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Effects of cubic BN addition and phase transformation on hardness of Al_2O_3–cubic BN composites

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Abstract

The Vickers hardness of dense Al_2O_3–cubic BN (cBN) composites prepared by spark plasma sintering under a moderate pressure of 100 MPa at 1200–1600 °C was investigated at indentation loads of 0.098–19.6 N. The BN grains in the Al_2O_3–BN composite prepared at 1300 °C showed no transformation from the cBN to hBN phase, and the hardness was 59 GPa at 0.098 N. The hardness of the Al_2O_3 matrix in the Al_2O_3–BN composites containing 10–30 vol% cBN prepared at 1300–1400 °C was around 25 GPa at 0.098 N, which was higher than monolithic Al_2O_3 bodies prepared at the same temperatures. The hardness of the Al_2O_3 matrix in the Al_2O_3–BN composites decreased with increasing sintering temperature. The increase in the hardness of the Al_2O_3 matrix may be due to the decrease in the size of Al_2O_3 grains in the Al_2O_3–BN composites owing to the addition of cBN particles and the decrease in sintering temperature. The Meyer exponents of the monolithic Al_2O_3 bodies and Al_2O_3–BN composites were 1.90–1.94 independent of cBN content.

Keywords: A. Sintering; B. Composites; C. Hardness; D. Nitrides

1. Introduction

Cubic boron nitride (cBN) and several ceramics such as Al_2O_3, TiN and Si_3N_4 are widely used as cutting tools for high-speed machining for hard materials. cBN and Al_2O_3 have high hardness, whereas their fracture toughness is lower than that of cutting tool material of WC–Co composite. Owing to the typical toughening mechanism of crack deflection, the fracture toughness can be improved by making composite materials. Next to diamond, cBN has the highest hardness, whereas it is hardly densified by conventional sintering mainly due to its strong covalent nature and phase transformation to low-hardness hexagonal BN (h-BN). In general, cBN sintered bodies are produced at an ultra-high pressure of more than 5 GPa and a high temperature of 1000–1400 °C with various additives such as Al, Ti, TiN and TiC [1–4]. Such an extreme high-pressure condition suppresses the phase transformation from cBN to hBN at high temperature. Therefore, it is difficult to prepare fully dense cBN [5–7] and cBN-based composites [8,9] under a moderate pressure of less than 100 MPa.

We have reported the preparation of Al_2O_3–cBN [10], βSiAlON–cBN [11], TiN–cBN [12] and mullite–cBN [13] composites containing 10–20 vol% cBN at a moderate pressure of 100 MPa by spark plasma sintering (SPS). The densification of these composites was achieved without the phase transformation from cBN to hBN. The hardness is a primal issue for the application to cutting tools.

In the present study, the Vickers micro-hardness of BN grains and Al_2O_3 matrix in Al_2O_3–BN composites prepared from Al_2O_3 and cBN powders by SPS were measured at different indentation loads, and the effects of cBN addition, phase transformation and microstructure on the hardness of the Al_2O_3–BN composites were studied.

2. Experimental procedure

Al_2O_3 (TM-DAR, Taimei Chemicals Co., Ltd., Nagano, Japan, average particle size: 0.2 μm) and cBN (SBN-F, Showa Denko K.K., Tokyo, Japan, average particle size: 2.8 μm) powders were used in the present study. The mixed powder was

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sintered at temperatures ranging from 1200 to 1600 °C for 600 s in a vacuum under a uniaxial pressure of 100 MPa at a heating rate of 1.7 °C/s using an SPS apparatus (SPS-210LX, SPS Syntex Inc., Kanagawa, Japan). The detailed procedure of the SPS process has been reported elsewhere [10]. The relative densities of the Al_2O_3 bodies reached more than 99% [10]. The relative densities of the Al_2O_3–BN composites were the same value as approximately 98% in all the composites [10]. The surface of specimens was ground with a diamond wheel and then finally polished with 1-μm diamond slurry. The Vickers hardness was measured at a load between 0.098 and 19.6 N using a micro-hardness tester (HM-221, Mitutoyo Corp., Kanagawa, Japan). The load was applied for 30 s. The hardness was calculated by the following formula:

