

Novel Development of High-Pressure Synthetic Diamonds “Ultra-hard Nano-polycrystalline Diamonds”

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We have succeeded in synthesizing a single-phase (binderless) ultra-hard nano-polycrystalline diamond (NPD) by direct conversion sintering from graphite under ultra-high pressure and high temperature. The hardness of NPD is considerably high, far surpassing that of single-crystal diamonds even at high temperature. In addition, NPD shows outstanding strength, possessing no cleavage features and no anisotropy of mechanical properties. The NPD consists of very fine grains of several tens nanometers without containing any secondary phases and binder materials which greatly affect the mechanical properties and thermal stability. These characteristics of NPD suggest potential applications of this novel material to innovative cutting tools and wear resistance tools. This report reviews our systematic studies concerning NPD in terms of its synthesis mechanism, characteristics and applications.

Keywords: diamond, hardness, nano-polycrystal, high pressure synthesis, direct conversion

1. Introduction

We have developed a novel diamond that far surpasses conventional diamonds in hardness, strength, and thermal stability. That is newly developed translucent polycrystalline diamond consists only of ultra-fine diamond grains of several tens of nanometers which are directly bonded to each other with extreme solidness. This single-phase polycrystalline diamond may be referred as binderless; however, it is not a mere sintered compact made by sintering diamond powders without binder materials. It is uniquely different from single-crystal diamonds or sintered diamonds, representing a novel diamond derived from a new process by evolving a direct conversion method utilizing the ultra-high pressures.

In general, the strength and hardness of crystals differ depending on directions. Even crystals of a cubic system have different crystal lattice intervals and in-plane atomic densities depending on crystal orientations. Thus, crystals of the cubic system have cleavage features and anisotropy of mechanical properties such as hardness and abrasive wear resistance. The crystals of diamonds, which are considered the hardest material, are also susceptible to fracture when impacted, depending on the orientations, due to cleavage features. The indentation hardness changes nearly twice depending on the crystal orientation. In addition, abrasive wear resistance is significantly different depending on the crystal orientation. Such cleavage features and the anisotropy of mechanical properties of single-crystal diamonds (hereinafter referred to as SCDs) pose significant problems in some applications. In contrast, polycrystalline diamonds do not have cleavage features; they are tough, and isotropic in mechanical properties. However, conventional polycrystalline diamonds (hereinafter referred to as PCDs) used in commercially available cutting tools and wear-resisting tools represent sintered compacts of diamond powders using sintering aids or binder materials such as Co. The PCDs contain the additives in the grain boundaries, which decrease mechanical properties and thermal stability, while significantly undermining the performance of tools. Single-phase polycrystalline diamonds,

free from such sintering aids and binders, are considered to be ideal hard materials, with hardness, strength, and thermal stability that are all well balanced. It is known that such single-phase polycrystalline diamonds can be obtained with the solid-phase sintering of diamond powders at ultra-high pressures/temperatures or with chemical vapor deposition (CVD). However, polycrystalline diamonds characterized by adequate performance as bulk materials for tools have not been obtained by these methods, due to such as voids in grain boundaries and insufficient intergranular binding.

We succeeded in producing a single-phase nano-polycrystalline diamond (hereinafter referred to as NPD) consisting of fine diamond grains of several tens of nanometers through the indirectly heated direct conversion sintering of high-purity graphite at high pressures of more than 15 GPa and high temperatures of 2,200-2,300°C^{(1), (2)}. NPD is free from secondary phases, inclusions and pores, with ultra-fine diamond grains bonded directly to each other with extreme solidness⁽³⁾. Thus, NPD is translucent, as shown in **Photo 1**. The effect of inhibiting or blocking the development of plastic deformation and microcracking at the grain boundaries lies behind high hardness, which surpasses that of SCDs⁽⁴⁾⁻⁽⁶⁾. In addition, NPD is characterized



Photo 1. Nano-polycrystalline diamonds synthesized by direct conversion from graphite under high pressure and high temperature

by high strength, having no cleavage features and no anisotropy of mechanical properties which are the disadvantages of SCDs. This single-phase NPD has also high thermal stability and heat resistance, along with hardness and strength that do not decrease significantly at high temperatures⁽⁷⁾⁻⁽⁹⁾. Due to these excellent characteristics, NPD has outstanding potential as a hard material suited for cutting tools and wear-resistant tools. Due to its translucency, NPD is also useful in applications for high-strength, environment-resistant optical components. We have been working to enlarge the size of NPD samples and to develop mass-production technology to apply NPD commercially. Recently, we have succeeded in developing a process for mass-producing NPD products at large sizes (8-10 mm), along with satisfactory quality. We evaluated the actual performance of NPD in various applications and obtained satisfactory results in all of the applications^{(7), (8)}. Projects are now underway to commercialize products for some of the applications.

This paper is intended to summarize the results of our systematic research on NPD from synthesis and characterization to application.

