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Mechanical properties of high purity polycrystalline cBN synthesized by direct conversion sintering method

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Mechanical properties of high purity polycrystalline cBN sintered bodies synthesized by the direct conversion method under high pressure and high temperature have been investigated by hardness and transverse rupture strength (TRS) measurement in the temperature range of 20–1200 °C. It was confirmed that the hardness and TRS of the polycrystalline cBN depends strongly on the cBN grain size and the amount of residual (compressed) hBN in the sintered body. The fine-grained (<0.5 μm) and high purity (cBN $>$ 99.9%) polycrystalline sintered body synthesized at 7.7 GPa, 2200–2400°C has highest hardness and TRS at any temperature. The TRS of the sintered body shows a positive temperature dependence up to 1200 °C. The high hardness and high TRS at high temperature of the fine-grained high purity polycrystalline cBN suggest that the sintered body has high potential in cutting tool uses.

1. Introduction

Cubic boron nitride (cBN) has high hardness and high thermal conductivity ranking next to diamond. With regard to chemical and thermal stability, cBN is superior to diamond. Because of those superior characteristics, cBN sintered compacts are widely used as cutting tools for cutting hardened steel, cast iron, ferrous powder metal and heat resisting alloy.

Conventional cBN sintered compacts contain binder materials of metal or ceramic composites of 10–50 vol %. The binder materials remarkably affect the mechanical and thermal properties. Therefore, the cutting performance of the cBN sintered compact depends strongly on the content and kind of binder material. A polycrystalline cBN, a single phase (binderless) sintered body of cBN, would exhibit excellent mechanical and thermal properties free from the effects of binder, and is expected to have high potential in cutting applications.

Catalytic or direct conversion sintering method started from hBN is known to be a suitable method for obtaining such polycrystalline cBN. A polycrystalline cBN sintered body synthesized by the catalytic conversion method using a small amount of Mg_3BN_3 as a catalyst [1] has been applied for heat sinks and TAB bonding tools owing to its high thermal conductivity [2–4]. However, mechanical strength and thermal stability of the polycrystalline cBN are inferior, because the sintered body contains some residual catalyst ($\sim$1 vol%) and the grain size is as large as 10 μm. Therefore, it is unsuitable for cutting tool uses. Although it is known that volatile materials [5] and HCl [6] and so on also act as effective catalysts for conversion sintering, the polycrystalline cBN obtained by these catalysts is thought to have the same problem as mentioned above.

On the other hand, a pure polycrystalline cBN sintered body can be obtained by the direct conversion sintering method in which substantially pure hBN is directly converted to polycrystalline cBN without adding any catalysts [7–9]. In the method, the pressure and temperature condition for synthesis of the polycrystalline cBN depends on the crystallite size or the degree of crystallization of the staring hBN material. Namely, the smaller grain size or lower crystallinity of starting hBN material makes the synthesis condition more mild [7, 10]. However, when such starting material is used, the polycrystalline cBN sintered body is ready to contain some impurities of boron oxide, which strongly affect the mechanical strength of the sintered body. If a high purity and well-crystallized hBN is used for the starting material, although a relatively high pressure and high temperature condition is needed for the process, a high purity polycrystalline cBN sintered body with a denser and finer structure can be obtained [9]. This high purity polycrystalline cBN is thought to exhibit excellent mechanical properties and superior thermal stability because the sintered body contains no secondary phases and consists of very small cBN grains. Therefore, the high purity polycrystalline cBN shows great promise to become a new cutting tool material with excellent cutting performance.

Hardness and transverse rupture strength (TRS) at high temperature are very important properties for a cutting tool, because they are closely related to the resistance of wearing and chipping of the cutting tool. Therefore, it is significant to investigate these properties of the polycrystalline cBN in order to determine its potential in cutting tools. However, very few reports on systematic investigations of this subject have appeared. The present paper describes the results of an investigation of these mechanical properties of the high purity polycrystalline cBN synthesized at various conditions, the objective of which was to evaluate its potential for cutting tool uses.