$$H_V = 1854\frac{P}{d^2}, \quad (1)$$

where P is the applied load and d is the average value of two diagonal lengths for Vickers indentation. The relationship between P and d can be expressed by the Meyer equation:

$$P = ad^n, \quad (2)$$

where a and Meyer exponent n are constant depending on the materials [14]. The relationship between H_V and P can be obtained from Eqs. (1) and (2) as follows:

$$H_V = 1854ad^{n-2}. \quad (3)$$

Hence, the hardness is independent of the indentation size at $n = 2$. The average value of 20 measurements at each specimen was used for the evaluation of the Vickers hardness. The indented surface was observed by scanning electron microscopy (SEM; S-3100H, Hitachi Ltd., Tokyo, Japan). The average size of Al_2O_3 grains in the specimens was determined from linear intercept length of 100 grains in the SEM images.

3. Results and discussion

3.1. Hardness of Al_2O_3 matrix and BN grains in the composites

Fig. 1 shows the Vickers hardness of the Al_2O_3 matrix and BN grains in the Al_2O_3–BN composites originally containing 10–30 vol% cBN and of monolithic Al_2O_3 bodies prepared at 1200–1600 °C at a load of 0.098 N. The hardness of monolithic Al_2O_3 bodies prepared at 1200–1400 °C was 19–20 GPa, and slightly decreased with increasing sintering temperature. When the sintering temperature was elevated from 1400 to 1600 °C, the hardness of the monolithic Al_2O_3 bodies significantly increased from 19 to 23 GPa. In contrast, it has been reported that the hardness of monolithic Al_2O_3 bodies at a load of 0.98 N decreased with increasing sintering temperature [10].

In the Al_2O_3–BN composite originally containing 20 vol% cBN, the hardness of BN grains reached 59 GPa without the phase transformation of cBN to hBN at 1300 °C. The cBN grains started to transform into the hBN phase at 1400 °C, and the Vickers hardness of the BN grains slightly decreased to 57 GPa. It was not possible to measure the hardness of BN grains prepared at 1500–1600 °C because of a porous microstructure resulting from the phase transformation into hBN [10].

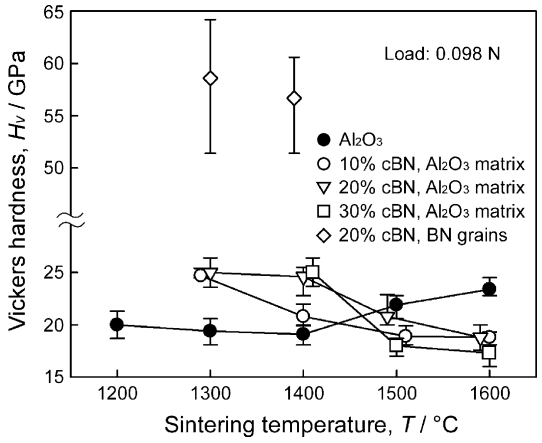

Fig. 1. Vickers hardness of Al_2O_3 matrix and BN grains in Al_2O_3–BN composites originally containing 10–30 vol% cBN and Al_2O_3 bodies sintered at 1200–1600 °C for 600 s at applied indentation load of 0.098 N.

The Al_2O_3 matrix in the Al_2O_3–BN composites containing 10–20 vol% cBN prepared at 1300 °C without the phase transformation into hBN had the highest hardness of 25 GPa. With increasing sintering temperature, the Vickers hardness of the Al_2O_3 matrix in the Al_2O_3–BN composites decreased. This was opposite to the trend of the monolithic Al_2O_3 bodies, as shown in Fig. 1.

3.2. Effect of size of Al_2O_3 grains on hardness of Al_2O_3 matrix

Fig. 2 demonstrates the effect of average size of Al_2O_3 grains in the monolithic Al_2O_3 bodies and the Al_2O_3–BN composites on Vickers hardness of the Al_2O_3 matrix at a load of 0.098 N. The hardness of the monolithic Al_2O_3 bodies decreased with increasing grain size from 0.6 to 4.5 μm obeying the Hall–Petch relationship [15,16], whereas the hardness significantly

