Microstructure and Mechanical Properties of SiC-BN Composites with Oxynitride Glass

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ABSTRACT

By using an oxynitride glass as a sintering additive, the effects of BN content on microstructure and mechanical properties of the hot-pressed and subsequently annealed SiC-BN composites were investigated. The microstructures developed were analyzed by image analysis. The morphology of SiC grains was strongly dependent on BN content in the starting composition. The aspect ratio of SiC decreases with increasing BN content and the average diameter of SiC shows a maximum at 5 wt% BN and decreases with increasing BN content in the starting powder. The fracture toughness increased with increasing BN content while the strength decreased with increasing BN content. The strength and fracture toughness of SiC or SiC-TiC composites were strongly dependent on the morphology of SiC grains, but the strength and fracture toughness of SiC-BN composites were strongly dependent on BN content rather than morphology of SiC grains. These results suggest that fracture toughness of SiC ceramics can be tailored by manipulating BN content in the starting composition. Typical fracture toughness and strength of SiC-10 wt% BN composites were 8 MPa·m$^{1/2}$ and 445 MPa, respectively.

Key words : Composites, Microstructure, Mechanical property, SiC-BN

1. Introduction

O ne approach for tailoring properties is to combine the properties of different materials. Examples are SiC-TiC composites for improving fracture toughness[1,2] and SiC-Si$_3$N$_4$ composites for improving strength.[3,4] A new approach that has received less attention is the incorporation of hexagonal boron nitride (h-BN) in SiC with an oxynitride glass additive. SiC has higher hardness and oxidation resistance, whereas BN has better thermal-shock behavior and machinability.[5,6] Previous studies[7-9] on SiC-BN composites were mostly focused on phase stability and phase transformation of SiC. Ruh et al.[7,8] suggested that BN stabilizes β-SiC, whereas Turan and Knowles[9] claimed that BN does not directly affect the stability of a particular SiC polytype. However, the 3C SiC (β-SiC) polytype can be indirectly stabilized by nitrogen produced from a decomposition of BN.[9] Additions of h-BN to Al$_2$O$_3$[10] and Si$_3$N$_4$[11,12] improved thermal shock resistance. These improvements may be due to microcracks that exist between basal planes in h-BN.[13]

In the present study, SiC composites that contained up to 30 wt% of dispersed h-BN particles were fabricated via hotpressing and subsequently annealing with an oxynitride glass. The effect of BN on microstructural development of SiC was investigated using image analysis. Mechanical

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evaluations of strength and fracture toughness of the resulting composites were determined at room temperature.

2. Experimental Procedure

Submicron α-SiC (grade A-1, Showa Denko, Tokyo, Japan), β-SiC (grade ultrafine, Ibiden Co., Ltd., Nagoya, Japan), and h-BN (grade A01, H. C. Starck, Goslar, Germany) powders were used as starting powders. A mixture of SiO$_2$ (Reagent Grade, Kanto Chemical Co., Inc., Tokyo, Japan), MgO (High-Purity Grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan), Y$_2$O$_3$ (99.9% pure, Shin-Etsu Chemical Co., Tokyo, Japan), Al$_2$O$_3$ (99.9% pure, Sumitomo Chemical Co., Tokyo, Japan), and AlN (Grade F, Tokuyama Soda Co., Tokyo, Japan) powders was prepared by ball milling in ethanol for 24 h to form an oxynitride composition of Y$_{0.124}$Mg$_{0.160}$Si$_{0.414}$Al$_{0.302}$O$_{1.400}$N$_{0.151}$. The oxynitride composition has an appreciable solubility of SiC at high temperatures.[14] Five batches of powder were mixed, each of which contained 10 wt% of oxynitride glass powder. The BN content in those batches was 0, 5, 10, 20 and 30 wt%. All individual batches were milled in ethanol for 24 h, using SiC media and a polyethylene container. After milling, the slurry was dried and hot-pressed at 1800°C for 1 h under a pressure of 25 MPa in a nitrogen atmosphere. The hot-pressed samples were heated further at 1950°C for 4 h under an applied pressure of 25 MPa in nitrogen atmosphere to enhance grain growth. The heating rate was 20°C/min, and the cooling rate was ~40°C/min from 1950°C to 1200°C. The batch compositions and sample designations are given in Table 1.