2. Experiment

2.1. Specimens

High purity polycrystalline cBN sintered bodies were synthesized by the direct conversion sintering method. A high purity hBN compact of 1.75 g/cm^3 in bulk density containing less than 0.03 wt % of impurity (B_2O_3) were prepared for the starting material. The hBN compact was set in Ta capsule, and converted and sintered to polycrystalline cBN under high pressure and high temperature conditions of 7.7 GPa and 1900–2700 °C for 15 min using a modified belt-type high pressure apparatus [11]. After the treatment, Ta capsule was removed by hydrofluoric acid treatment.

The X-ray diffraction patterns of the polycrystalline cBN sintered bodies are shown in Fig. 1. Strongly sintered bodies were obtained at more than 2000 °C, and single phase polycrystalline cBN sintered bodies were obtained at more than 2300 °C. The sintered bodies synthesized at 2000–2200 °C contained small amounts of compressed hBN, which is ascribed to hBN trapped under high pressure in the polycrystalline cBN matrix [12]. The amount of compressed hBN was found to increase with decreasing synthesis temperature. At lower temperatures than 2000 °C or lower pressure than 7.5 GPa, a normal hBN phase remained in the sintered bodies. The strength of the sintered bodies containing the hBN phase was moderate. In this study, the strongly sintered bodies obtained at 7.7 GPa and higher temperature than 2000 °C were subjected to investigations. The cBN grain size of the polycrystalline sintered body is related to the synthesis temperature. Fig. 2 shows the SEM images of fracture surfaces of polycrystalline cBN sintered bodies obtained at various temperatures under 7.7 GPa. The grain size of polycrystalline cBN sintered bodies obtained at lower temperatures than 2300 °C was as small as less than 0.5 μm, however, the cBN grains became larger rapidly above 2400 °C, growing to above 5 μm at 2700 °C. In Fig. 3, the amount of the compressed hBN and the cBN grain size are plotted against the synthesis temperature. Here, the amount of compressed hBN was estimated from the ratio of the X-ray reflection intensity of the compressed hBN (002) peak ($d = 0.31$ nm) to that of cBN (111) peak.

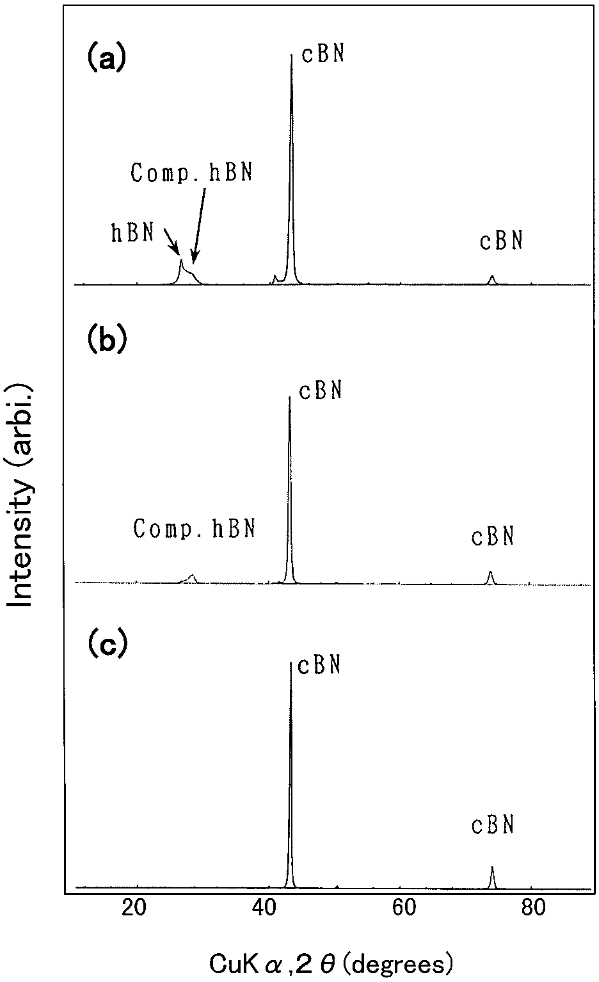

Figure 1 X-ray diffraction patterns of polycrystalline cBN sintered bodies obtained by the direct conversion sintering method at 7.7 GPa and various temperatures; (a) 1910°C, (b) 2060°C and (c) 2220°C.