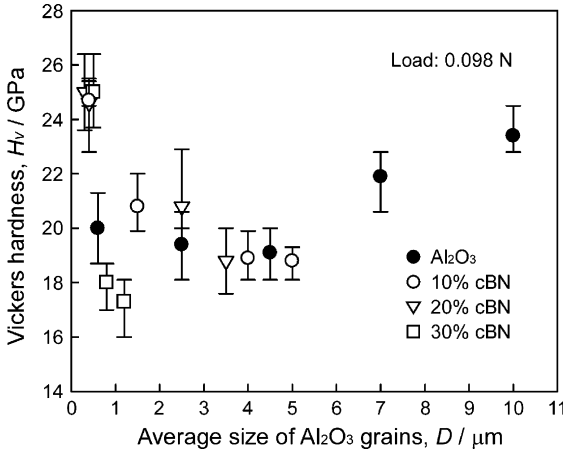

Fig. 2. Effect of average size of Al_2O_3 grains in the monolithic Al_2O_3 bodies and the Al_2O_3–BN composites on Vickers hardness of the Al_2O_3 matrix at a load of 0.098 N.

increased with an increase in grain size ranging from 4.5 to 10 μm. The Vickers hardness of ceramics such as Al_2O_3 and MgO first decreased with increasing grain size, then increased toward that of single-crystals as the grain size increased to more than the indentation size [17]. The indentation size measured at a load of 0.098 N in the monolithic Al_2O_3 bodies and the Al_2O_3 matrix in the Al_2O_3–BN composites was around 3 μm. Consequently, the calculated hardness value of the monolithic Al_2O_3 bodies with the grain size of 4.5–10 μm prepared at 1400–1600 °C might indicate the hardness of one crystal grain (i.e., Al_2O_3 single-crystal), resulting in the increase of the hardness with further increase of the grain size.

The hardness of the Al_2O_3 matrix in the Al_2O_3–BN composites decreased with increasing size of the Al_2O_3 grains. When sintering temperature increased, the size of Al_2O_3 grains in the Al_2O_3 bodies and the Al_2O_3–BN composites increased [10]. Hence, the reduction of the hardness of Al_2O_3 matrix in the Al_2O_3–BN composites with increasing sintering temperature in Fig. 1 would be caused by the increase of the size of the Al_2O_3 grains. The addition of cBN to Al_2O_3 led to the decrease of the size of Al_2O_3 grains in the Al_2O_3–BN composites [10]. Thus, the increase in the hardness of Al_2O_3 matrix in the Al_2O_3–BN composites by the addition of cBN in Fig. 1 would be attributed to the decrease in the size of the Al_2O_3 grains.

The Vickers hardness of ceramics might have been affected by many parameters, such as grain size, residual porosity, indentation load and bonding strength among grains [17]. Whereas all the specimens had high density of over 98%, the density of the Al_2O_3–BN composites was slightly lower than that of the monolithic Al_2O_3 bodies. The decrease of the density would be attributed to the existence of residual pores at the interface between BN and Al_2O_3 matrix due to the addition of low-sinterable cBN to Al_2O_3. Consequently, the Al_2O_3 matrix in the Al_2O_3–BN composites might be fully dense, although the Al_2O_3–BN composites had slightly lower density compared with the monolithic Al_2O_3 bodies.

3.3. Vickers indents in Al_2O_3 body and Al_2O_3–BN composite

Fig. 3 shows SEM micrographs of the surfaces of a monolithic Al_2O_3 body prepared at 1200 °C and a Al_2O_3–20 vol% cBN composite prepared at 1300 °C after Vickers indentation at loads of 0.98 and 9.8 N. The black phase is BN grains. The hardness value of the Al_2O_3–BN composites measured at the indentation load of 0.98 and 9.8 N was confirmed to include hardness of both Al_2O_3 matrix and BN grains. The indentation size of the Al_2O_3–BN composite was smaller than that of the monolithic Al_2O_3 body at 0.98 N, demonstrating that the hardness of the Al_2O_3–cBN composite was higher than that of the monolithic Al_2O_3 body. Therefore, the improvement of the hardness of Al_2O_3–BN composites measured at indentation load of 0.98 N by the addition of cBN particles might be due to the existence of high-hardness cBN particles in the Al_2O_3–BN composites and the increase in hardness of Al_2O_3 matrix, as shown in Figs. 1 and 2. In fact, in the Al_2O_3–BN composite originally containing 30 vol% cBN prepared at 1400 °C, the Vickers hardness of the Al_2O_3–BN composite at 0.98 N reached maximum value of 26 GPa, although the cBN phase in the composite slightly transformed to hBN [10]. This might be caused by the small size of Al_2O_3 grains of 0.5 μm in the Al_2O_3–BN composite. Although some cracks can be seen at the Al_2O_3/cBN interface in the Al_2O_3–BN composite, it was possible for bonding between the Al_2O_3 matrix and the cBN grains to remain strong even under the high indentation load of 9.8 N.