2. Synthesis of NPD with Direct Conversion

Today, most industrial synthetic diamonds are manufactured using solvents (catalysts) of ferrous metals, under conditions of 5-6 GPa and 1,300-1,400°C. On the other hand it is known that graphite can be directly converted to diamond without solvents (non-catalytic phase transition) at high pressures of more than 10 GPa and high temperatures of more than 2,000°C^{(10), (11)}. Sintering simultaneously with the direct conversion is likely to produce solid, single-phase polycrystalline diamonds without binders. It has been confirmed that direct conversion sintering at such ultra-high pressures and temperatures can produce single-phase (binderless) polycrystalline cubic boron nitride (cBN: a substance with crystal structures and properties similar to those of diamonds) under conditions at 8 GPa and at 2,200-2,300°C^{(12), (13)}. Despite various attempts, however, solid single-phase polycrystalline diamonds have not been successfully obtained primarily because: (i) it is difficult to stably generate ultra-high pressures above 10 GPa and (ii) graphite heating elements (those that are commonly used) are converted to diamond at ultra-high pressures, which makes heating impossible. Although attempts were made to ensure heating by direct electrification^{(11), (14), (15)} and laser radiation⁽¹⁶⁾, these methods are inevitably accompanied by partially unconverted graphite and inhomogeneous sintering, due to short heating time and highly irregular temperature distribution.

Meanwhile, in high-pressure science and geoscience research, ultra-high pressure generation technology using multi-anvil apparatuses and indirect heating technology using refractory metal heaters have been developed, which has opened up possibilities to generate pressures of approximately 20 GPa and temperatures of 2,000-3,000°C in laboratories. By applying these technologies, we have succeeded in generating ultra-high pressures and tempera-

tures for industrial applications, along with synthesizing high-hardness NPD consisting of fine diamond grains of several tens of nanometers through a systematical development of the direct conversion sintering process encompassing the conditioning of starting materials (graphite) and the optimization of synthesis conditions^{(1), (2)}. The specimens we obtained in the initial stage of our development were very small, of only 1 mm, with many cracks and defects. Recently, the improvement and enlargement of pressure vessels and specimen chambers, as well as the enhancement of production technologies, have enabled us to stably produce ultra-hard NPD of large sizes (8-10 mm) and with satisfactory quality. The overview of this process is discussed below.

High-purity graphite compacts (purity of 99.99% or higher) consisting of hexagonal graphite particles of several micrometers in diameter oriented in a random direction are used as a starting material. A system consisting of a Kawai-type (6-8 type) multi-anvil apparatus and a specimen chamber, as shown in **Fig. 1 (b)**, is employed to generate ultra-high pressures and temperatures. Conventionally, anvil-cylinder type (belt type) pressure vessels, as shown in **Fig. 1 (a)**, were used. These conventional pressure vessels, however, can generate pressures of only up to approximately 8 GPa in industrial applications. In a Kawai-type multi-anvil apparatus, eight anvils are pressurized isotropically; each anvil is subject predominantly to compressive stress (with limited tensile stress). For this reason, ultra-high pressures exceeding 20 GPa can be stably generated without breaking anvils. Successful production of an NPD of satisfactory quality with high reproducibility depends primarily on the: (i) adequate selection of purity and the crystallinity of the starting material, (ii) stabilization of indirect heating by using a high-melting-point refractory heater, and (iii) optimization of synthesis pressures and temperatures. **Figure 2** shows the results of experiments to achieve direct conversion to diamond under various conditions. Conversion to cubic diamond (c-Dia) starts near the broken line in this graph; hexagonal diamond (h-Dia) is also recovered. Unconverted graphite remains as compressed graphite. As temperatures rise, the amount of c-Dia generated increases, with unconverted graphite and h-Dia decreasing. Direct conversion to diamond is completely achieved, and solidly

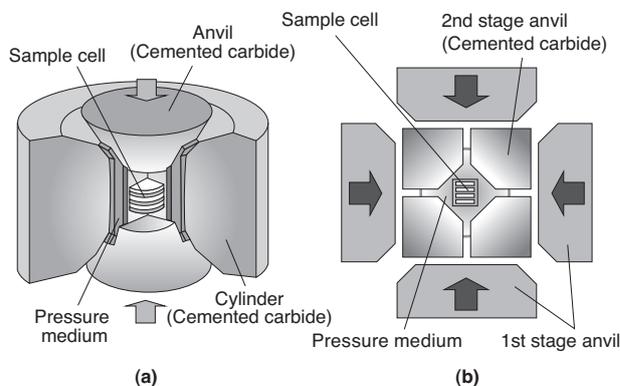


Fig. 1. Anvil-cylinder type (belt type) high pressure apparatus (a), and Kawai type (6-8 type) multi-anvil apparatus (b)

