Innovative Ultra-hard Materials: Binderless Nano-polycrystalline Diamond and Nano-polycrystalline Cubic Boron Nitride

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We have succeeded in the production of novel ultra-hard materials: single-phase (binderless) nano-polycrystalline diamond and nano-polycrystalline cubic Boron Nitride (cBN). These nano-polycrystals were synthesized under static ultra-high pressure and high temperature using a new method, direct conversion sintering. The new hard materials consist of fine grains of several tens of nano-meters without containing any secondary phases or binder materials. They thus have high hardness and high strength that surpass those of single crystals and conventional sintered compacts containing binder materials. The fine microstructure containing no secondary phases and the outstanding mechanical properties of these new hardmaterials are promising for applications to next-generation high-precision and high-efficiency cutting tools.

Keywords: diamond, cubic-Boron-Nitride (cBN), nano-polycrystalline, high pressure and high temperature, direct conversion

1. Introduction

As part of efforts to reduce production costs and enhance production efficiency, use of highly durable, hard-to-cut materials is expanding in the automotive, aircraft, medical, electronics, and other industries. Under such circumstances, these industries have increasing needs for harder and tougher cutting tool materials in order to enhance cutting efficiency by increasing cutting speed, as well as to cut hard-to-cut materials. Ceramic and cemented carbide tools, which have been widely used, cannot meet these needs.

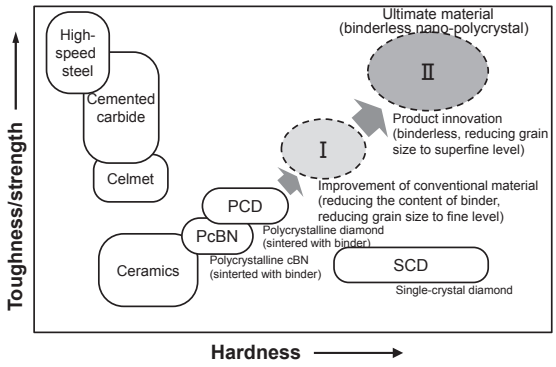


Fig. 1. Mechanical Properties of Currently Available Tool Materials and Direction of Innovative Ultra-hard Material Development

Development of higher-hardness and tougher cutting tool materials using ultra-hard cBN and diamond as base materials has been promoted according to the concept shown by an arrow in Fig. 1. The problem to be solved in the development is to increase hardness by reducing the amount of binder materials to be added and to increase strength by refining the constituent grains (Ⅰ in Fig. 1). The ideal ultimate target material is a nano-polycrystalline body in which nano-sized grains of diamond or cBN are directly bound tightly to one another without containing any binder materials (Ⅱ in Fig. 1). The ultimate material can be formed into high-precision cutting edges alike single crystal diamond. In addition, the non-cleavability of this material gives the cutting edges strength exceeding that of single crystals. Owing to these outstanding features, this material is promising for precision- and micro- machining applications. However, such an innovative nano-crystalline material cannot be created by merely extending conventional technologies. Instead, development of an innovatively new process (product innovation) is essential.

We started research and development of nano-polycrystalline diamond and nano-polycrystalline cBN aiming at the creation of the ultimate cutting tool materials suitable for higher-speed, higher-efficiency, and higher-precision cutting applications. After years of efforts, we succeeded in the creation of these innovative hard materials by establishing a new ultra-high pressure technology and a new technology called direct conversion sintering process. This paper details the development of these new ultra-hard materials, as well as their features and applications.

2. Development Concept and Approach

Sintered polycrystalline diamond (PCD) and sintered polycrystalline cubic boron nitride (PcBN), both of which are widely used as tool materials, are made by sintering powdered diamond and cBN in the pressure range of 5 to 6 GPa and in the temperature range of 1,300°C to 1,500°C using cobalt or other metals, or hard ceramics as binder materials. When the binder is added to the powdered diamond or powdered

cBN, it lies on the boundaries of diamond grains or cBN grains, and significantly affects the mechanical properties and thermal stability of the sintered compact. Developing techniques for sintering powdered diamond and cBN without using a binder has been tried. However, these techniques have not been put to practical use as of today because binding diamond grains or cBN grains tightly to one another is difficult.