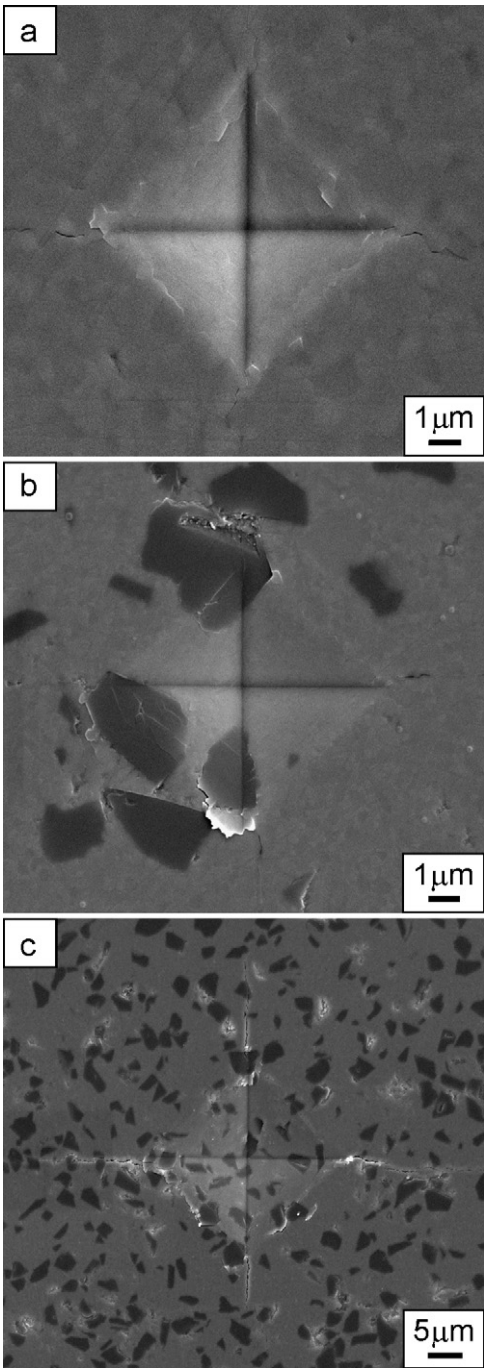

Fig. 3. SEM micrographs of indented surface of Al_2O_3 body sintered at 1200 °C at a load of 0.98 N (a), Al_2O_3–BN composite originally containing 20 vol% cBN sintered at 1300 °C at load of 0.98 N (b) and that at load of 9.8 N (c).

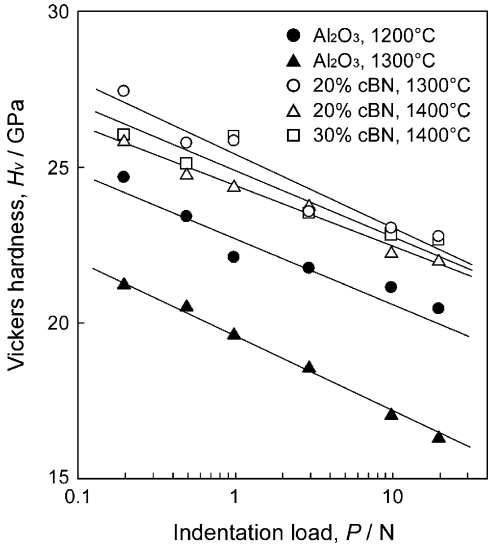

Fig. 4. Vickers hardness of Al_2O_3–BN composites originally containing 20–30 vol% cBN and Al_2O_3 bodies sintered at 1200–1400 °C as a function of applied indentation load.

