Densification and microstructure of Al_2O_3 -cBN composites prepared by spark plasma sintering

Mikinori HOTTA and Takashi GOTO

Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577

Al_2O_3 -cubic boron nitride (cBN) composites were prepared from Al_2O_3 and cBN powders by spark plasma sintering (SPS) at temperatures of 1200 to 1600°C for 600 s under a pressure of 100 MPa. Densification, phase transformation, microstructure and mechanical properties of the Al_2O_3 -cBN composites were investigated. Fully dense Al_2O_3 -cBN composites containing 10 to 20 vol% cBN with a relative density of more than 98% were obtained at 1300°C for 600 s without the phase transformation from cBN to hexagonal BN (hBN). The transformation of cBN was more greatly accelerated in the Al_2O_3 -cBN composite than in cBN. The cBN phase to Al_2O_3 inhibited the grain growth of Al_2O_3 in the Al_2O_3 -cBN composite. Vickers hardness of dense Al_2O_3 -cBN composites containing 10 to 20 vol% cBN sintered at 1300°C showed the maximum value of 26 GPa. The Al_2O_3 -cBN composite containing 20 vol% cBN sintered at 1300°C had the highest fracture toughness of 4.1 $\text{MPa}\cdot\text{m}^{1/2}$.

©2008 The Ceramic Society of Japan. All rights reserved.

Key-words : Cubic boron nitride, Alumina, Composite, Cutting tools, Spark plasma sintering, Densification, Microstructure

[Received March 10, 2008; Accepted April 17, 2008]

1. Introduction

Cutting tools should be able to endure harsh conditions such as high temperature, severe friction and chemical reaction with work materials during the machining process.¹⁾ Therefore, high hardness, fracture toughness and excellent thermal stability are required for these tools. A wide variety of materials for cutting tools, including high-speed steels, hard metals, cermets, ceramics, cubic boron nitride (cBN) and diamond are available for machining. Ceramics tools, in particular, such as Al_2O_3 , TiN and Si_3N_4 , are widely adopted because of their excellent high-temperature stability under high-speed rotating conditions. Al_2O_3 could be suitable for machining cast iron because of high hardness, less reactivity with iron and its abundance as a raw material.

Next to diamond, cBN has the highest hardness and thermal conductivity and is more thermally stable and less reactive with iron than diamond. These characteristics enable the application of cBN to cutting tools for hardened steel and cast iron.²⁾ However, it is difficult to obtain high-density cBN materials because of the strong covalent bonding and low self-diffusion coefficients of B and N. In addition, cBN transforms to hexagonal BN (hBN) with low-hardness at high temperature.³⁻⁵⁾ Therefore, fully dense cBN bodies for cutting tools have been commonly fabricated by sintering under an ultra-high pressure of more than 5 GPa and with various kinds of additives such as Al and Ti.⁶⁻⁹⁾ However, as the ultra-high pressure process is costly, an economic process using a moderate pressure less than 100 MPa should be useful for a wide range of applications of cBN-based cutting tools.^{10,11)} cBN and common ceramics possess high hardness, whereas their fracture toughness is lower than that of cermets, hard metals and high-speed steels. Composites of ceramics and cBN would thus be promising cutting tools having excellent mechanical properties of high hardness and toughness.

Spark plasma sintering (SPS) is possible for heating specimens rapidly using pulsed direct current.¹²⁾ The current would pass through a die and punch rods made of graphite. Hence, the

grain growth could be suppressed, and a low-sinterability material such as cBN could be densified easily at moderate temperatures. Hardly sinterable oxides, nitrides and carbides have been produced in a fully dense form by SPS.¹³⁻¹⁷⁾ Moreover, the phase transformation of cBN to hBN might be inhibited due to the short sintering time of the SPS process.

In this work, Al_2O_3 -cBN composites were prepared from Al_2O_3 and cBN powders using SPS under a pressure of 100 MPa, and effects of sintering temperature and cBN content on the densification, phase transformation, microstructure and mechanical properties were investigated.

