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Effects of additive amount on microstructure and mechanical properties of silicon carbide-silicon nitride composites

YOUNG-IL LEE, YOUNG-WOOK KIM*
Department of Materials Science and Engineering, The University of Seoul, Seoul 130-743, South Korea
E-mail: ywkim@uoscc.uos.ac.kr

HEON-JIN CHOI, JUNE-GUNN LEE
Division of Ceramics, Korea Institute of Science and Technology, Seoul 130-650, South Korea

Powder mixtures of β-SiC-α-Si_3N_4 in a weight ratio of 1 : 1 containing 5–20 wt% Y-Mg-Si-Al-O-N oxynitride as a sintering additive were liquid-phase sintered at 1800°C for 3 h by hot-pressing. These materials had a microstructure of "*in situ*-toughened composites" as a result of the $\alpha \rightarrow \beta$ phase transformation of Si_3N_4 during sintering. The introduction of larger amount of additives accelerated the grain growth of elongated β-Si_3N_4 grains with higher aspect ratio, resulting in the improved fracture toughness and strength. Typical flexural strength and fracture toughness of SiC-Si_3N_4 composites containing 15 wt% oxynitride glass were 860 MPa and 5.7 $MPa \cdot m^{1/2}$, respectively.

1. Introduction

Densification of SiC-based composites such as SiC-TiB_2 and SiC-Si_3N_4 without the aids of high pressure or sintering additives is very difficult owing to the covalent nature of their bond. Therefore, sintering additives such as metals, oxides, and non-oxide ceramics are usually added to densify the composites [1–7]. Composites of SiC-Si_3N_4 can be fabricated by hot-isostatic pressing with the aid of La_2O_3 and Y_2O_3 [5] or hot-pressing with Al_2O_3 and Y_2O_3 [8] to a nearly full density at temperatures in excess of 1800°C. The role of additives for the sintering of covalent-bonded ceramics can be regarded as not only densification aids but also key elements for the microstructural development, since the related properties of the materials are influenced by the kinds and the amount of additives [7, 9–11].

Recently, using an Y-Mg-Si-Al-O-N oxynitride as a sintering additive, a microstructure consisting of uniformly distributed, elongated β-Si_3N_4, equiaxed β-SiC grains, and an amorphous grain boundary was obtained [12]. The flexural strength and fracture toughness of the SiC-35 wt% Si_3N_4 composites were 1020 MPa and 5.1 $MPa \cdot m^{1/2}$, respectively. The reduced defect size and the enhanced bridging and deflection by the elongated β-Si_3N_4 grains have been identified as the principal elements of the improved mechanical properties [12].

In this study, we present the influence of additive amount on microstructure and mechanical properties of SiC-Si_3N_4 composites with an Y-Mg-Si-Al-O-N oxynitride as a sintering additive.

2. Experimental procedure

Commercially available β-SiC (Ultrafine grade, Ibiden Co. Ltd., Nagoya, Japan) and α-Si_3N_4 (E10 grade, Ube Industries, Tokyo, Japan) powders were used as starting powders. A mixture of SiO_2 (reagent grade, Kanto Chemical Co., Tokyo, Japan), MgO (high-purity grade, Wako Pure Chemical Industries, Ltd., Osaka, Japan), Al_2O_3 (99.9% pure, Sumitomo Chemical Co., Tokyo, Japan), Y_2O_3 (99.9% pure Shin-Etsu Chemical Co., Tokyo, Japan), and AIN (Grade F, Tokuyama Soda Co., Tokyo, Japan) powders was prepared by ball milling in ethanol to form an oxynitride composition of $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.4}N_{0.151}$. The oxynitride composition has an appreciable solubility of SiC at high temperatures [13] and a good potential for crystallization control [14]. Four batches of powder were mixed, each containing 5, 10, 15 and 20 wt% oxynitride powder and SiC : Si_3N_4 in a weight ratio of 1 : 1. The sample designations and batch compositions are shown in Table I. All individual batches were milled in ethanol for 24 h, using Si_3N_4 grinding balls. The milled slurry was dried, sieved and hot-pressed at 1800°C for 3 h under a pressure of 25 MPa in a nitrogen atmosphere. The heating rate was 20°C/min, and the cooling rate was ~60°C/min from 1800°C to 1200°C.

The sintered density was determined by using the Archimedes method. The theoretical densities of the

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* Author to whom all correspondence should be addressed.

TABLE I Composition and characteristics of SiC-Si_3N_4 composites

Sample designation	Composition(wt %)			Relative density (%)	Si_3N_4 grain	
	SiC	Si_3N_4	Oxynitride*		Aspect ratio	Diameter
SCN1	47.5	47.5	5	97.3	3.4	0.24
SCN2	45	45	10	98.6	4.2	0.23
SCN3	42.5	42.5	15	99.7	5.1	0.24
SCN4	40	40	20	99.5	6.1	0.22

* The composition of the oxynitride is $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.4}N_{0.151}$.

specimens were calculated according to the rule of mixtures (the theoretical density of the oxynitride glass was 3.18 g/cm^3) [14]. Crystalline phases in the sintered specimens were determined by X-ray diffractometry (XRD) using Cu-K_α radiation. The microstructure was observed by scanning electron microscopy (SEM) for the polished and etched specimens. The length and diameter of Si_3N_4 grains were determined from the longest and shortest grain diagonals, respectively, in the two-dimensional image [15, 16]. The bar samples, with dimensions of 2.5 mm × 3 mm × 25 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 estimated by measuring the lengths of cracks that were generated by a Vickers indenter [17]. The variation of fracture toughness with indentation load (R-curve-like behavior) was estimated by changing the indentation load over a range of 98–294 N, and the toughness values that were measured in the steady-state region were reported in this study.