Table 1. Batch Composition, Relative Density and Crystalline Phase of the Hot-pressed and Annealed SiC-BN Composites

Sample designation	Batch composition (wt%)	Relative density (%)	Crystalline phase	
			Major	Trace
SB0	89% β-SiC[a] + 1% α-SiC[b] + 10% oxynitride glass[c]	99.0	α-SiC	β-SiC
SB1	84.05% β-SiC + 0.95% α-SiC + 5% BN[d] + 10% oxynitride glass	99.5	α-SiC	h-BN, β-SiC
SB2	79.1% β-SiC + 0.9% α-SiC + 10% BN + 10% oxynitride glass	99.6	β-SiC	h-BN, α-SiC
SB3	69.2% β-SiC + 0.8% α-SiC + 20% BN + 10% oxynitride glass	99.6	β-SiC, h-BN	
SB4	59.3% β-SiC + 0.7% α-SiC + 30% BN + 10% oxynitride glass	99.1	β-SiC, h-BN	

[a]The average particle size is ~0.27 μm.
[b]The average particle size is ~0.45 μm.
[c]The composition of oxynitride glass is $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.400}N_{0.151}$.
[d]The average particle size is ~1.5 μm.

The sintered density was determined by using the Archimedes method. The theoretical densities of the materials were calculated according to the rule of mixtures.[14] The hot-pressed and annealed materials were cut and polished, then etched by a plasma of CF_4 containing 7.8% O_2. The microstructure was observed by Scanning Electron Microscopy(SEM). Grain diameters (d) and apparent lengths (L) of two-dimensionally exposed SiC grains were evaluated using an image analyzer (Image-Pro Plus, Media Cybernetics, Silver Spring, MD, U.S.A.).[15] The diameter and length of each grain were determined from the shortest and the longest diagonal, respectively. The mean value of the observed aspect ratio (L/d) was considered as an average aspect ratio.[16] A total of 900–1200 grains was used for statistical analysis of each material.

X-Ray Diffractometry(XRD) using Cu$K\alpha$ radiation was performed on the ground powders to determine crystalline phases. The bar samples, with dimensions of 25 mm×3 mm

×2.5 mm, were machined to a 1 μm finish for flexural testing. Bend tests were performed at room temperature on five specimens at each condition, using a four-point bending method with outer and inner spans of 10 and 20 mm, respectively, and a crosshead speed of 0.5 mm/min. The fracture toughness was measured by the indentation-strength method with an applied load of 196 N for 15 s. The strength of the indented specimen was measured with the four-point bending configuration mentioned above. The equation of Chantikul et al.[17] was used to calculate the fracture toughness.