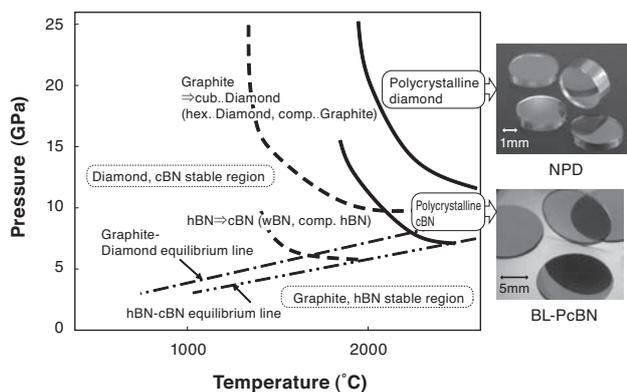


Fig. 2. High-pressure and high-temperature conditions for direct conversion from graphite and hBN to diamond and cBN, respectively.

sintered NPDs are obtained in the area toward high pressures (15 GPa or higher) and high temperatures (2,200°C or higher) from the solid line in the graph. The X-ray diffraction patterns of products obtained in this area indicate that only c-Dia diffraction lines are present; graphite and h-Dia diffraction lines are not observed.

It is noteworthy that pressures and temperatures at which conversion to c-Dia commences change depending on the starting material's graphite grain size and crystallinity. The smaller the graphite grain size is, or the lower the crystallinity is, the more easily the diffusion-type phase transition process occurs, as discussed in the next section; the synthesis temperature and pressure conditions become less demanding, and the amount of h-Dia decreases. For example, if amorphous carbon or glassy carbon is used as a starting material, conversion to diamond occurs at 10 GPa and 1,800°C, or at 15 GPa and approximately 1,600°C^{(17), (18)}. Carbon materials other than graphite, such as fullerenes (C₆₀) and carbon nanotubes (CNTs), can also be employed to achieve direct conversion to diamond^{(19), (20)}. These non-graphitic carbon materials are completely converted to c-Dia at low pressures and low temperatures equivalent to those for low-crystallinity or amorphous graphite; the formation of h-Dia is not observed at all. Polycrystalline diamonds consisting of ultra-fine diamond grains (10 nm or less) can be obtained at synthesis temperature conditions of 1,600-1,800°C⁽²¹⁾. It should be noted, however, that such polycrystalline diamonds derived from these starting materials tend to be characterized by weak intergranular binding and low mechanical properties because such polycrystalline diamonds are sintered at low temperatures and are affected by impurities in the starting materials, among others^{(5), (6)}.

For comparison, **Fig. 2** shows the experimental results of direct conversion to cBN using high-purity hexagonal boron nitride (hBN) as a starting material⁽²²⁾. Both solidly sintered, dense, polycrystalline diamond and polycrystalline cBN can be obtained at the minimum temperatures of approximately 2,300°C. However, the pressures required for diamond are 1.5-2 times higher than those required for cBN. It is known that the pressures and temperatures required for direct conversion from hBN to cBN depend largely on the crystallinity of the starting materials^{(23), (24)}; a

similar trend is observed in the case of diamond, as discussed above.

3. Microstructure and Conversion Mechanism

Photo 2 shows a transmission electron microscope (TEM) image of an NPD obtained from high-purity graphite under conditions of 16 GPa and 2,300°C. Characterized by a dense, ultra-fine structure, NPD consists mainly of amorphous diamond grains of several tens of nanometers in diameter. Lamellar structures may be partially observed depending on the grain size, crystallinity, and synthesis conditions of the starting materials. Such lamellar structures consist of c-Dia, but respective diamonds have not automorphic forms. The electron diffraction image shows that the orientation of the granular diamond is completely random, while all the stacking directions of the lamellar diamond are aligned with the <111> orientation⁽³⁾. The percentage of lamellar structures depends on the crystallinity and grain size of the graphite of the starting material. The higher the graphite crystallinity is, the higher the percentage of lamellar structures becomes; the lower the graphite crystallinity is, or the smaller the grain size is, the lower the percentage of lamellar structures becomes. As discussed below, these lamellar structures are not observed at all if non-graphitic carbon without graphite structures is used as a starting material. In-depth TEM and electron diffraction investigations have revealed that these lamellar structures are converted from graphite to h-Dia and eventually to c-Dia via diffusionless phase transition⁽³⁾. In other words, diffusionless phase transition contributed to c-Dia in lamellar structures, reflecting the shape of the graphite (the starting material). It is noteworthy that the homogeneous structures consisting of granular diamond that accounts for most of the structure are formed via a diffusion phase transition process: the breaking of the graphite's atomic bonds ⇒ the transfer of atoms ⇒ the reorganization to diamond lattices. Thus, respective grains have random orientations. In the diffusion phase transition process, crystals are formed in a manner minimizing the surface energy, which leads to polyhedral, automorphic granular crystals.