2. Experimental procedure

Al_2O_3 (TM-DAR, Taimei Chemicals Co., Ltd., an average particle size of 0.2 μm) and cBN (SBN-F, Showa Denko K. K., an average particle size of 2.8 μm) powders were used as starting materials. cBN powder was mixed with Al_2O_3 in compositions of 0 to 50 vol% cBN. The powders were ball-milled in a plastic pot with balls and a small amount of ethanol for 48 h. The slurry was dried and passed through a sieve with an opening size of 150 μm . The mixed powder was filled in a graphite die 10 mm in inner diameter and 3 mm in thickness, and then the mixture was sintered using an SPS apparatus (SPS-210LX, SPS SYNTEX INC.) under a uniaxial pressure of 100 MPa in vacuum. Pulsed direct current (pulses of 60 ms on/10 ms off) was applied during the sintering process. The specimens were heated to a sintering temperature of 1200 to 1600°C at a rate of 1.7°C/s. After being held for 600 s at a specific sintering temperature, the specimens were cooled at a rate of about 1.5°C/s. The temperature of the surface of the die was measured by an optical pyrometer. Linear shrinkage of the specimens during the SPS process was continuously monitored. Phase transformation of cBN to hBN was analyzed by X-ray diffractometry (XRD; Geigerflex, Rigaku Corp.) with $\text{CuK}\alpha$ radiation. Bulk densities were determined by an Archimedes' method, and converted to relative densities using theoretical densities of Al_2O_3 (3.99 g/cm^3)¹⁸⁾ and cBN (3.49 g/cm^3).¹⁹⁾ The fractured and polished surfaces of the spec-

imens were observed by scanning electron microscopy (SEM; S-3100H, HITACHI Ltd.). Vickers hardness (H_V) and fracture toughness (K_{IC}) at room temperature were evaluated by a hardness tester (HM-221, Mitutoyo Corp.) at loads (P) from 0.98 and 9.8 N. The fracture toughness was calculated by eq. (1) using the half length of the crack (c) formed around the corners of indentations²⁰⁾:

$$K_{IC} = 0.073 \times (P/c^{1.5}) \quad (1)$$

3. Results and discussion

The shrinkage of specimens due to densification during the SPS process was monitored by the displacement of the punch rods. **Figure 1** shows the shrinkage of Al_2O_3 -cBN composites containing 0 to 50 vol% cBN at 800 to 1400°C. The isothermal shrinkage at 1400°C up to 600 s is shown in Fig. 1. The shrinkage of Al_2O_3 started at 900°C and finished at 1250°C. The starting temperature of shrinkage for Al_2O_3 -cBN composites containing 10 to 50 vol% cBN was higher than that of the Al_2O_3 body and became higher with increasing cBN content. There was no further shrinkage of the Al_2O_3 -cBN composites at 1350 to 1400°C. The temperature increased with increasing cBN content.

Figure 2 shows the XRD patterns of Al_2O_3 -cBN composites containing 20 vol% cBN sintered at 1300 to 1600°C for 600 s. No transformation of cBN to hBN was detected at 1300°C, and the transformation started at 1400°C. The hBN peak became clearly higher with increasing sintering temperature. No change of cBN peak was evident because the strongest peak of (111) cBN was overlapped by that of (113) Al_2O_3 . Phase transformation of cBN was observed at 1650°C in the cBN body. The cBN phase in the Al_2O_3 -cBN composites transformed to hBN at a lower temperature than that in the cBN body. No chemical reaction between Al_2O_3 and cBN occurred at 1300 to 1600°C. We as well as other researchers have reported that TiN and TiC significantly reached with cBN to form TiB_2 ,^{21),22)} AlN, AlB_2 and $\alpha\text{-AlB}_{12}$ were also formed in Al-cBN composites at 1200 to 1400°C.⁶⁾⁻⁸⁾ Since the reacted products at the interface are commonly brittle and porous, the cBN phase would be easily deleted from the matrix. Therefore, the non-reactivity of Al_2O_3 with cBN is advantageous for fabrication of fully dense and strongly bonded cBN-based composites.

Fig. 1. Effect of sintering temperature on the displacement of Al_2O_3 -cBN composites containing 0 to 50 vol% cBN at 800 to 1400°C, and the time dependence of isothermal displacement at 1400°C up to 600 s.

Fig. 2. Change in XRD pattern of Al_2O_3 -cBN composite containing 20 vol% cBN sintered at 1300°C (a), 1400°C (b), 1500°C (c) and 1600°C (d) for 600 s.