Meanwhile, several research papers report that polycrystalline bodies consisting of fine grains being bonded directly with one other could be created on an experimental basis.[1]-[8] In the experiment, the normal-pressure phase of graphite, hexagonal boron nitride (hBN), or other material was used as a starting material. The starting material was directly converted to the high-pressure phase of diamond or cBN under ultra-high pressure and high temperature conditions,[1],[2] and the high-pressure phase was sintered simultaneously in this phase conversion process. However, the properties of experimentally created materials have not been clarified sufficiently and these experimental processes use ultra-high pressure and high temperatures two to three times of those required in conventional processes. Due to higher cost and lower mass-productivity, these experimental processes have not been put to practical use until today.

We believed that the above ultra-high pressure direct conversion process would be useful for creating the high-hardness, tough, binderless polycrystalline body we intended to develop. We began to develop a new ultra-high pressure and high temperature generation technology with confidence that we would be able to economically and stably generate ultra-high pressure and high temperature conditions by applying the technologies we had accumulated over a number of years. At the same time, we carried out a systematic study on the effects of the properties and synthesis conditions of the starting material in a direct conversion process on the structure and properties of the created polycrystalline body. As a result, we succeeded in the creation of nano-polycrystalline cBN[9]-[11] and then nano-polycrystalline diamond.[12]-[15] In these materials, fine grains are directly and tightly bonded to one another as we intended to achieve.

The synthesis of these innovatively new hard materials, as well as their properties and applications, are discussed below.

3. Synthesis Method and Formation Mechanism

Since diamond and cBN resemble each other in a crystalline structure and thermodynamic energy state, the direct conversion processes can be discussed from the same standpoint. This section details their synthesis methods while comparing them as needed.

First, we developed a new ultra-high pressure technology and succeeded in spreading the usable pressure and temperature ranges from 5–6 GPa and 1,300–1500°C to 8–20 GPa and 2,000–2,500°C, respectively. Next, we determined the high pressure and high temperature conditions for direct conversion from graphite and hBN to the high-pressure phases. The synthesis regions we obtained from experiments are shown in Fig. 2. According to this figure, each starting material begins to be converted from the normal-pressure phase to the high-pressure phase in the regions above the dotted line (regions A' and B'), and the conversion to cubic crystal forms completes in the regions upper right of the solid line (regions A and B). The conditions required for completion of the conversion are as follows; Pressure: 8 GPa or higher for cBN and 15 GPa or higher for diamond, Temperature: 2,100°C or higher for both cBN and diamond. This temperature corresponds to the energy for activating the diffusion of atoms.

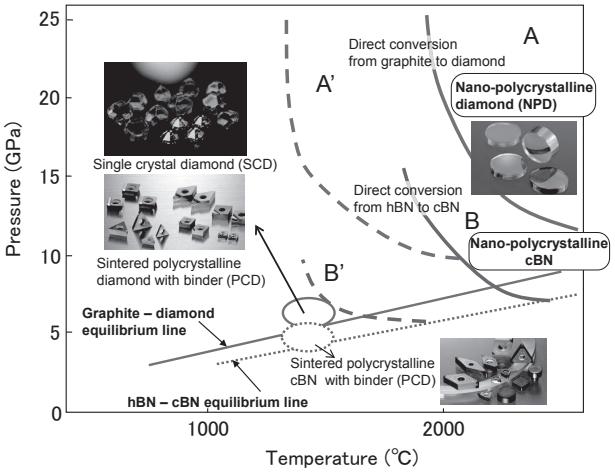


Fig. 2. Nano-polycrystalline Diamond/cBN Synthesis Regions

In the conversion mechanism of both nano-polycrystalline diamond and cBN, diffusive phase transition and non-diffusive phase transition compete with each other.[14],[16] However, the phase transition pathway of each starting material changes depending on its properties and pressure and temperature conditions. As the crystallization degree of starting materials and the synthesis pressure increase, non-diffusive transition becomes dominant in a low-temperature range. In such a case, hexagonal diamond or wurtzite boron nitride (wBN), a metastable phase, is formed temporarily as an intermediary phase in the conversion process. When the process temperature is raised continuously, almost all of the phases change to cubic diamond or cBN when the temperature exceeds 2,100°C.