3. Results and Discussion

3.1. Microstructure

The relative densities of the hot-pressed and annealed materials are shown in Table 1. As shown, all of the materials could be sintered to nearly full density (≥99.0% of theo-
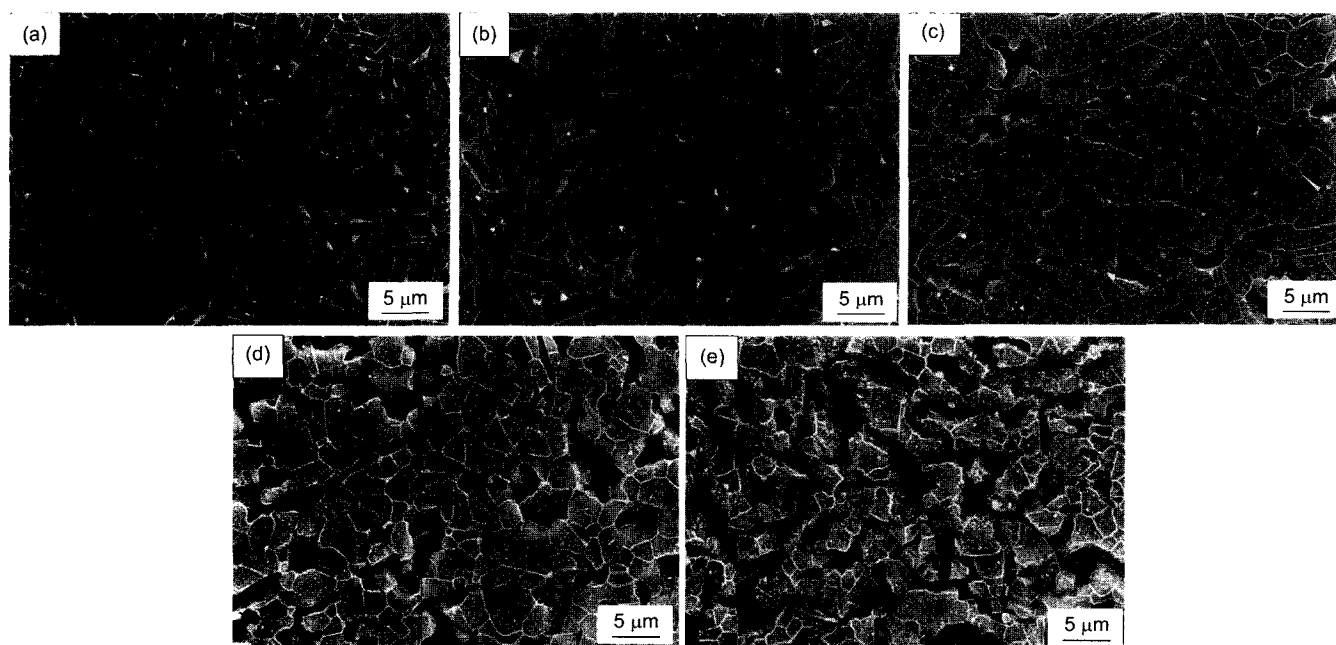

Fig. 1. Microstructures of the hot-pressed and annealed SiC-BN composites: (a) SB0, (b) SB1, (c) SB2, (d) SB3, and (e) SB4 (refer to Table 1).

retical density) by hot-pressing at 1800°C for 1 h and subsequently annealing at 1950°C for 4 h.

The microstructures of the hot-pressed and annealed materials are shown in Fig. 1. The pore-like dark grains are BN because they are etched away by CF_4 plasma. As shown, the microstructures are strongly dependent on the starting composition. The microstructures of the materials fabricated from SiC without BN (SB0) and SiC with 5 wt% BN (SB1) consisted of plate-shaped α-SiC grains, referring to the phase analysis in Table 1. In contrast those of the materials fabricated from SiC with ≥10 wt% BN consisted of mostly equiaxed β-SiC grains. The growth of plate-shaped α-SiC grains is evidently related to the occurrence of the β→α phase transformation of SiC, as shown in Table 1. When the BN content was increased, the shape of the SiC grains changed from plate-shaped to equiaxed grains and the aspect ratio of the grains decreased. In addition, the size of the plate-shaped grains prepared from SiC without BN (SB0) and SiC with 5 wt% BN (SB1) appeared to be larger than that of equiaxed grains from SiC with ≥10 wt% BN. These results suggest that BN addition critically affect the development of plate-shaped grains, in turn the occurrence of the β→α phase transformation.

The changes of diameter and aspect ratio of SiC grains for the annealed materials as a function of BN content are shown in Fig. 2. The aspect ratio of SiC grains decreased with increasing BN content and the diameter of SiC grains showed a maximum at 5 wt% BN and decreased with increasing BN content in the starting powder. It indicated that BN suppresses the growth of SiC grains as well as the suppression of the phase transformation, referring to the XRD analysis in Table 1. It is noteworthy to point out that the addition of a small amount of BN (≤5 wt%) increases the diameter but decreases the aspect ratio (Fig. 2), indicating the role of BN as a grain growth inhibitor in the composites.

