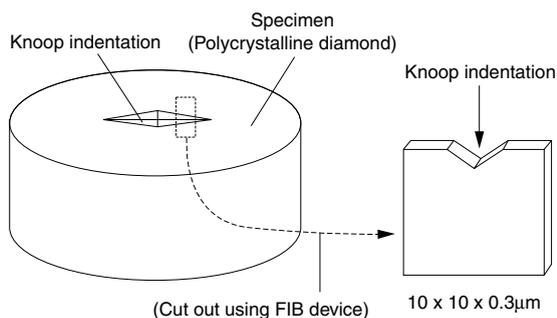
No.	Starting material	PT conditions	Product (X-ray)	Particle size (nm)	Hk (GPa)
1	Gr	15 GPa, 2400°C, 78 sec	c-Dia 100%	10-30 (+lamellar)	128-138
2	Gr	18 GPa, 2500°C, 10 sec	c-Dia 98%+h-Dia	10-30 (+lamellar)	120-140
3	Gr	21 GPa, 2300°C, 10 min	c-Dia 100%	10-30 (+lamellar)	113-139
4	a-C	18 GPa, 2000°C, 20 min	c-Dia 100%	10-200	97-119
5	a-C	21 GPa, 1800°C, 10 min	c-Dia 100%	5-10	70-74
6	GC	21 GPa, 2250°C, 6 min	c-Dia 100%	50-200	95-112
7	GC	18 GPa, 2000°C, 20 min	c-Dia 100%	5-10	66-86
8	C <sub>60</sub>	18 GPa, 1800°C, 30 min	c-Dia 100%	5-10	70-85
9	C <sub>60</sub>	18 GPa, 2000°C, 35 min	c-Dia 100%	20-100	93-104
Ref. material: Synthetic IIa single crystal (001)<100>					110-135



**Fig. 10.** Knoop hardness values (measured under 4.9 N load) of polycrystalline diamonds obtained directly from (A) graphite at 15-21 GPa and 2300°C-2400°C and (B) non-graphitic carbon at 15-21 GPa and below 2000°C, compared to those of various synthetic and natural diamond crystals (SD IIa: synthetic type IIa diamond, SD Ib: synthetic type Ib diamond, ND Ia: natural type Ia diamond)

from non-graphitic carbon material at low temperatures (2000°C or less), the Knoop hardness values of polycrystalline diamonds consisting of single nanosize grains is about 70-90 GPa, which are clearly lower than those of polycrystalline diamonds synthesized from graphite (specimens No. 5, No. 7, and No. 8). These values are nearly equal to the hardness values measured in the softest direction of single crystal diamonds (indicated as region B of **Fig. 10**). Note that hardness tends to increase with synthesis temperatures, and that hardness values exceeding 100 GPa are obtained at synthesis temperatures of 2000°C or higher (specimens No. 4, No. 6, and No. 9). However, even these hardness values are somewhat low when compared with those of polycrystalline diamonds obtained from graphite.

To investigate the mechanism by which the hardness of nano-polycrystalline diamonds is influenced in this manner by the starting material and synthesis conditions, a TEM was employed for detailed study of deformation and fracture around the indentations. As shown in **Fig. 11**, from the indented area formed on the polished surface of each of the polycrystalline diamonds, a thin plate were cut out using an FIB device and the microstructure was observed with a TEM.



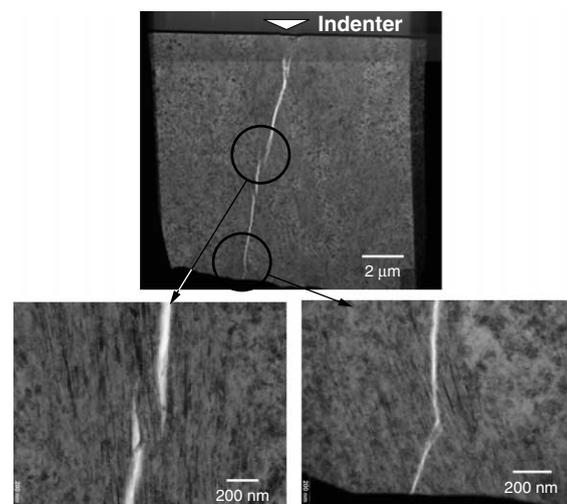
**Fig. 11.** Preparation of thin plate specimen for TEM observation

**Figures 12 and 13** show the TEM images of the indented areas of polycrystalline diamonds obtained from graphite and  $C_{60}$ , respectively. Cracks near the indentations can be categorized into large cracks running vertically directly under the indentation (median cracks) and the countless microscopic cracks of 100 nm or less (nanocracks).