In the regions A and B in Fig. 2, 100% pure polycrystalline diamond and 100% pure polycrystalline cBN are synthesized, respectively. However, the microstructures and properties of the synthesized materials change significantly depending on their synthesis conditions. The following three are major influential factors: 1) starting material, 2) pressurization and heating process conditions, and 3) conversion sintering

temperature. Densely structured polycrystalline materials having the desired high hardness and toughness are obtained by optimizing and properly controlling these factors, as described in the following section.

4. Characteristics

4-1 Microstructure

The polycrystalline bodies of diamond and cBN that are synthesized at 2,100°C–2200°C under the conditions A and B shown in Fig. 2 consist of fine grains of several tens of nanometers. When graphite or hBN consisting of finer grains or lower crystallinity grains is used as a starting material, a polycrystalline body consisting of a perfectly converted high-pressure phase is synthesized even under a lower temperature condition in the regions A' and B'. When a polycrystalline body is synthesized at a temperature of 2,000°C or below, its grain size further decreases (to approximately 10 nm). However, its hardness decreases due to insufficient sintering.[17],[18] On the other hand, if the synthesis temperature exceeds approximately 2,300°C, the diffusion velocity of atoms increases rapidly and the grains of both the diamond and cBN begin to grow.[17],[18] In particular, the grain size of cBN increases abnormally to several μm.

4-2 Mechanical properties

When nano-polycrystalline diamond (NPD or BL-PCD) or nano-polycrystalline cBN (binderless PcBN (BL-PcBN)) is synthesized by accurately controlling its grain size and sinterability, its hardness is far higher than that of conventional PCD and PcBN containing binders, as shown in Fig. 3.

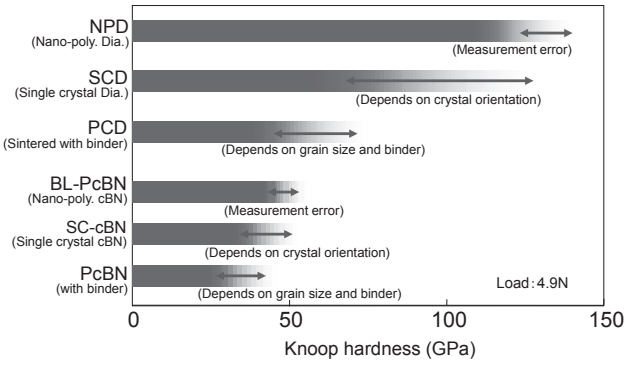


Fig. 3. Knoop Hardness of Nano-polycrystalline Diamond/cBN

The hardness of a single crystal differs greatly depending on the crystallographic orientation. The hardness of nano-polycrystals is higher than the mean hardness of a single crystal and they do not have such hardness anisotropy as that of a single crystal. A nano-polycrystal maintains high hardness even when exposed to high temperatures. In particular, the hardness of NPD at approximately 1,000°C is nearly two times the hardness of a single crystal.[13],[14] The transverse rupture strength (TRS)*1 of nano-polycrystals is also higher than that of conventional PCD and PcBN, as shown in Fig. 4.[13],[14] Nano-polycrystals maintain their high TRS even when exposed to high temperatures. Specifically, they tend to increase their TRS slightly in a temperature range of higher than 800°C-1,000°C. The TRS of conventional PcBN and PCD containing binders drops sharply at around 800°C and 500°C, respectively. The reason is that they generate fine cracks at several hundred degrees centigrade due to a difference in thermal expansion between the binders and cBN or diamond.