The difference in microstructures of materials with 0–30 wt% BN reflects different phase transformation behavior of SiC grains in the composites. Previous results[18,19] have shown that the oxynitride glass maintains β-SiC up to 2000°C and microscopically, β-SiC has equiaxed morphology in nitrogen-containing glass. However, the introduction of α-SiC seeds into fine β-SiC with an oxynitride glass accelerated the growth of plate-shaped α-SiC grains.[20] In contrast, Zangvil and Ruh suggested that BN stabilizes β-SiC.[7] Turan and Knowles[9] suggested that nitrogen arising from BN dissociation during processing stabilized β-SiC if there was a liquid-phase. Thus, it is interesting to observe whether the plate-shaped α-SiC grains can grow in the presence of both BN and Y-Mg-Si-Al-O-N glass, in turn, whether the β→α phase transformation can occur. Present results suggest that the growth of plate-shaped α-SiC grains, i.e., the occurrence of β→α phase transformation of SiC, was strongly dependent on the BN content in the composites.

The BN addition as well as the oxynitride glass[7,8,18] stabilizes β-SiC, but the addition of α-SiC to β-SiC accelerates the growth of plate-shaped grains,[20] i.e., the phase transformation of SiC. Thus, BN and α-SiC affect the phase transformation and the growth of plate-shaped grains in opposite manner. The net effect was strongly dependent on the BN content, i.e., when ≤5 wt% BN was added, the phase transformation occurred and resulted in the growth of plate-shaped grains, whereas ≥10 wt% BN addition suppressed the phase transformation and resulted with equiaxed grains. The effect of α-SiC content was investigated previously[21] and further addition of α-SiC might decrease the tendency for the growth of plate-shaped grains because of the impingement of growing grains.

Based on the microstructural observation and XRD analysis, the effect of BN addition on microstructural development and phase transformation can be summarized as follows: (1) the growth of plate-shaped α-SiC grains, i.e., the occurrence of β→α phase transformation of SiC, was strongly dependent on the BN content in the composites; (2) the plate-shaped α-SiC grains can be grown in the presence of both BN and Y-Mg-Si-Al-O-N glass if 1 wt% α-SiC is added as seeds and BN content is equal to or less than 5 wt% in the composites; (3) BN stabilizes β-SiC in the presence of oxynitride glass if BN content is equal to or higher than 10 wt% in the composites containing 1 wt% α-SiC as seeds; and (4) BN suppresses the grain growth of SiC both directly by acting as grain growth inhibitor in the composites and indirectly via suppressing the phase transformation of SiC.

3.2. Mechanical Properties

Fig. 3 shows the variation of fracture toughness and strength as a function of BN content. The fracture toughness increased with increasing BN content while the strength decreased with BN content. SB0, which was composed of relatively large, plate-shaped α-SiC grains, had a fracture toughness of 5.5–5.9 $MPa \cdot m^{1/2}$ and a flexural strength of 450–550 MPa. In contrast, SB4, which was
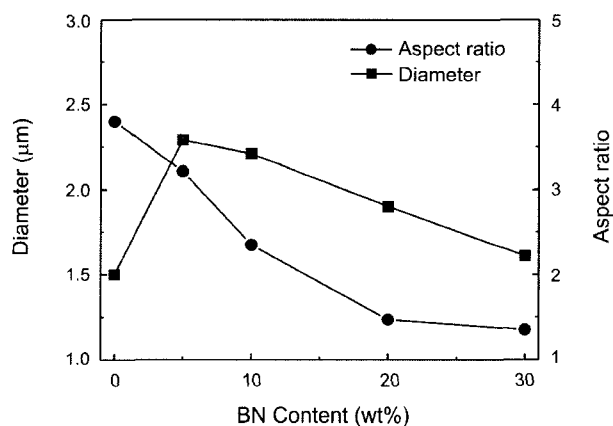