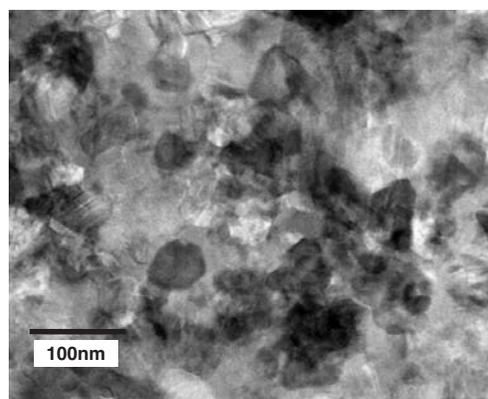


Photo 2. TEM image of microstructure of nano-polycrystalline diamond

Two phase transitions of different mechanisms are considered to take place concurrently due to the different orientations of the maximum compression stress and shear stress applied to respective graphite grains, resulting in the deformation of the respective graphite grains in different ways⁽⁶⁾. The deformation patterns determine the conversion paths (i.e., a diffusion phase transition or a diffusionless phase transition), which leads to the formation of composite structures as discussed above. Diffusionless phase transition is likely to take place when graphite (a starting material) has high crystallinity and is compressed dominantly in the c axis direction. Dominant compression in the a-b axis direction leads to diffusionless phase transition. On the other hand, lower graphite crystallinity or smaller graphite grain size results in less conversion process in the diffusionless phase transition, which leads to less lamellar structures. If carbon materials without graphite structures (so called “non-graphitic carbon,” such as amorphous carbon, fullerenes, and CNTs) are used as a starting material, such materials are entirely converted to diamond via diffusion phase transition; lamellar structures are not observed^{(6), (21)}.

4. Properties of NPD

As discussed above, NPD is characterized by a dense structure in which ultra-fine diamond grains are bonded solidly and directly to each other. For this reason, NPD has unique and outstanding properties beyond those of conventional diamond. This section discusses some distinctive properties of NPD derived from high-purity graphite with direct conversion under conditions at 16 GPa and 2,300°C. Note that polycrystalline diamonds consisting of ultra-fine diamond grains, obtained directly from low-crystallinity graphite and non-graphitic carbon materials, are not discussed in this section because the properties of such polycrystalline diamonds are significantly affected by impurities and adsorbed gases, etc., in the starting materials. For details about these polycrystalline diamonds, see references^{(5), (6)}.

4-1 Hardness

It is difficult to properly evaluate the hardness of NPD because NPD is very hard and ordinary natural SCD indenters are immediately destroyed. To evaluate NPD hardness more accurately, we used high-hardness Knoop indenters made from synthetic type IIa SCD characterized by high-hardness orientations⁽²⁵⁾. The hardness of these indenters in the axial direction (001) <110> is higher than 150 GPa⁽²⁵⁾. **Figure 3** shows the Knoop hardness of NPD in comparison with that of natural and synthetic SCDs. The hardness of NPD is approximately 130 GPa (± 10 GPa), which is higher than that of type I (containing nitrogen impurities) SCD (70-120 GPa)—the most common diamond, such as natural type Ia and synthetic type Ib SCDs. NPD’s high hardness is considered to be derived from the fact that the structure with fine grains solidly bonded to each other helps to inhibit the development of plastic deformation and microcracking at the grain boundaries. Furthermore, NPD is polycrystalline with randomly orientated grains; thus, unlike SCDs, NPD has no anisotropy of hardness and no cleavage fea-

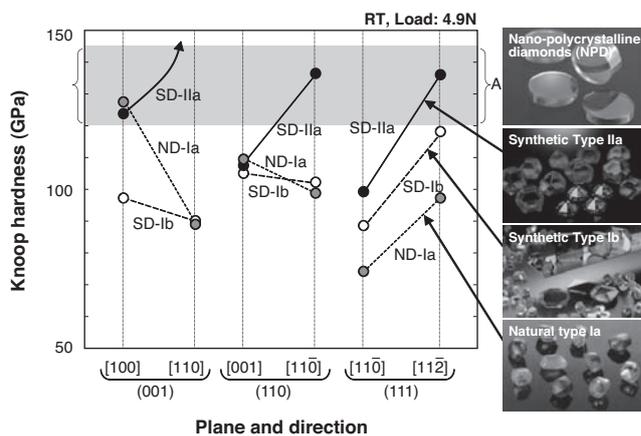


Fig. 3. Knoop hardness of nano-polycrystalline diamond (A) comparing to those of various synthetic and natural single crystal diamonds (SD-IIa; synthetic type IIa diamond, SD-Ib; synthetic type Ib diamond, ND-Ia; natural type Ia diamond). Load: 4.9N

tures. In addition, TEM observations of microcracking near the indentations have revealed that transgranular fractures are dominant in terms of fracture mode, indicating the intergranular binding is extremely strong, and crack propagation resistance (fracture toughness) is high because the development of microcracking is inhibited at the grain boundaries^{(5), (6)}.