Figure 3 demonstrates the effect of cBN content on the relative density of Al_2O_3 -cBN composites sintered at 1200 to 1400°C for 600 s. The relative density at 1400°C was calculated by assuming two phases of Al_2O_3 and cBN in the composite, although a small amount of hBN was found at 1400°C as shown in Fig. 2. At 1200°C, the relative density of the Al_2O_3 body was more than 99%. The 10 vol% cBN of the Al_2O_3 -cBN composite had a density of about 85%. Although at 1300 to 1400°C, the density of Al_2O_3 -cBN composites containing 10 to 20 vol% cBN were slightly lower than that of Al_2O_3 , the density of the Al_2O_3 -cBN composites reached a level of over 98%. The density sharply decreased at 1300 and 1400°C at the cBN content of 30 and 40 vol%, respectively, and then further reduced from 80 to 85% at 50 vol% cBN. Martinez and Echeberria¹¹⁾ investigated the sintering behavior of WC-Co-cBN composites containing up to 50 vol% cBN and found the densification of WC-Co to be significantly retarded by the addition of cBN.

Figure 4 shows SEM micrographs of the polished surface of

Fig. 3. Effect of cBN content on the relative density of Al_2O_3 -cBN composites sintered at 1200 to 1400°C for 600 s.

Fig. 4. SEM images of the polished surface of Al₂O₃-cBN composite containing 20 vol% cBN sintered at 1300°C (a), 1400°C (b), 1500°C (c) and 1600°C (d) for 600 s.

Al₂O₃-cBN composites containing 20 vol% cBN sintered at 1300 to 1600°C for 600 s. The black phase is BN grains, which were uniformly dispersed in the Al₂O₃ matrix. The angular edges of cBN particles remained as shown in Fig. 4 (a), implying the absence of a chemical reaction of cBN with the Al₂O₃ matrix. At 1400°C, as illustrated in Fig. 4 (b), the cracks and pores at the interface between Al₂O₃ and cBN grains were observed. The crack formation and the porous microstructure of the BN grains at 1500 to 1600°C, as shown in Figs. 4 (c) and (d), could be caused by the difference of thermal expansion coefficient between Al₂O₃ and hBN particles and the degradation of hardness by the transformation of cBN to hBN.

Figure 5 demonstrates SEM micrographs of the fractured surface of Al₂O₃-cBN composites containing 20 vol% cBN sintered at 1200 to 1600°C for 600 s. At 1200°C, non-sintered Al₂O₃ particles less than 0.2 μm remained, and the Al₂O₃ particles hardly bonded with BN. At 1300 to 1400°C, Al₂O₃ grains with a size of 0.2 to 0.5 μm, which bonded with BN grains, were observed. At 1500 and 1600°C, Al₂O₃ grains significantly grew and BN grains changed to a flake morphology similar to graphite, as indicated by the arrows in Figs. 5 (d) and (e). Hence, the phase transformation of cBN to hBN in the Al₂O₃-cBN composites could proceed at 1400 to 1500°C as shown in Figs. 4 and 5.

Figure 6 shows SEM micrographs of the fractured surface of an Al₂O₃ body sintered at 1200 to 1600°C for 600 s. The grain size of the dense Al₂O₃ sintered at 1200°C was less than 1 μm (Fig. 6 (a)). Al₂O₃ grains grew with increasing sintering temperature and the grain size at 1600°C reached 5 to 15 μm.

Figure 7 shows SEM micrographs of the fractured surface of Al₂O₃-cBN composites containing 0 to 30 vol% cBN sintered at 1300°C for 600 s. The size of the Al₂O₃ grains in the Al₂O₃ body was 1 to 2 μm. The size of the Al₂O₃ grains in the Al₂O₃-cBN composites containing 10 to 20 vol% cBN, on the other hand, was less than 0.5 μm. The growth of Al₂O₃ grains in the Al₂O₃-cBN composites was suppressed by the effect of cBN. At a cBN content of 30 vol%, the sintering of Al₂O₃ particles hardly proceeded.