Fig. 2. Change of grain diameter and aspect ratio of SiC grains for the hot-pressed and annealed SiC-BN composites as a function of BN content in the starting powder.
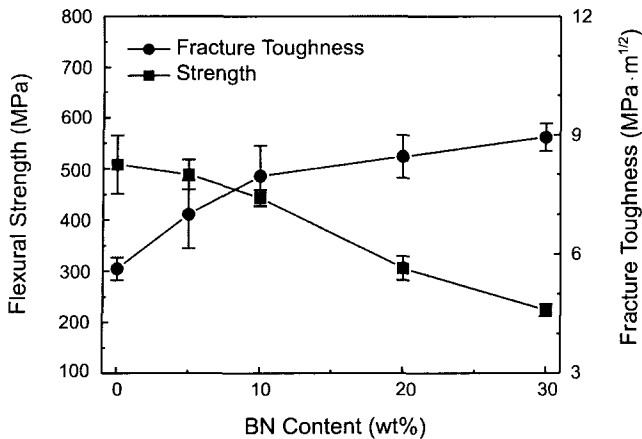
Fig. 3. Flexural strength and fracture toughness of the hot-pressed and annealed SiC-BN composites as a function of BN content in the starting powder.

composed of relatively small, equiaxed β-SiC grains and platelike BN grains, had a fracture toughness of 8.7–9.2 MPa·m$^{1/2}$ and flexural strength of 210–230 MPa. Previous studies[2,21-23] suggested that the growth of plate-shaped SiC grains improved fracture toughness and decreased the strength values in self-reinforced SiC ceramics and SiC-TiC composites. In the present study, BN addition changed the morphology of SiC grains from plate-shaped to equiaxed, but increased the toughness. Thus, BN addition showed opposite tendency in toughness of self-reinforced SiC ceramics. It indicated that the improvement in toughness was directly related to the BN addition. Fig. 4 shows the fracture surfaces of SiC ceramics (SB0) and SiC-BN composites

(SB1-4). As shown, the interactions between BN grains (platelike grains 3 to 6 μm in length and 0.1 to 0.4 μm in thickness) and cracks are clearly shown. Crack deflection by platelike BN grains is responsible to the increase in toughness. Trice and Halloran[6] also observed the toughening, owing to the crack defection by platelike BN grains in h-BN-oxide ceramic composites. Therefore, the effect of BN addition on fracture toughness in SiC-BN composites is duplex: BN addition inhibits the grain growth of plate-shaped α-SiC grains by suppressing the β→α phase transformation of SiC, resulting the decrease in the contribution of plate-shaped SiC grains to toughening; on the other hand, it deflects the cracks, resulting the improved toughness. Comparison of fracture toughness of SB0 (a typical self-reinforced SiC ceramics) and SB4 (SiC-30 wt% BN composite) suggested that the contribution of crack deflection by BN grains overwhelmed the contribution by plate-shaped SiC grains. Thus, the improvement of toughness with increasing the BN content was mainly due to the crack deflection by platelike BN grains.