Figure 4 shows the results of comparison between the high-temperature Knoop hardness of NPD and that of synthetic type IIa SCD, which has the highest hardness of all SCDs⁽⁷⁾⁻⁽⁹⁾. It should be noted that Knoop indenters prepared from NPD⁽²⁶⁾ were used to measure high-temperature hardness because SCD indenters undergo plastic deformation at high temperatures. As shown in **Fig. 4**, NPD’s hardness decrease gently with increasing temperature; high hardness of more than 100 GPa is maintained at 800°C. On the other hand, the Knoop hardness of synthetic type IIa SCD (001) <110> is extraordinarily high of more than 150 GPa at room temperature, and thus indentations are not formed⁽²⁷⁾. As the temperatures are increased, how-

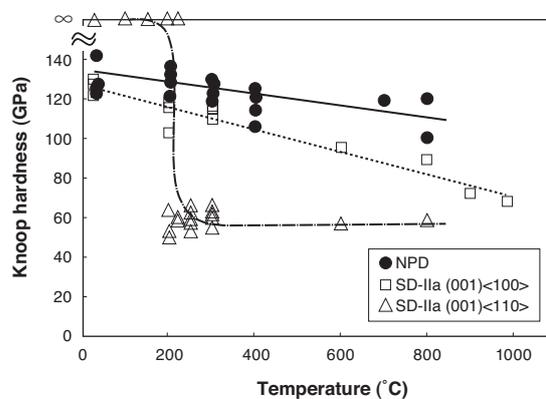


Fig. 4. High temperature Knoop hardness of nano-polycrystalline diamond (NPD) compared with Knoop hardnesses in (001)<100> and (001)<110> of single crystal synthetic type IIa single crystal diamonds (SD-IIa)

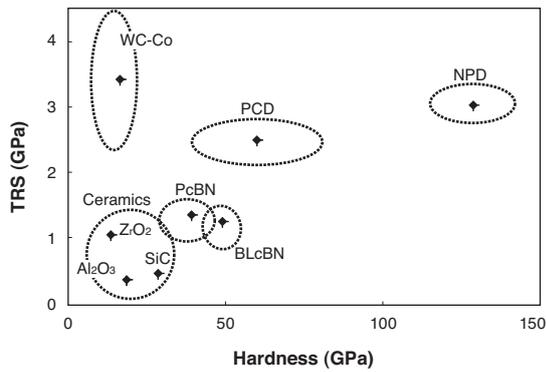


Fig. 5. TRS and hardness of nano-polycrystalline diamond (NPD) and other hard materials at room temperature. PCD; conventional polycrystalline diamond containing binder, PcBN; conventional polycrystalline cBN containing binder, BL-PcBN; binderless polycrystalline cBN synthesized by direct conversion, Span length: 4 mm

ever, plastic deformation is thermally activated from 200–300°C. The hardness rapidly decreases, down to approximately 60 GPa (equivalent to the hardness of type Ib SCD) at 300°C or higher⁽²⁸⁾. As a result, the Knoop hardness of NPD at 800°C is approximately twice as high as that of synthetic type IIa SCD (001) <110>. In the case of SCDs, plastic deformation is promoted at high temperatures due to a dislocation slip caused primarily by the (111) <110> slip system, leading to significant reduction in hardness. In contrast, in the case of NPD, plastic deformation inhibition effects at grain boundaries work effectively at high temperatures, resulting in high-temperature hardness far beyond that of SCDs. Conventional PCDs (sintered diamond compacts containing binders) deteriorate significantly at 600–700°C, leading to considerably lower hardness (refer to sections 4-2 and 4-4).

4-2 Strength

Figure 5 shows the transverse rupture strength (TRS) and hardness at room temperature for NPD, a conventional PCD containing Co binder, and other hard ceramic materials. The TRSs of NPD and PCD were measured with a jig made from SiC (span length: 4 mm). The TRS of NPD at room temperature is approximately 3 GPa, which is higher than the TRS of other ceramic materials and conventional binder-containing PCDs, and close to that of cemented carbide. In **Fig. 5**, NPD is located in the top right corner, indicating that NPD is a superbly hard material characterized by both high hardness and high toughness. NPD has high TRS because intergranular binding is very strong and transgranular cracking grows (not at the grain boundaries)^{(5), (6)}, and some of the development of microcracks is inhibited at the grain boundaries.

As shown in **Fig. 6**, the TRS of NPD hardly decreases at high temperatures, and it increases slightly at 1,000°C or higher⁽⁹⁾. To the contrary, the TRS of conventional binder-containing PCDs sharply decreases at around 500°C. The increased TRS of NPD at high temperatures of 1,000°C or higher is considered to be attributed to microscopic plastic deformation (dislocation movement) in diamond grains at high temperatures that relaxes the localized stress at a