Two typical kinds of conventional commercial cBN sintered compacts containing binder phases were used for comparison. One is a high cBN content (cBN: 85–90 vol%) type compact in which cBN grains are bonded together (type A), and the other is a low cBN content (50–55 vol%) type in which cBN grains are dispersed in the ceramic binder matrix (type B).

Furthermore, conventional commercialized polycrystalline cBN containing no binder material synthesized by the catalytic conversion sintering method using Mg_3BN_3 as the catalyst (type C) was also used for comparison. The polycrystalline cBN consists of 3–10 μm cBN grains, which contains 1.0 vol% of Mg_3BN_3 in the grain boundaries. The details of the process and characteristics of the material are described in our previous papers [3, 4].

2.2. Investigation of mechanical properties

The specimens were subjected to investigations of hardness and TRS in the temperature range of 20–1200°C. The hardness was measured by the indentation method using the Knoop or Vickers indenter. The indentations were made on a polished surface of the specimens with a normal load of 500 g applied for 15 s. Hardness measurements at high temperatures were carried out in a vacuum under 10^{-3} torr using a high temperature hardness tester with the Vickers indenter. For measuring the TRS, test pieces with the dimensions of 6 × 3 × 0.7 mm were prepared from specimens. The side surfaces of the test pieces were fine finished by grinding with a diamond wheel, and the side edges were neatly chamfered by 0.1 mm. TRS measurements were carried out by a three-point bending method with the span length of 4 mm (SiC supporter) using an Instron-type high