The change in strength (Fig. 3) is quite similar to that of the diameter (Fig. 2). The BN addition decreased the strength. Previous results on liquid-phase-sintered SiC [21,23,24] showed that the equiaxed microstructure has a superior strength to the self-reinforced microstructure consisted of plate-shaped grains because of the decreased flaw size in the equiaxed microstructure. But the present results show that the self-reinforced microstructure (SB0) has superior strength, compared to the equiaxed microstructure (SB4). BN grains would act as pre-existing flaws, either due to the intrinsic weakness between basal planes or due to microcracks that exist between basal planes in h-BN,[12,13] resulting
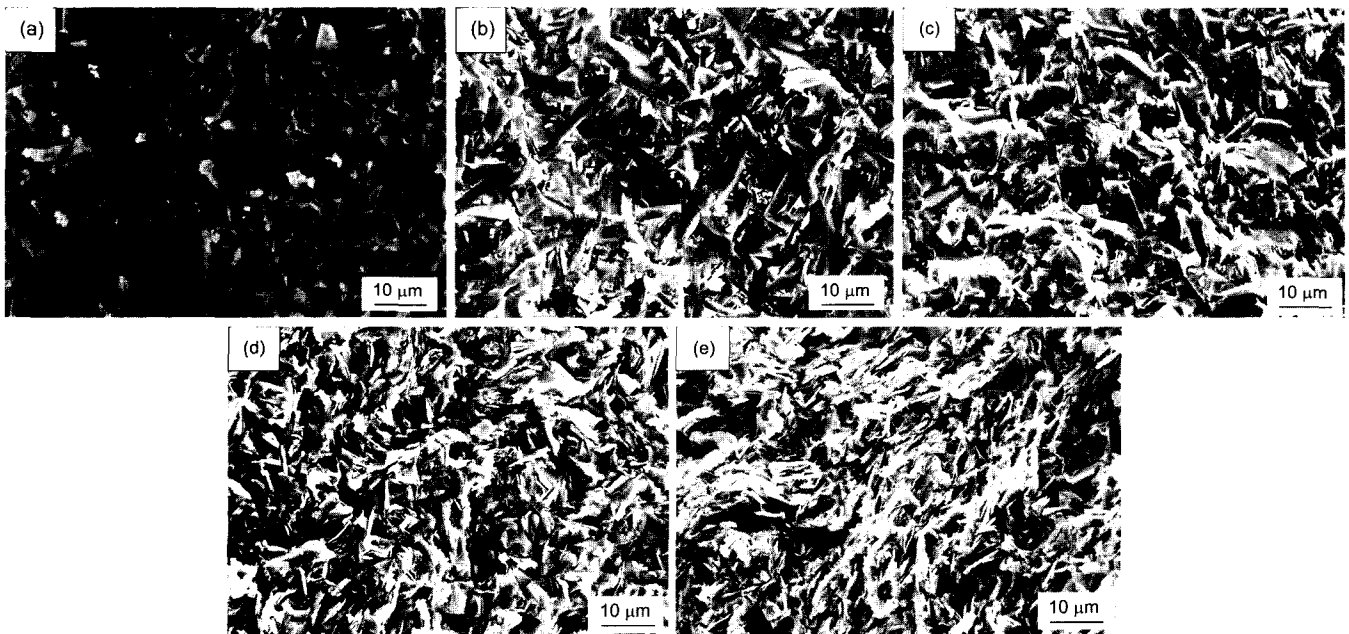

Fig. 4. SEM micrographs of the fracture surfaces of the hot-pressed and annealed SiC-BN composites: (a) SB0, (b) SB1, (c) SB2, (d) SB3, and (e) SB4 (refer to Table 1).

the decrease in the strength.

The present results suggest that the mechanical properties of SiC-BN composites with an Y-Mg-Al-Si-O-N glass are not dependent on their microstructure, but mainly on the BN content added. The BN addition into liquid-phase-sintered SiC produces the improved toughness, but decreased strength. Thus, the mechanical properties of SiC ceramics can be tailored to some extent by manipulating the BN content.

4. Conclusions

SiC composites that contained up to 30 wt% of dispersed BN particles were fabricated via hot-pressing and subsequent annealing with an oxynitride glass. The BN addition into liquid-phase-sintered SiC ceramics suppressed the grain growth of SiC both directly by acting as a grain growth inhibitor in the composites and indirectly via suppressing the $\beta \rightarrow \alpha$ phase transformation of SiC. The fracture toughness of SiC has been improved by adding BN particles, owing to crack deflection by BN grains, but the strength of SiC, owing to the intrinsic weakness of BN grains, has been decreased by adding BN. Typical fracture toughness and strength of SiC-10 wt% BN composites were 8 MPa·m$^{1/2}$ and 445 MPa, respectively.

Acknowledgment

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