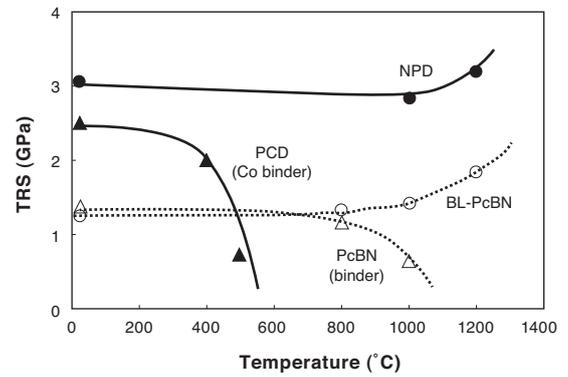


Fig. 6. TRS of nano-polycrystalline diamond (NPD) and other hard materials at high temperature. PCD; conventional polycrystalline diamond containing binder, PcBN; conventional polycrystalline cBN containing binder, BL-PcBN; binderless polycrystalline cBN synthesized by direct conversion, Span length: 4 mm

crack tip. Such a tendency can also be observed in the case of ceramic materials such as SiC, Si₃N₄ derived from CVD⁽²⁹⁾ and also binderless polycrystalline cBN synthesized by direct conversion⁽³⁰⁾ that do not have impurity phases in grain boundaries and in which intergranular binding is sufficiently solid (i.e., the transgranular fracture is dominant). As discussed above, it has been confirmed that transgranular fracture is dominant in NPD. Such effect is not observed if intergranular binding is insufficient because cracking propagates in grain boundaries. The rapid decrease in the TRS of PCDs at around 500°C is attributed to thermal stress and microcracking due to thermal expansion differences between binders and diamonds.

4-3 Abrasive wear resistance

NPD's abrasive wear properties were evaluated in grinding experiments using a metal-bonded diamond grinding wheel. **Figure 7** shows the test conditions and experiment results^{(7), (8)}. Other diamond materials were also evaluated under the same conditions for comparison. The abrasive wear resistance of NPD is comparable to that of high-pressure synthetic type Ib SCD (112) <110> (the high abrasive wear resistance direction), and is approximately

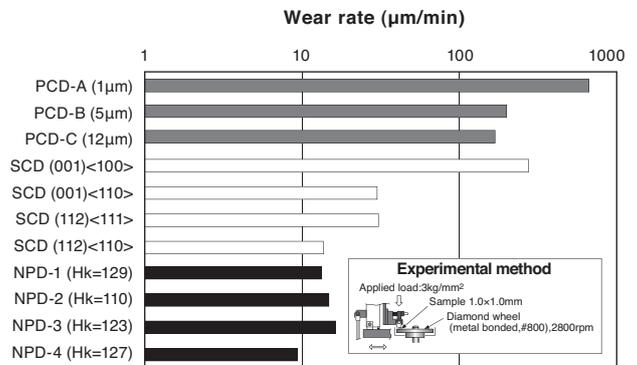


Fig. 7. Wear resistance of nano-polycrystalline diamond (NPD), conventional polycrystalline diamond (PCD) and synthetic single crystal (type Ib) diamond (SCD)

10 times higher than that of the SCD (001) <100> (the low abrasive wear resistance direction) and 10-20 times higher than that of conventional binder-containing PCDs. Observation of NPD's grinding surface with high-resolution SEM revealed that traces of fallen grains are not seen in large numbers; instead, many grain surface structures that are considered to be the high abrasive wear resistance crystal planes of (111), etc., stand slightly higher (several nanometers) than the surrounding surface in large numbers. In the case of NPD, grains are less likely to fall because respective diamond grains are bonded very solidly^{(5), (6)}. In addition, diamond grains of NPD are randomly orientated, which is why the high abrasive wear resistance grain surfaces discussed above appear on the NPD surface in large numbers. For these reasons, NPD is considered to have shown high abrasive wear resistance. Note that, in the case of SCDs, abrasive wear progresses due to the accumulation of cleavages, and significant abrasive wear occurs depending on the crystal orientation. In the case of PCDs, abrasive wear progresses much more than the case of NPD due to microcracks and falling grains as influenced by binders.

4.4 Thermal properties

The results of the X-ray diffraction, Raman spectrum, and hardness measurement of NPD specimens recovered after being heated to 1,500°C in an inert atmosphere remained unchanged from those before heating. NPD specimen surfaces were partly graphitized at 1,600°C. It is known that, in an inert atmosphere, pure SCDs are stable up to 1,500-1,600°C and graphitized at higher temperatures⁽³¹⁾. Thus, the thermal stability of NPD is almost equivalent to that of SCDs. In the case of PCDs, heating causes thermal stress due to thermal expansion differences between binders and diamond; microcracking occurs at temperatures around 400-500°C; PCDs deteriorate at 800-900°C⁽³²⁾. In addition, in the case of PCDs, diamonds are converted into graphite at temperatures of 700°C or higher due to the catalytic action of binders⁽³¹⁾. Thus, as discussed above, the hardness and TRS of PCDs are drastically reduced. To sum up, the thermal stability of NPD is equivalent to that of SCDs, and is far beyond that of conventional PCDs.