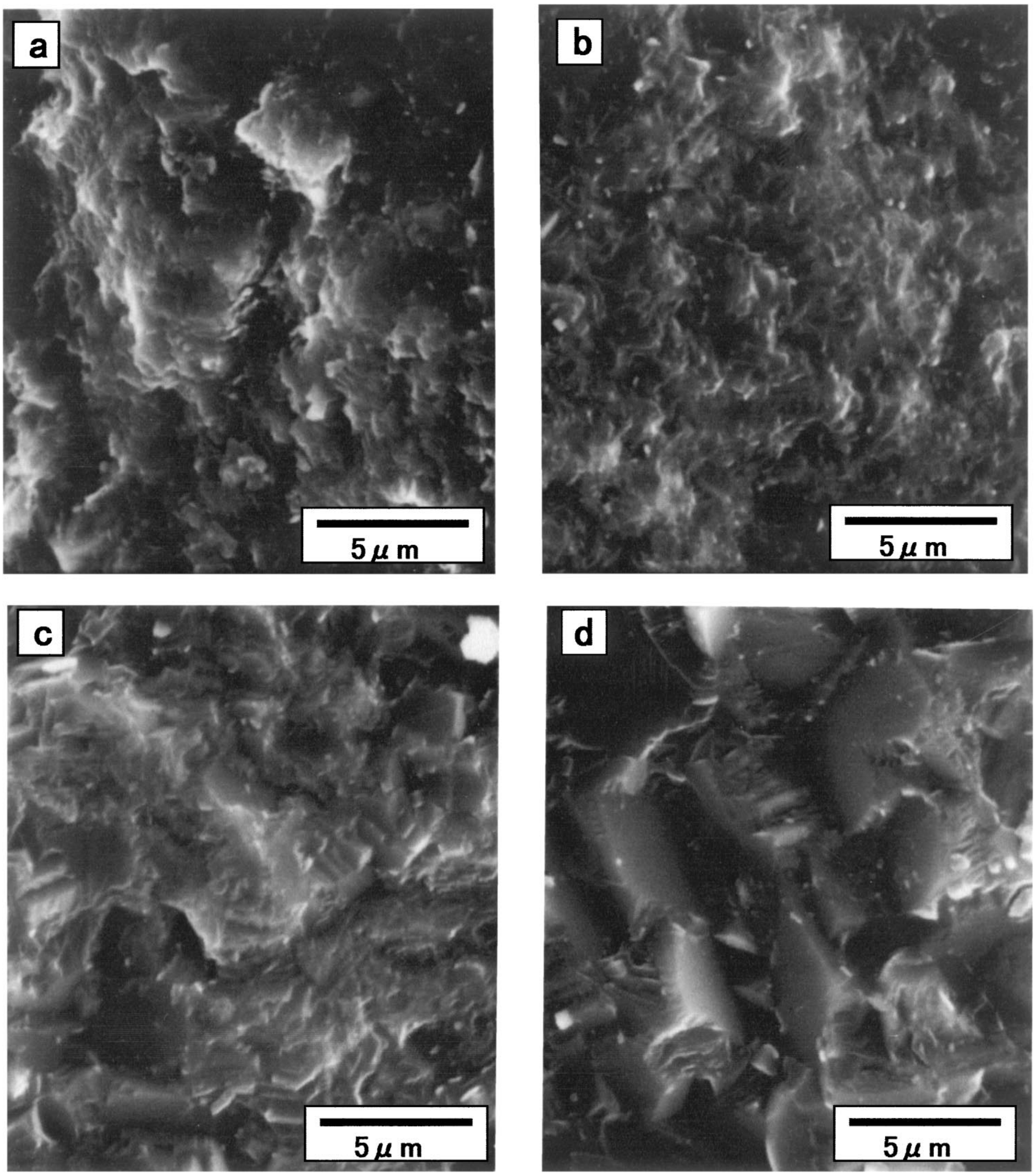

Figure 2 SEM images of fracture surfaces of polycrystalline cBN sintered bodies by the direct conversion sintering method at 7.7 GPa and various temperatures; (a) 2060°C, (b) 2420°C, (c) 2500°C and (d) 2680°C.

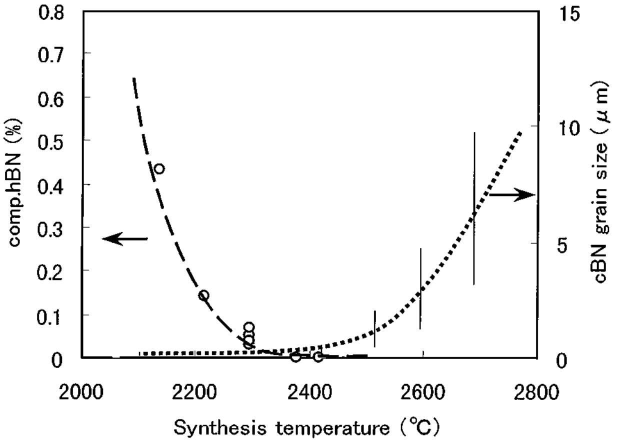

Figure 3 Amount of compressed hBN and cBN grain size of polycrystalline cBN sintered bodies with synthesis temperature. Here, the amount of compressed hBN was estimated from the ratio of the X-ray reflection intensity of the compressed hBN (002) peak to that of cBN (111) peak.

temperature material testing machine. High temperature TRS was measured in a flow of nitrogen gas. The hardness and TRS values were obtained from the average of at least three measurements.