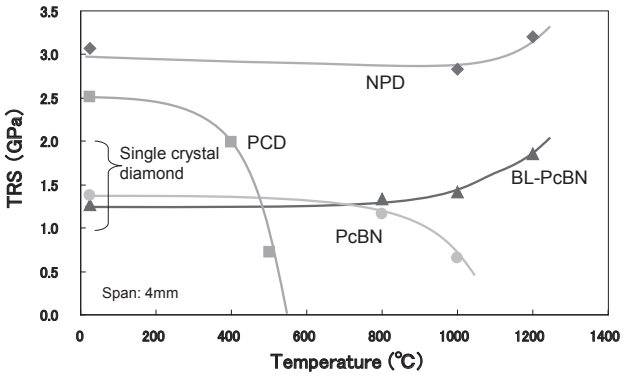


Fig. 4. Transverse Rupture Strength (TRS) of Nano-polycrystalline Diamond/cBN

Diamond crystal undergoes plastic deformation or cleavage cracking along a specific crystal orientation and resulting plastic deformation and cleavage cracking, thereby accelerating deformation/fracture. In contrast, the polycrystal accelerates breakage due to intergranular slip and/or cracking, therefore the hardness of polycrystals is usually lower than that of single crystals. However, when the intergranular bond is sufficiently strong, transgranular fracture dominates over intergranular fracture. In this condition, plastic deformation and crack propagation generated in each grains are suppressed by grain boundaries where atoms are arranged discontinuously. As a result, polycrystals exhibit mechanical properties superior to those of single crystals.

Owing to optimization of the starting materials, pressurization/heating processes, and temperature conditions, the newly developed nano-polycrystalline diamond and nano-polycrystalline cBN have extremely high intergranular bonding force (grain boundary strength), thereby making transgranular fracture dominant.[10],[17] Therefore, these new nano-polycrystals demonstrate higher hardness and TRS than those of single crystals. In addition, microscopic transgranular plastic deformation that occurs at high temperatures suppressed the concentration of stress at crack edges. These phenomena are considered to prevent these nano-polycrystals from lowering their high hardness

and TRS even when they are exposed to high temperatures. These phenomena can be observed only when grain boundary strength is high and transgranular fracture is dominant.[10),(13)]

Figure 5 is a schematic illustration of grain boundary conditions. In a high-strength nano-polycrystal, the crystal lattices of each grain are intertwined complexly with one another. As a result, grain boundary strength increases dramatically and transgranular fracture becomes dominant. In contrast, when the sintering degree is degraded due to an inappropriate synthesis condition or when the grain growth is developed, grain boundary strength will decrease and intergranular fracture will become dominant.

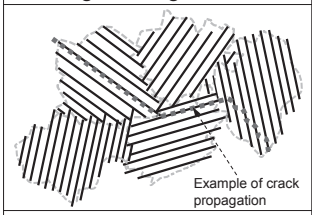
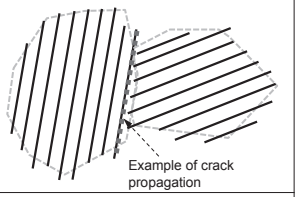
High-strength NPD	Low-strength NPD
	
Complexly intertwined (deeply-indented or sawtooth) grain boundary	Less intertwined linear grain boundary (Conventional polycrystalline diamond has this type of grain boundary.)
High grain boundary strength (Hard to be broken at grain boundary ⇒Transgranular fracture mode)	Low grain boundary strength (Easy to be broken at grain boundary ⇒Intergranular fracture mode)

Fig. 5. Schematic Illustration of the Microscopic Structure of Nano-polycrystalline Diamond/cBN

The relationships between the hardness and TRS of nano-polycrystalline diamond and nano-polycrystalline cBN that were synthesized under optimal conditions are shown with those of other materials in Fig. 6. Binderless nano-polycrystalline materials have a hardness and toughness exceeding those of conventional materials,

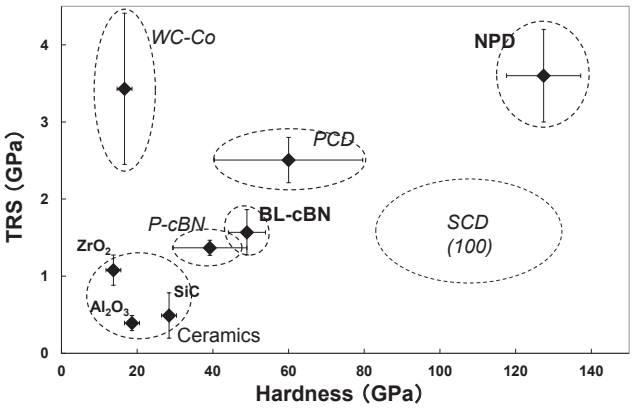


Fig. 6. Relationship between Hardness and TRS of Various Hard Materials

constituting the ultimate materials (Ⅱ in Fig. 1) we discussed at the beginning of this paper.