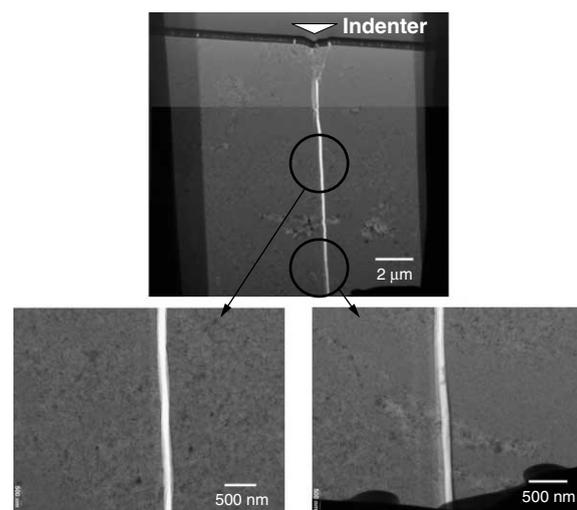
Median cracks just below the indentations are not seen at the time of indentation, but they are formed due to delayed fracture resulting from residual stress around the indentation when thin plates were cut out from the diamond specimens using the FIB device. The fracture toughness of the diamond specimens can be qualitatively evaluated from the shape of the median cracks. As apparent in **Fig. 12**, the course of median crack propagation in a polycrystalline diamond synthesized from graphite is deflected or ends at the lamellar structure. On the other hand, in the homogeneous fine structure obtained from  $C_{60}$  (**Fig. 13**), the crack propagates linearly. Polycrystalline diamonds synthesized

from other non-graphitic carbons also show the same behavior as the latter. This demonstrates that polycrystalline diamonds consisting only of the homogeneous structure obtained from non-graphitic carbons have poorer fracture toughness than the polycrystalline diamonds containing the lamellar structure obtained from graphite. In other words, the existence of the lamellar structure plays a major role in defining the mechanical properties of polycrystalline diamonds.

Next, the authors focused on the microscopic nanocracks found around the indentations. Deformation at the indented area arised from plastic deformation and generated nanocracks. Therefore, some of the factors that influence hardness can be ascertained through the behavior of these nanocracks. **Figure 14** is a TEM image



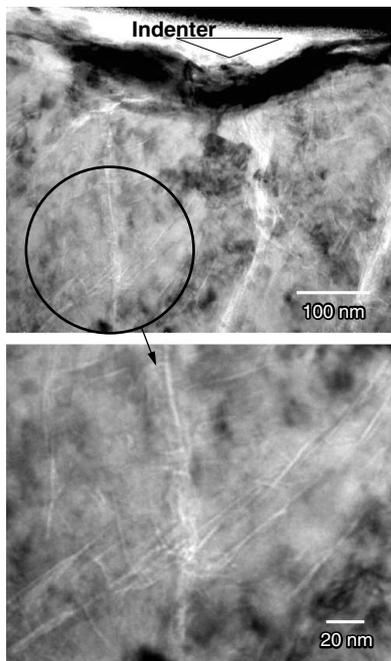
**Fig. 12.** TEM images of thin plate cut out from near Knoop indentation of polycrystalline diamond synthesized directly from graphite at 15 GPa, 2400°C (Hk = 128-138 GPa) (Images at bottom are enlarged views of areas enclosed in circles in image at top)



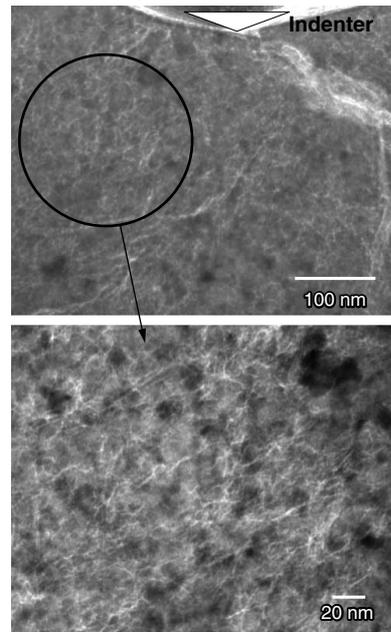
**Fig. 13.** TEM images of thin plate cut out from near Knoop indentation of polycrystalline diamond synthesized directly from  $C_{60}$  at 18 GPa, 1800°C (Hk = 70-85 GPa) (Images at bottom are enlarged views of areas enclosed in circles in image at top)

of an area near an indentation in a hard polycrystalline diamond specimen obtained from graphite under conditions of 15 GPa and 2400°C (hardness  $H_k = 128-138$  GPa). The propagation of nanocracks was irrespective of grain boundaries, indicating that transgranular fractures were predominant. **Figure 15** is a TEM image of an area near an indentation in a relatively soft polycrystalline diamond obtained from  $C_{60}$  under conditions of 21 GPa and 1800°C (hardness  $H_k = 70-74$  GPa). It can be seen that most of the nanocracks propagated along grain boundaries, reflecting intergranular fracture. These results point to the fact that grain boundary cohesion is very strong in the former case (**Fig. 14**), and relatively weak in the latter (**Fig. 15**), suggesting that intergranular cohesion greatly influences hardness in the polycrystalline diamonds. Through a series of experiments at varying synthesis temperatures, it is also found that in the low temperature range of 2000°C or less, intergranular fractures are more dominant, and the higher the temperature, intergranular cohesion is improved with synthesis temperature.