3. Results and discussion

3.1. Hardness

Fig. 4 shows the hardness at room temperature of polycrystalline cBN sintered bodies synthesized at various temperatures plotted against the amount of the compressed hBN. The hardness increases with decreasing the amount of compressed hBN. A high purity polycrystalline cBN sintered body containing compressed hBN less than 0.5% (synthesized at temperatures above 2100°C) has high hardness of about 5000–5500 kg/mm^2. This hardness value is almost equal to that of a polycrystalline sintered body synthesized by

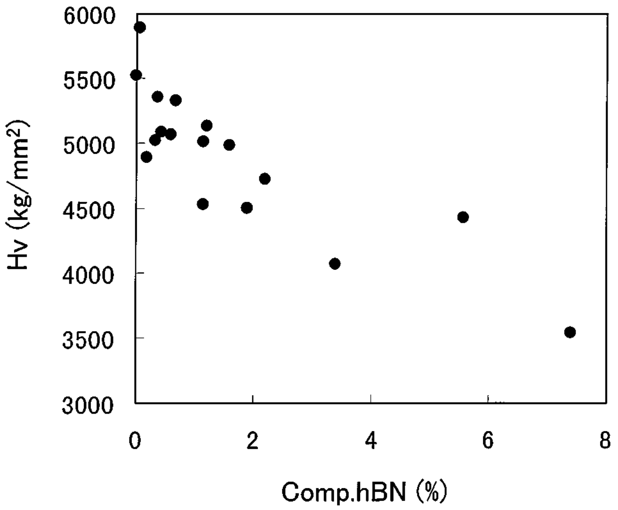

Figure 4 Hardness at room temperature of polycrystalline cBN sintered bodies synthesized at various temperatures.

catalytic conversion sintering with Mg_3BN_3 catalyst (type C), and considerably higher than those of conventional cBN compacts containing binder phases (3000–4000 kg/mm^2). A definite dependence of the cBN grain size or synthesis temperature on the hardness was not observed in the high purity sintered bodies synthesized above 2200 °C. An excess of compressed hBN is thought to deteriorate the bonding strength of cBN grains and lower the hardness of sintered body, but a small amount of compressed hBN ($<0.5\%$) does not affect the hardness at room temperature.

Fig. 5 shows the temperature dependence of hardness of two typical kinds of high purity polycrystalline cBN: a fine-grained (H-1, <0.5 μm) and a coarse-grained (H-2, 2–5 μm) sintered bodies obtained at 2300 °C and at 2600 °C respectively. The high temperature hardness of conventional type A and type B compacts containing binder phases are also plotted in the figure for comparison. The hardness of both of the high purity polycrystalline cBN decreases with increasing temperature, however, the decreasing rate depends on the cBN grain size. The hardness of the coarse-grained sintered body (H-2) decreases more rapidly with increasing temperature than that of the fine-grained one (H-1). A similar temperature dependence of polycrystalline cBN hardness on the grain size was reported by Novikov *et al.* [13]. In the high temperature range above 500 °C, the hardness of the coarse-grained sintered body become lower than those of conventional sintered compacts.

When indentations are made on the high purity polycrystalline cBN, plastic deformation due to the slip system may occur in the cBN crystal grains. The active slip systems of cBN crystal are considered to be $\{111\}\langle 110\rangle$ [14]. The slip deformation of crystal is ready to occur under high temperature. That brings the deterioration of hardness of the polycrystalline cBN at high temperature. On the other hand, the development of the slip deformation ceases at the grain boundaries. Therefore, the fine-grained polycrystalline cBN, which has a high degree of grain boundaries, has less deformation at high temperature than the coarse-grain polycrystalline cBN. This explains the higher hardness of the fine-grained sintered body compared to that of the coarse-grain one.

Conventional cBN compacts of type B, has low hardness (~3000 kg/mm^2) at RT, but the decreasing rate of the hardness at high temperature is less than that of high purity polycrystalline cBN. The temperature dependence of hardness of the type B compact is ascribed to the mechanical behavior of the binder phase rather than that of cBN, because cBN particles disperses in the binder matrix.