5. Applications

5-1 Nano-polycrystalline diamond

As discussed in the preceding section, nano-polycrystalline diamond (NPD) synthesized from an appropriately selected and adjusted starting material under optimized synthesis conditions is remarkably hard and tough. Different from single crystalline diamond (SCD), NPD is free from cleavage fracture and anisotropy in mechanical properties. NPD is also superior to conventional sintered diamond (PCD) containing a binder in wear resistance and thermal stability (heat resistance).[13),(14)] The characteristics of NPD are summarized in Fig. 7, comparing with those of conventional diamond. Owing to these exceptional properties, NPD is promising for use as a diamond cutting tool material and wear-resistant tool material. We fabricated various NPD cutting tools shown in Photo 1 and evaluated their practical performances in cutting. In this evaluation test, each tool demonstrated cutting performance as expected.[12),(15),(21)]

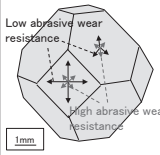
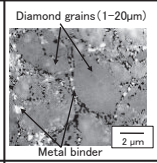
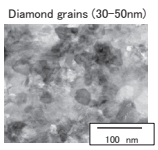
	SCD	PCD	NPD
			
Micro structure or Image			
Hardness	80-120GPa	50GPa	**110-130GPa**
Isotropy	Anisotropic	Isotropic	**Isotropic**
Strength	Low (cleavage)	High	**Very high**
Thermal stability	1600°C	600°C	**1600°C**
Edge accuracy	50nm	~0.5μm	**<50nm**
Transparency	Transparent	Opaque	**Transparent**

Fig. 7. Characteristics of Nano-polycrystalline Diamond and Conventional Diamond Materials

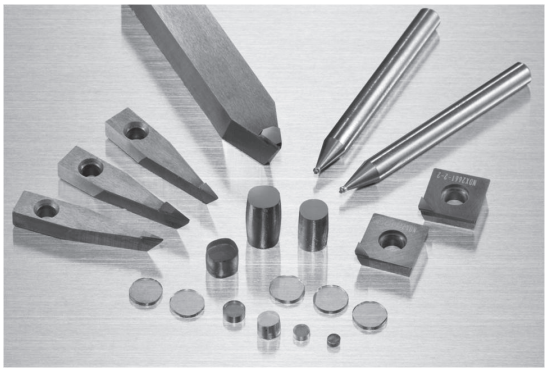


Photo 1. Cutting Tools Made of Nano-polycrystalline Diamond

Figure 8 shows the result of a test for turning cemented carbide with NPD tools. The single crystal diamond tool was chipped off due to cleavage at the initial stage of cutting, while the NPD tool did not show any notable fracture.

Figure 9 shows an example of an ultra-hard die for optical component applications that was finished precisely with a NPD ball-nosed end mill (0.5 mm in radius). This cutting test confirmed that NPD ball-nosed end mills ensure high-quality finished surfaces equivalent to polish-finished surfaces and also make it possible to mirror-finish cemented carbide, which has been difficult to achieve.