4.5 Optical properties

Next, NPD's optical properties⁽³³⁾ are discussed. **Figure 8** shows the transmission spectrum for the ultraviolet and visible region of NPD and various types of SCDs at 1 mm in thickness⁽³⁴⁾. Continuous absorption is observed in the range of 700-800 nm or at shorter wavelengths. This pattern is similar to the continuous absorption attributed to extended defects as observed in SCDs with many dislocation defects and internal strains⁽³⁵⁾. This continuous absorption is considered to be attributed to dislocation defects in NPD grains and lattice defects that are present in large numbers at grain boundaries. Due to the continuous absorption, NPD looks yellowish brown. The absorption observed at 611 nm and 669 nm corresponds to luminescence due to structural defects. Absorption is also observed from around 500 nm, which is considered to be attributed to other crystal defects. NPD sliced down to 50 μm shows optical transparency to the absorption edge corresponding to the indirect energy band gap of 225 nm. It should be noted, however, that absorption attributed to isolated substitutional nitrogen impurities (270 nm) as observed in conven-

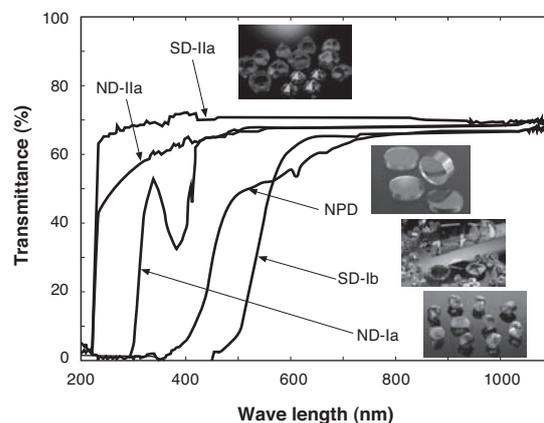


Fig. 8. UV and visible transmission spectra of nano-polycrystalline diamond (NPD) and various single crystal diamonds (SD-IIa; synthetic type IIa diamond, SD-Ib; synthetic type Ib diamond, ND-IIa; natural type IIa diamond, ND-Ia; natural type Ia diamond). Thickness: 1 mm

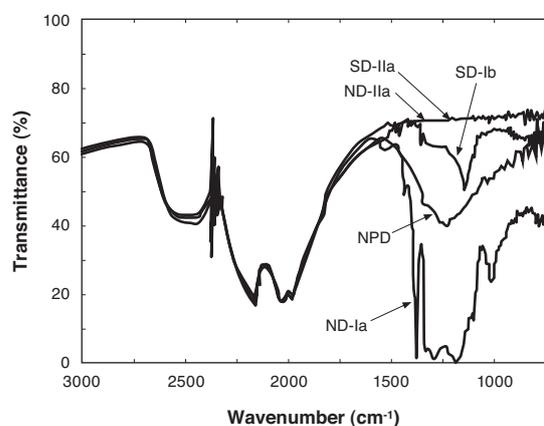


Fig. 9. IR transmission spectra of nano-polycrystalline diamond (NPD) and various single crystal diamonds (SD-IIa; synthetic type IIa diamond, SD-Ib; synthetic type Ib diamond, ND-IIa; natural type IIa diamond, ND-Ia; natural type Ia diamond). Thickness: 1 mm

tional synthetic type Ib SCD as well as in the absorption of aggregated nitrogen impurities as observed in natural type Ia SCD were not clearly observed⁽³³⁾. In photo luminescence measurement, some color centers such as N3 centers, in which aggregated nitrogen impurities are involved, and some spots of luminescence that are considered to be attributed to dislocation defects are observed⁽³³⁾.

Figure 9 shows the transmission spectrum of NPD in the infrared region. In the case of NPD, absorption (1,220 cm⁻¹) that is considered to be attributed to 6H-type h-Dia⁽³⁶⁾ is observed, in addition to absorption attributed to multiphonon of the diamond lattice. On both sides of this absorption, weak absorption is observed at positions where type IaA (nitrogen atom pairs) absorption (1,282 cm⁻¹) and type IaB (clusters of four nitrogen atoms) absorption (1,175 cm⁻¹) appear, as observed in natural diamond. Type Ib absorption (1,130 cm⁻¹) attributed to isolated substitutional nitrogen impurities, which is well known in the case

of synthetic diamond, is not clearly observed.

As discussed above, absorption attributed to isolated substitutional nitrogen impurities are not clearly observed both in the ultraviolet and infrared regions, while signals of nitrogen atom pairs and clusters of four nitrogen atoms were slightly observed. In SIMS analyses of impurities in NPD, nitrogen of 50-100 ppm was detected; in ESR analyses, isolated substitutional impurities were 1 ppm or less⁽³³⁾. Thus, most of the nitrogen impurities in NPD are considered to be present in the aggregated forms as observed in natural diamond, not in the form of isolated substitutional impurities as observed in conventional synthetic diamond. NPD is synthesized at high temperatures of more than 2,200°C; thus, it is considered that most of the nitrogen atoms diffuse and aggregate during the synthesis process, and that clusters of two to four nitrogen atoms remain in the grains.