Micro cracks were produced above 1000 °C in the type A and B compacts. In the case of the polycrystalline cBN obtained by catalytic conversion sintering (type C), many cracks were recognized above 600–700 °C. Secondary constituents or impurities are thought to cause the deterioration of the sintered bodies at high temperature. In contrast with this, no cracks were observed in high purity polycrystalline cBN even at 1350 °C, demonstrating the sintered body's high heat resistance.

3.2. Transverse rupture strength (TRS)

We measured TRS of high purity polycrystalline cBN sintered bodies synthesized at various temperatures at 7.7 GPa. Fig. 6 shows the variation of TRS at 20 °C

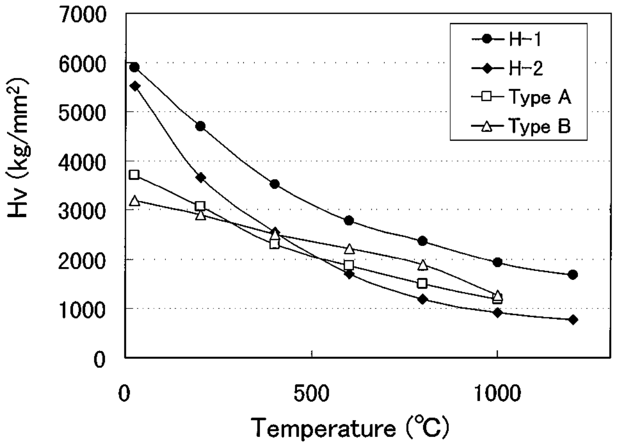

Figure 5 Temperature dependence of hardness of high purity polycrystalline cBN sintered bodies (H-1: fine-grained, H-2: coarse-grained) and conventional type A and type B sintered compacts.

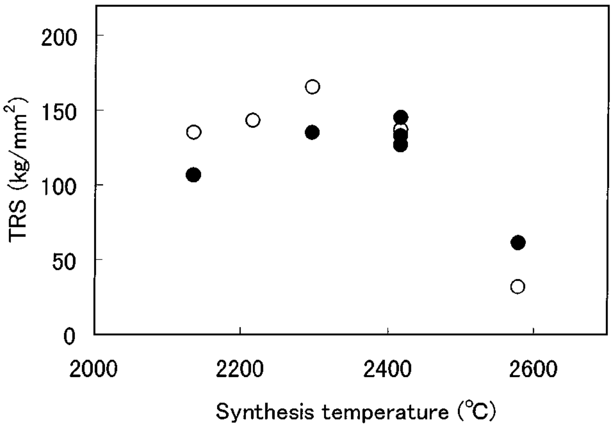

Figure 6 Variation of TRS of polycrystalline cBN sintered bodies at room temperature (●) and 1000°C (○) with the synthesis temperatures.

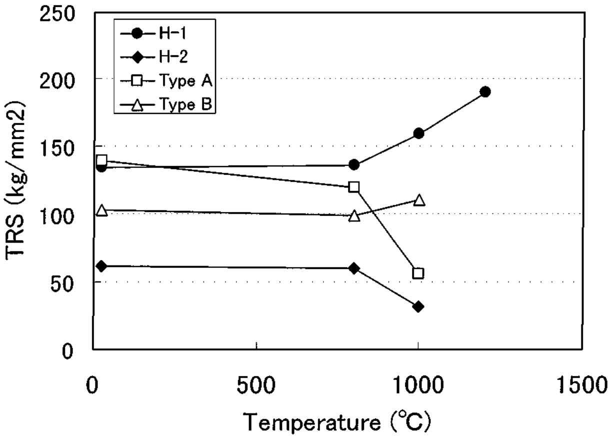

Figure 7 Temperature dependence of TRS of high purity polycrystalline cBN sintered bodies (H-1: fine-grained, H-2: coarse-grained) and conventional type A and type B sintered compacts.

(room temperature) and 1000 °C with the synthesis temperature. Each TRS at 20 °C and 1000 °C has a maximum when the synthesis temperature is about 2300°C, above which they decrease rapidly. In the case of the polycrystalline cBN synthesized at 2100–2300°C, the TRS at 1000°C is higher than that at 20°C. In contrast, the TRS at 1000°C of the polycrystalline cBN synthesized at 2600°C is low as half as that at room temperature.