The results of the above are summarized in **Fig. 16**. According to the results of this experiment, polycrystalline diamonds synthesized at pressures of 15 GPa or higher and temperatures of 2300°C or higher using graphite as a starting material possess the highest hardness and fracture toughness. When non-graphitic carbon is used as the starting material, the temperature required for complete conversion to c-Dia falls to 1600°C, meaning that it is possible to synthesize extremely fine textured polycrystalline diamonds of 10 nm or less in grain size in a low temperature range (2000°C or lower) where grain growth does not occur. However, it



**Fig. 14.** TEM images of nanocracks under Knoop indentation formed on polycrystalline diamond synthesized from graphite at 15 GPa, 2400°C ( $H_k = 128-138$  GPa) (Image at bottom is enlarged view of area enclosed in circle in image at top)



**Fig. 15.** TEM images of nanocracks under Knoop indentation formed on polycrystalline diamond synthesized from a-C at 21 GPa, 1800°C ( $H_k = 70-74$  GPa) (Image at bottom is enlarged view of area enclosed in circle in image at top)

Starting Material	Synthetic Temperature (°C), at P=15-21 GPa			Median crack
	1500	2000	2500	
Graphite	Unconverted	c-Dia, h-Dia, Gr(comp.) 10-30nm (homogeneous + lamellar) $H_k=110-145$ GPa	c-Dia (+h-Dia)	Blocked by lamellar structure ↕ Propagates in straight line (linearly)
Non-graphitic carbons	Unconverted	c-Dia 5-10nm (homogeneous) $H_k=70-90$ GPa	20-200nm (homogeneous) $H_k=90-135$ GPa	

Micro- (nano-) crack    Interganular fracture (low bonding strength)    ↔    Transgranular fracture (high bonding strength)

**Fig. 16.** Microstructure, hardness and fracture mode of polycrystalline diamonds obtained by direct conversion from graphite and non-graphitic carbons

was found that the hardness and fracture toughness of nano-polycrystalline diamonds obtained in this temperature range are not so high. In the relationship between grain size and hardness of polycrystalline materials, finer grains generally contribute to higher hardness (the Hall-Petch effect). On the contrary, however, when grains are smaller than a certain size (approximately 10 nm or less), grain boundary sliding predominates and there is a decrease in hardness (the reverse Hall-Petch effect)<sup>(17)</sup>. Nevertheless, in the case of the nano-polycrystalline diamonds obtained from non-graphitic carbon in this study, the decrease in hardness of the polycrystalline diamond consisting of fine grains (10 nm or less) was not caused by grain boundary sliding, but rather by the marked occurrence of intercrystalline cracks (such as those seen in **Fig. 15**) induced by insufficient grain boundary cohesion due to low temperature

sintering. Synthesizing polycrystalline diamonds with high hardness requires conversion by sintering at temperatures high enough to activate atomic diffusion (more than 2000-2200°C) in order to strengthen grain boundary cohesion. Furthermore, the presence of lamellar that blocks crack propagation produces higher hardness, and may improve fracture toughness.

## 5. Conclusion

Nano-polycrystalline diamonds were synthesized using various carbon starting materials, and the relationship between their microstructural features and mechanical properties was studied to explain the mechanism behind the high hardness of nano-polycrystalline diamonds synthesized by direct conversion from graphite at ultra-high pressure and high temperature, and for higher hardness and further stability. The experiment results showed that while the hardness values of nano-polycrystalline diamonds synthesized directly from graphite starting materials were 120 GPa or higher, the hardness values of homogeneous polycrystalline diamonds consisting only of single nanoscale (less than 10 nm) fine grains synthesized directly from non-graphitic carbon by sintering in a low temperature range (1600°C to 2000°C) were significantly lower (70-90 GPa). From TEM observations of deformation and fracture around indentations, it was found that transgranular fracture predominates in polycrystalline diamonds sintered at high temperatures, intergranular fracture predominates in polycrystalline diamonds sintered at lower temperatures, and grain boundary cohesion (sintering temperature) is a factor influencing hardness. Also found was that in polycrystalline diamonds obtained from graphite, microscopic crack propagation was blocked by lamellar structure, showing that lamellar structure is effective in improving fracture toughness. According to the results of this experiment, polycrystalline diamonds synthesized at pressures of  $\geq 15$  GPa and temperatures of  $\geq 2300^\circ\text{C}$  using graphite compacts as starting materials have the highest hardness and superior fracture toughness. It may be possible to improve the mechanical properties of these polycrystalline diamonds by further controlling and optimizing fine structure through choice of starting material, synthesis conditions, and other factors.

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