Figure 8 illustrates the effect of sintering temperature on the Vickers hardness of Al₂O₃-cBN composites containing 0 to 30

Fig. 5. SEM images of the fractured surface of Al₂O₃-cBN composite containing 20 vol% cBN sintered at 1200°C (a), 1300°C (b), 1400°C (c), 1500°C (d) and 1600°C (e) for 600 s.

vol% cBN sintered for 600 s. The hardness of fully dense Al₂O₃-cBN composites containing 10 to 20 vol% cBN sintered at 1300°C without the transformation of cBN to hBN reached 26 GPa, higher than that of the fully dense Al₂O₃ body. The hardness of the Al₂O₃ body decreased from 22 to 20 GPa with increasing sintering temperature from 1200 to 1600°C. The grain growth of Al₂O₃, as shown in Fig. 6, may have caused the decrease of hardness. Shen et al.¹⁶⁾ have reported that the Vickers hardness of the Al₂O₃ body by SPS decreased from 21 to 16 GPa with increasing grain size from 2 to 18 μm. Therefore, the increase in the hardness of the Al₂O₃-cBN composites was the main cause of the uniformly dispersed cBN particles in the Al₂O₃ matrix. The decrease in the size of Al₂O₃ grain in the matrix, as illustrated in Fig. 4 (a) and Fig. 5 (b), might slightly affect the increase in the hardness. In the Al₂O₃-cBN composite containing 30 vol% cBN sintered at 1400°C, the hardness had a high value of 26 GPa. This could be mainly due to a high density of more than 98% in the composite and small Al₂O₃ grains, in spite of the slight transformation from cBN to hBN. In WC-Co-cBN composites, a high hardness of 25 GPa has been reported.¹¹⁾ In the case of cBN-TiN-Al composites, the hardness increased to 30 GPa by the addition of 75 vol% cBN.⁶⁾ These cBN-based composites were produced under pressures of 150 to 200 MPa by hot isostatic pressing and an ultra-high pressure of about 6 GPa. We achieved the high hardness of 22 to 26 GPa under a moderate pressure of 100 MPa in the fully dense Al₂O₃-cBN composite.

Figure 9 shows the effect of sintering temperature on the fracture toughness of Al₂O₃-cBN composites containing 0 to 30

Fig. 6. SEM images of the fractured surface of Al_2O_3 bodies sintered at 1200°C (a), 1400°C (b) and 1600°C (c) for 600 s.

Fig. 7. SEM images of the fractured surface of an Al_2O_3 body (a), Al_2O_3 -cBN composites containing 10 vol% (b), 20 vol% (c) and 30 vol% (d) cBN sintered at 1300°C for 600 s.

Fig. 8. Effect of sintering temperature on the Vickers hardness of Al_2O_3 -cBN composites containing 0 to 30 vol% cBN sintered for 600 s.

vol% cBN sintered for 600 s. The fracture toughness of the composites was improved by the addition of cBN. The toughness of the sintered Al_2O_3 body was 2.1 to 2.7 $\text{MPa}\cdot\text{m}^{1/2}$, almost independent of sintering temperature. The highest fracture toughness was 4.1 $\text{MPa}\cdot\text{m}^{1/2}$ for the Al_2O_3 -cBN composite containing 20 vol% cBN sintered at 1300°C for 600 s. Crack deflection was

Fig. 9. Effect of sintering temperature on the fracture toughness of Al_2O_3 -cBN composites containing 0 to 30 vol% cBN sintered for 600 s.

observed around the cBN grains. This could possibly have resulted in the increase in fracture toughness. On the other hand, it was observed that cracks propagated straight through BN grains transformed from cBN to hBN. This might have caused the decrease of the fracture toughness. The addition of cBN to WC-Co increased the toughness from 7.3 to 15.4 $\text{MPa}\cdot\text{m}^{1/2}$.¹¹⁾ Since W is a rare element, intensive study on the substitution of W in cutting tools has been conducted. Although the mechanical properties of Al_2O_3 -cBN composite are still lower than those of the WC-Co-cBN composite, Al_2O_3 -cBN may be a good candidate for cutting tools with further optimization of the microstructure and sintering conditions in SPS.

4. Conclusions

Al_2O_3 -cBN composites were prepared by SPS at sintering temperatures of 1200 to 1600°C for 600 s under a pressure of 100 MPa using Al_2O_3 and cBN powders. The phase transformation of cBN to hBN in the Al_2O_3 -cBN composites was more greatly accelerated than that in the cBN body. Dense Al_2O_3 -cBN composites with a relative density of more than 98% without transformation of cBN to hBN phase were obtained at a cBN content of 10 to 20 vol% at 1300°C. The grain growth of Al_2O_3 was inhibited by the addition of cBN. The Vickers hardness of fully dense Al_2O_3 -cBN composites containing 10 to 20 vol% cBN sintered at 1300°C reached 26 GPa. The fracture toughness of the Al_2O_3 -cBN composite containing 20 vol% cBN sintered at 1300°C was 4.1 $\text{MPa}\cdot\text{m}^{1/2}$.