As mentioned above, the grain size of the polycrystalline cBN rapidly increases with increasing the synthesis temperature above 2400°C. The coarsening of the grain is thought to lower the TRS. The type C polycrystalline sintered body which consists of large cBN grains such as 3–10 μm also had low TRS. When the synthesis temperature is as low as below 2200°C, the polycrystalline cBN contains some compressed hBN ($>$0.1%). Because of the compressed hBN, the TRS becomes lower. Therefore, the optimum synthesis temperature for obtaining a high strength polycrystalline cBN is considered to be 2200–2400°C.

In Fig. 7, the TRS of the fine-grained (H-1) and coarse-grained (H-2) high purity polycrystalline cBN, that synthesized at 2300°C and 2600°C respectively, is plotted against temperature. For comparison, the TRS of conventional types A and B compacts is also plotted in the figure. TRS of all samples does not change with the temperature up to 800°C, above which that of the fine-grained polycrystalline cBN increases with increasing temperature. In contrast, the TRS of the coarse-grained one decreases as temperature rises. The TRS of the type A compact also decreases rapidly above 800°C. TRS at 1000°C of the coarse-grain polycrystalline cBN or type A compact is almost halved of that at room temperature. The TRS of the type B compact increases gradually as temperature increases. The fine-grained polycrystalline cBN has the highest TRS of all samples at temperatures above 800°C.

The strength increasing with an increase in temperature also has been reported for high purity polycrystalline Si_3N_4 and SiC [15]. It is explained this increasing in strength at high temperature by assuming small plastic deformations at the crack tips in the grain. Namely, micro plastic deformation occurs in the grain crystal at high temperature, and this relaxes the localized stress at a crack tip and prevents the development of the crack. Consequently, the TRS increases at high temperature. In this case, it is said that the intra-granular fracture is dominant. Fig. 8 shows the typical microstructures of the fracture surfaces of the fine-grained (H-1, Fig. 8a) and coarse-grained (H-2, Fig. 8b) polycrystalline cBN sintered bodies after TRS tests at 1000°C. From the examinations of the fracture surfaces, it is revealed that the fracture of the fine-grained polycrystalline cBN is based on intra-granular fracture, whereas inter-granular fracture is dominant for the coarse-grained one. It seems that the bonding strength of the cBN particles in coarse-grained polycrystalline cBN is inferior, and the bonding strength is weakened considerably at high temperature. In this case, the effect of relaxation of the localized stress by micro plastic deformation in the cBN grain does not arise, because most fractures occur in the grain boundaries, not in the cBN grains.

The decrease of TRS of the conventional type A compact at high temperature is ascribed to the heat stress due to the difference of the thermal expansion coefficient between the cBN and binder material. In contrast, the TRS of conventional type B compact gradually