3.4. Load dependence of hardness of Al_2O_3 bodies and Al_2O_3–BN composites

Fig. 4 shows the load dependence of Vickers hardness of monolithic Al_2O_3 bodies and Al_2O_3–BN composites originally containing 20–30 vol% cBN prepared at different temperatures. The hardness of both the monolithic Al_2O_3 bodies and the Al_2O_3–BN composites increased with decreasing indentation load. The hardness generally increases with decreasing indentation load, as has been reported in Si_3N_4, SiC, cBN and Ce–ZrO_2 [18–21]. This is often termed the indentation size effect. Krell [19] has reported that a fully dense Al_2O_3 body with a grain size of 0.45 μm exhibited an increase in hardness with decreasing load and that the hardness reached its highest value of 22 GPa at 6 N. At each indentation load of 0.196–19.6 N, the hardness of the monolithic Al_2O_3 body prepared at 1200 °C was 2–4 GPa higher than that prepared at 1300 °C. The grain size of Al_2O_3 bodies prepared at 1200 °C and 1300 °C was less than 1 μm and about 3 μm, respectively [10]. On the contrary, Krell and Blank [16] have reported that the hardness of the fully dense Al_2O_3 body at load of 100 N decreased with increasing grain size. The hardness of Al_2O_3–BN composites originally containing 20–30 vol% cBN prepared at 1300–1400 °C was higher than that of monolithic Al_2O_3 bodies at each indentation load.

Table 1 summarizes the Meyer exponents determined by the results shown in Fig. 4 in comparison with literature data [22]. The Meyer exponents of the monolithic Al_2O_3 bodies and Al_2O_3–cBN composites were 1.90–1.94, close to those of common oxide ceramics such as ZrO_2 and mullite, but greater than those of SiC and Si_3N_4. This implies that SiC and Si_3N_4 show more significant load dependence of hardness. Although the physical meaning of the Meyer exponent is not fully understood, it may be related to several deformation characteristics such as partial elastic deformation and viscous flow of materials. It can be assumed that a different Meyer exponent means a different deformation mechanism. The deformation mechanism during the Vickers hardness measurement may be independent of cBN content in the Al_2O_3–BN composites, whereas it can be slightly different from that of more covalent bonding ceramics such as SiC and Si_3N_4.

Table 1
Values of the Meyer exponent of Al_2O_3–BN composites originally containing 20–30 vol% cBN and of Al_2O_3 bodies sintered at 1200–1400 °C.

Specimens	Sintering temperature, T (°C)	Meyer exponent, n
Al_2O_3	1200	1.92
Al_2O_3	1300	1.90
Al_2O_3–20 vol% cBN	1300	1.93
Al_2O_3–20 vol% cBN	1400	1.93
Al_2O_3–30 vol% cBN	1400	1.94
Al_2O_3[a]	–	1.89
ZrO_2[a]	–	1.91
Mullite[a]	–	1.98
SiC[a]	–	1.79
Si_3N_4[a]	–	1.84

[a] Data of Gong et al. [22].

4. Conclusions

The Vickers hardness of dense Al_2O_3–cBN composites prepared by SPS at a moderate pressure of 100 MPa was characterized at indentation loads from 0.098 to 19.6 N. The hardness of BN grains in the Al_2O_3–BN composite prepared at 1300 °C without the phase transformation of cBN to hBN was 59 GPa at load of 0.098 N. The hardness of the BN grains decreased to 57 GPa at 1400 °C due to a slight phase transformation from cBN to hBN. The hardness of the Al_2O_3 matrix in the Al_2O_3–BN composites increased with decreasing sintering temperature. The hardness of the Al_2O_3 matrix in Al_2O_3–BN composites originally containing 10–30 vol% cBN prepared at 1300–1400 °C increased by about 5 GPa compared with that of monolithic Al_2O_3 bodies prepared at the same temperature. The improvement of the hardness of the Al_2O_3 matrix in the Al_2O_3–BN composites may be attributed to the decrease in the size of Al_2O_3 grains due to the decrease in sintering temperature and due to the addition of cBN particles. The hardness of both the monolithic Al_2O_3 bodies and the Al_2O_3–BN composites increased with a decrease in indentation load. The Meyer exponents were 1.90–1.94, independent of cBN content.

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