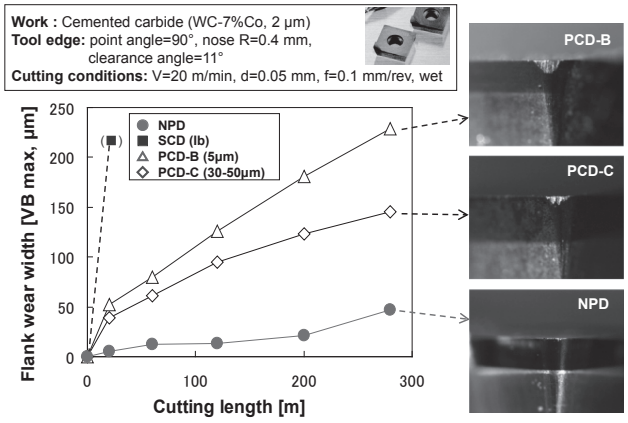


Fig. 8. Result of Turning Test on Cemented Carbide With NPD Tool

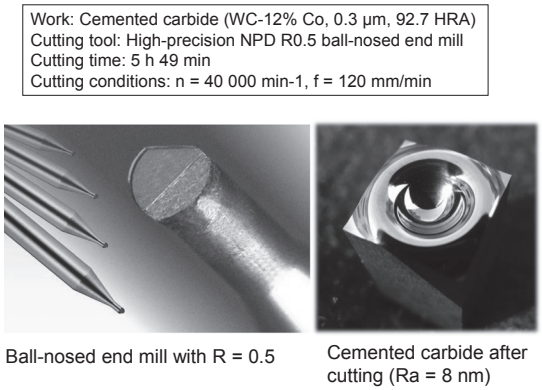


Fig. 9. Example of Cemented Carbide Die Cutting with NPD Ball-nosed End Mill

We also carried out machining tests for a high-strength Al-Si alloy, ceramic, and various types of cemented carbide under various cutting conditions, and confirmed in each test that NPD tools are far superior to PCD and SCD tools in cutting performance and cutting accuracy.[12),(15),(21)]

5-2 Nano-polycrystalline cBN

Similarly to diamond, nano-polycrystalline cBN made by appropriately optimizing and controlling the starting material and synthesis conditions has hardness (Fig. 3) and strength (Figs. 4 and 6) surpassing those of conventional sintered cBN containing binders (PcBN) and single crystal cBN, and maintains high hardness and TRS even at a high temperatures. In addition, nano-polycrystalline cBN is superior to conventional sintered cBN in thermal conductivity and thermal stability.[10)]

Because of these superior mechanical and thermal properties, nano-polycrystalline cBN is highly promising for cutting tool applications. In particular, we have confirmed that nano-polycrystalline cBN exhibits high performance when used for high-speed, high-efficiency, high-accuracy cutting of ferrous materials. For example, such high performance was verified in a test where gray cast iron was turned at high speed with a nano-polycrystalline cBN cutting tool. In contrast to conventional sintered cBN cutting tools, which are chipped off at the edges at the initial stage of cutting, the nano-polycrystalline cBN cutting tool seldom generated thermal cracks and cut the workpieces continuously for sufficiently a long time.[9)]

We also carried out a test for cutting high-hardness hardened steel with a ball-nosed end mill made of nano-polycrystalline cBN. In the test, the ball-nosed end mill produced high-quality cut surfaces having a roughness of Ra 20 nm or better (Fig. 10).[18),(22)]

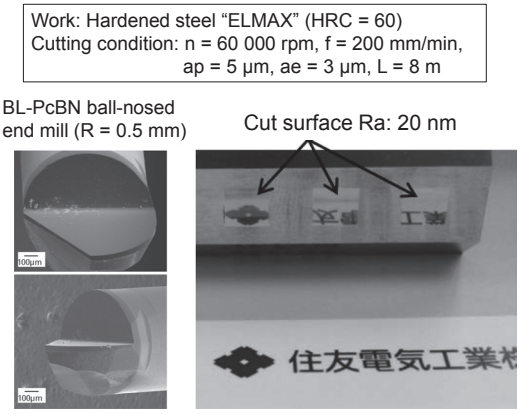


Fig. 10. Example of Cutting High Strength Steel with BL-PcBN Ball-nosed End Mill

6. Conclusion

We have succeeded in the development of binderless nano-polycrystalline diamond and nano-polycrystalline cBN, which are innovatively hard materials and superior in toughness and thermal stability. These nano-polycrystalline materials are synthesized by direct conversion sintering under ultra-high pressure and high temperature with optimized and accurately controlled starting materials and synthesis conditions.

These nano-polycrystalline bodies have a hardness surpassing that of single crystals, and are free from cleavage and anisotropy that are characteristic of single crystals. At high temperatures, their hardness and strength far surpass those of single crystals and conventional sintered compacts. Thus, the nano-polycrystalline diamond has a high potential for precision-cutting of nonferrous metals, hard ceramics, and cemented carbide, while the nano-polycrystalline cBN has a high potential for cutting ferrous materials. They are highly promising for use as the materials for next-generation high-precision and high-efficiency cutting tools and wear-resistant tools. These new hard materials are expected to contribute to the development of manufacturing industries in the world.

Technical Term

∗1 Transverse rupture strength: A measure of the strength of a material, which is determined from the maximum load applied to break the test piece in a three-point bending test.

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