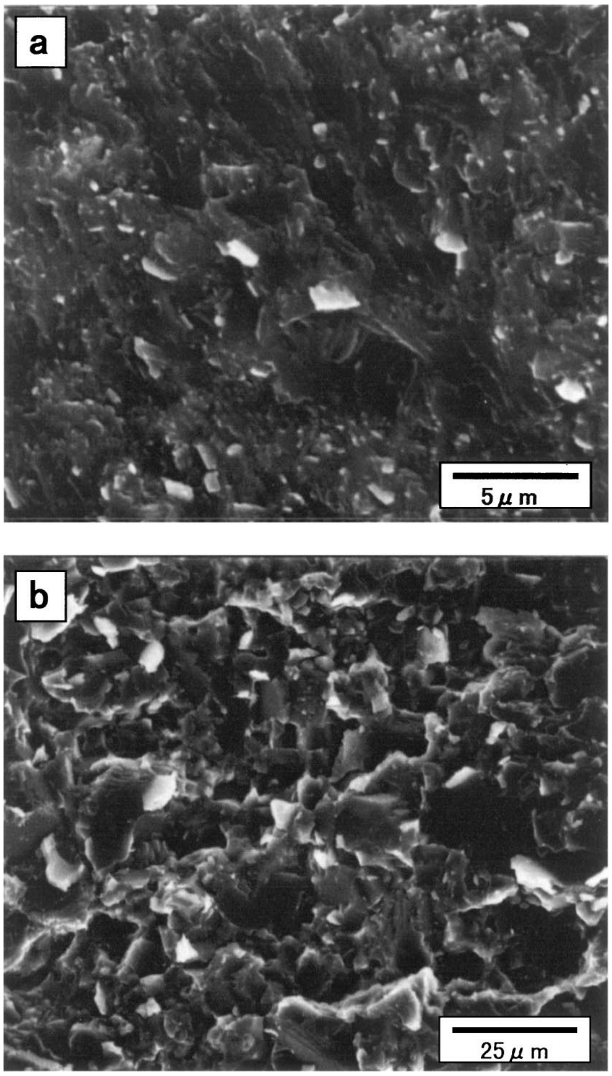

Figure 8 SEM images of fracture surfaces of polycrystalline cBN sintered bodies after high temperature TRS test at 1000°C. Synthesis temperature is (a) 2300°C and (b) 2600°C.

TABLE I Summary of mechanical properties of high purity polycrystalline cBN

		High purity polycrystalline cBN		Conventional sintered cBN		
		H-1 (fine)	H-2 (coarse)	Type A	Type B	Type C
cBN (vol%)		>99.9	>99.9	85–90	50–55	~ 99
cBN grain size (μm)		<0.5	2–5	1–3	1–3	3–10
Other constituents		– (comp.hBN)	– (comp.hBN)	Binder (Co etc)	Binder (TiN etc)	Mg_3BN_3
Process		Direct conv.	Direct conv.	cBN + binder	cBN + binder	Catalytic conv.
Hardness (kg/mm^2)	R.T.	5000–5500	5000–5500	3500–4000	3000–3500	5000–5500
	1000°C	2000	1000	1200	1200	—
TRS[a] (kg/mm^2)	R.T.	135	60	140	105	60
	1000°C	160	30	55	110	—
Thermal stability (°C in air)		1350	1350	1000	1000	700

[a] Transverse rupture strength. Span length; 4 mm.

increases with increasing temperature. The reason is thought to be that thermal softening of the binder matrix phase becomes prominent under high temperature. A similar behavior of TRS of the conventional cBN compact like type B also has been reported by Shintani *et al*. [16].

4. Conclusions

We have investigated the mechanical properties of the high purity polycrystalline sintered bodies synthesized under various conditions by the direct conversion method by measuring hardness and TRS in the temperature range of 20–1200 °C. The following conclusions were derived from the results and discussion.

(1) The hardness and TRS of the polycrystalline cBN depends strongly on the cBN grain size and the amount of residual compressed hBN in the sintered body. The fine-grained (<0.5 μm) and high purity (cBN$>$99.9%) polycrystalline sintered body synthesized at 7.7 GPa, 2200–2400°C has highest hardness and TRS at any temperature.

(2) The TRS of the fine-grained high purity polycrystalline cBN increases with increasing temperature. The reason is thought to be that micro plastic deformations relax the localized stress at a crack tip in the cBN grains at high temperature.

(3) The hardness and TRS of the coarse-grained high purity polycrystalline cBN synthesized at higher temperature ($>$2500 °C) are inferior and decrease as temperature rises. The polycrystalline cBN synthesized at low temperature ($<$2200°C) has low hardness and TRS because of the effect of the residual compressed hBN.

The typical experimental results are summarized in Table I. The mechanical properties at high temperature of the fine-grained high purity polycrystalline cBN are superior to other conventional cBN compacts. These results suggest that this material has high potential in cutting tool uses.

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