5. Applications

As discussed above, NPD is characterized by extremely high hardness and high strength, as well as superb abrasive wear resistance and thermal stability, having no cleavage features and no anisotropy, unlike SCDs. Thus, NPD can be applied to diamond tools in general, including cutting tools and wear-resisting tools such as dressers, scribes, styli, dies, and nozzles. NPD is also useful as a material for high-strength optical windows (e.g., pressure-proof windows and ultra high-pressure diamond anvils for research applications), due to its excellent strength and translucent properties. We evaluated the performance of NPD in practical applications, and satisfactory results were obtained in respective applications^{(7), (8), (37)}. Summarized below are the performance evaluation results of NPD as used in cutting tools.

Photo 3 shows some cutting tools manufactured from NPD. Cutting tests were conducted on various work materials such as high-strength Al-Si alloy, ceramics, and cemented carbide under different conditions. It was found that NPD has excellent cutting performance several times higher than that of conventional binder-containing PCDs and SCDs in all the cases^{(7), (8)}. NPD is not subject to binder-induced deterioration as observed in PCDs. Unlike SCDs, NPD has no cleavage features and no anisotropy against

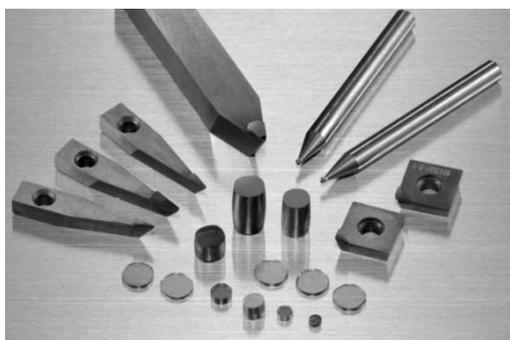


Photo 3. Cutting tools prepared from nano-polycrystalline diamond

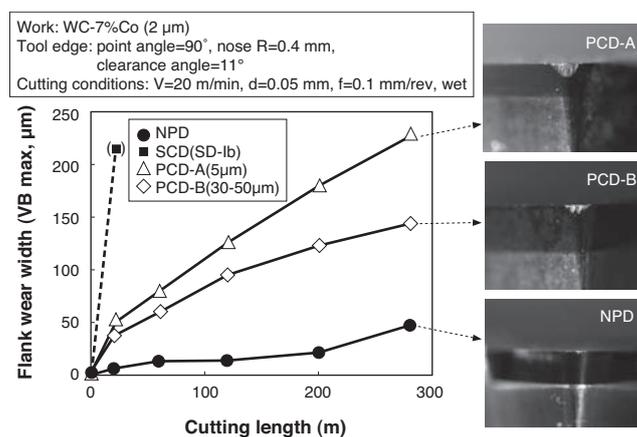


Fig. 10. Cutting performance of NPD cutting tool in cutting of WC-based cemented carbide

abrasive wear, leading less chipping and less uneven wear, respectively. In all the cutting tests, NPD showed excellent cutting performance, with minimal damage on blade tips and abrasion. **Figure 10** shows some of cutting performance evaluation results on cemented carbide. SCD tools sustained significant damage in the early stage of cutting, while NPD tools did not show remarkable damage with minimal abrasive wear. The abrasive wear resistance of NPD tools is five times higher than that of PCD tools A (grain size: 5 μm) and three times higher than that of PCD tools B (grain size: 30-50 μm), indicating superb cutting performance.

NPD is a binderless polycrystalline substance with very fine grains bonded directly and solidly to each other. For this reason, NPD is considered to demonstrate high performance regarding the precision cutting of brittle materials with sharp-edged cutting tools, in particular. NPD is expected to enable cutting of cemented carbide metal molds for precision optical elements which has not been attained with conventional PCDs and SCDs.

6. Conclusions

We succeeded in synthesizing NPD of extremely high hardness from graphite by direct conversion sintering at ultra-high pressures. The hardness of NPD, which surpasses that of SCDs, does not show a significant drop at high temperatures. NPD is also characterized by excellent strength, having no cleavage features and no anisotropy of mechanical properties, unlike SCDs. In addition, NPD is free from binders and secondary phases that significantly affect mechanical properties and thermal stability. Thus, NPD is an innovative hard material that is characterized not only by extreme hardness but also by high toughness and excellent thermal stability. NPD has very high potential as a material for tools and unlimited potential in its applications. In particular, NPD has outstanding potential for applications regarding next-generation high-performance cutting tools and wear-resistant tools. We hope that the ultra-hard NPD that we have developed will be used in many fields and con-

tribute in no small way to the development of industries. Applications of the NPD process (direct conversion at ultra-high pressures and temperatures) technology may also lead to the creation of functional diamonds and new materials. We will stay committed to opening up new possibilities and taking up challenges to create new diamonds.

7. Acknowledgements

We would like to express our deepest appreciation to Prof. Tetsuo Irifune of the Geodynamics Research Center at Ehime University, in collaboration with whom the research on the synthesis of NPD was conducted.

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