Acknowledgments This work was supported by a Grant-in-

Aid for Young Scientists (Start-up) (No.18860009), Asian CORE Program and Global COE Program from the Japan Society for the Promotion of Science and Rare Metal Substitution Materials Development Project from New Energy and Industrial Technology Development Organization. We also appreciate the financial support by Mitsubishi Materials Corporation.

References

- 1) P. A. Dearnley, *Transactions of the ASME. Series H, J. Eng. Mater. Technol.*, **107**, 68–82 (1985).
- 2) R. H. Wentorf, R. C. DeVries and F. P. Bundy, *Science*, **208**, 873–880 (1980).
- 3) F. P. Bundy and R. H. Wentorf, *J. Chem. Phys.*, **38**, 1144–1149 (1963).
- 4) F. R. Corrigan and F. P. Bundy, *J. Chem. Phys.*, **63**, 3812–3820 (1975).
- 5) V. L. Solozhenko, V. Z. Turkevich and W. B. Holzapfel, *J. Phys. Chem. B*, **103**, 2903–2905 (1999).
- 6) X. Z. Rong and O. Fukunaga, *Advanced Materials '93, I / B*, Ed. by M. Homma et al., Elsevier Science B.V., *Trans. Mater. Res. Soc. Jpn.*, **14B**, 1455–1458 (1994).
- 7) X. Z. Rong and T. Yano, *J. Mater. Sci.*, **39**, 4705–4710 (2004).
- 8) X. Z. Rong, T. Tsurumi, O. Fukunaga and T. Yano, *Diam. Relat. Mater.*, **11**, 280–286 (2002).
- 9) P. Klimczyk, E. Benko, K. Lawniczak–Jablonska, E. Piskorska, M. Heinonen, A. Ormaniec, W. Gorczynska-Zawislan and V. S. Urbanovich, *J. Alloy Compd.*, **382**, 195–205 (2004).
- 10) H. Moriguchi, K. Tsuduki and A. Ikegaya, *Metal Powder Report*, **59**, 26–30 (2004).
- 11) V. Martinez and J. Echeberria, *J. Am. Ceram. Soc.*, **90**, 415–424 (2007).
- 12) M. Tokita, *J. Soc. Powder Technol. Jpn.*, **30**, 790–804 (1993).
- 13) J. Tatami, M. Iguchi, M. Hotta, C. Zhang, K. Komeya, T. Meguro, M. Omori, T. Hirai, M. E. Brito and Y.-B. Cheng, “*Key Engineering Materials*,” **237**, 105–110 (2003).
- 14) D. Hiratsuka, J. Tatami, T. Meguro, K. Komeya, I. Hayashi, J. F. Yang and M. Omori, *Key Engineering Materials*, 317–318, 633–636 (2006).
- 15) Y. Zhou, K. Hirao, M. Toriyama and H. Tanaka, *J. Am. Ceram. Soc.*, **83**, 654–656 (2000).
- 16) Z. Shen, M. Johnsson, Z. Zhao and M. Nygren, *J. Am. Ceram. Soc.*, **85**, 1921–1927 (2002).
- 17) M. Suganuma, Y. Kitagawa, S. Wada and N. Murayama, *J. Am. Ceram. Soc.*, **86**, 387–394 (2003).
- 18) JCPDS, International Centre for Diffraction Data, No.10–173.
- 19) JCPDS, International Centre for Diffraction Data, No.25–1033.
- 20) B. R. Lawn and E. R. Fuller, *J. Mater. Sci.*, **10**, 2016–2024 (1975).
- 21) E. Benko, J. S. Stanislaw, B. Krolicka, A. Wyczesany and T. Barr, *Diam. Relat. Mater.*, **8**, 1838–1846 (1999).
- 22) F. Ueda, M. Yageta and I. Tajima, *J. Hard Mater.*, **2**, 233–243 (1991).