3. Results and discussion

The characteristics of the SiC-Si_3N_4 composites are summarized in Table I. Relative densities of >97% were achieved by hot-pressing with a holding time of 3 h at 1800°C. Higher amounts of additive addition resulted in increase of the sintered density because of the increased amount of liquid phase during hot pressing. Phase analysis of the hot-pressed composites by XRD showed that the major phases of all specimens were β-SiC and β-Si_3N_4. These results show that $\alpha \rightarrow \beta$ phase transformation of Si_3N_4, which usually accelerates the grain growth of elongated grains, has taken place during heating and hot-pressing at 1800°C.

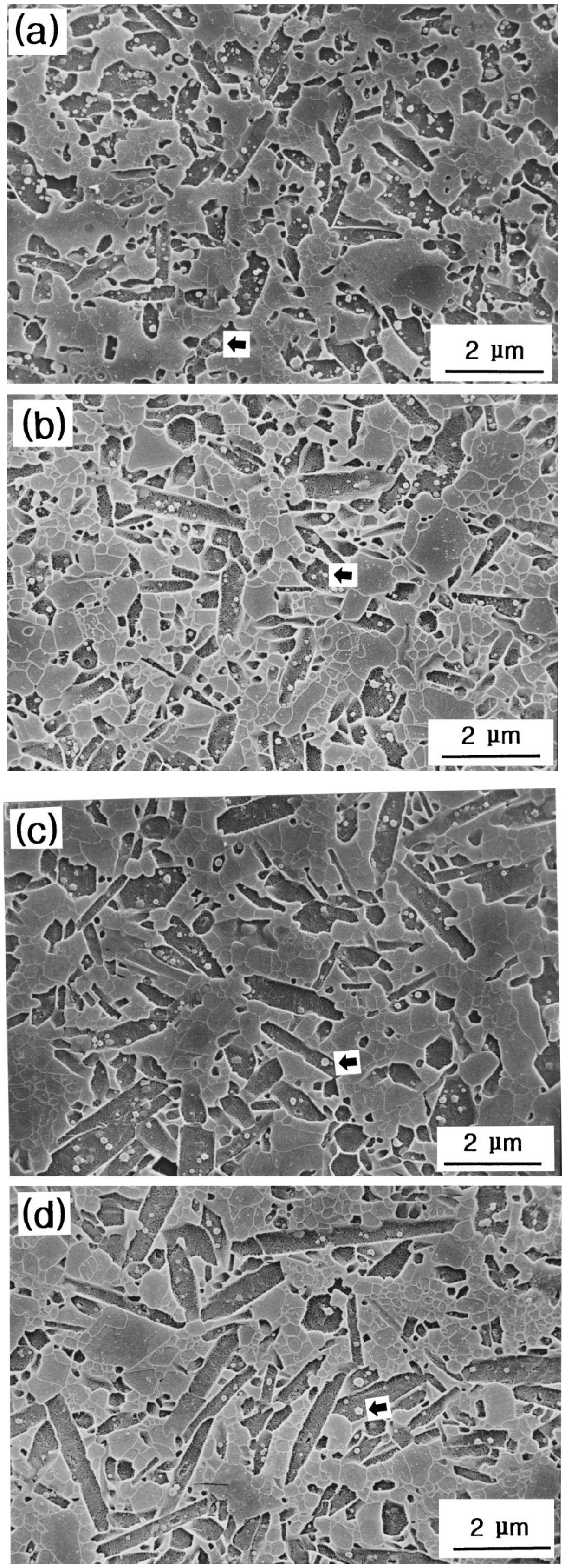

Figure 1 Microstructures of hot-pressed specimens: (a) SCN1, (b) SCN2, (c) SCN3, and (d) SCN4 (refer to Table 1). Note the relatively small (30–200 nm) SiC particles are trapped in the Si_3N_4 grains (marked by arrows).

Fig. 1 shows the microstructure of the SiC-Si_3N_4 composites after hot pressing. The SiC-Si_3N_4 composites were two-phase composites that consisted of randomly distributed, elongated β-Si_3N_4 grains and equiaxed β-SiC grains. The Si_3N_4 grains can be identified in the micrographs that are shown in Fig. 1 based on their concave nature, because of the faster etching rate of Si_3N_4. During hot pressing, the $\alpha \rightarrow \beta$ phase transformation of Si_3N_4 led to the *in situ* growth of elongated β-Si_3N_4 grains. The $\beta \rightarrow \alpha$ phase transformation of SiC was inhibited, because of the low-temperature sintering and a nitrogen-containing liquid [15, 16, 18]. The grain size and morphology of SiC grains were not changed significantly with the variation in the amount of additives. In contrast, the morphology of Si_3N_4 grains was dependent on the amount of the additives; aspect ratio of Si_3N_4 grains increased, i.e., from 3.4 for SCN1 to 6.1 for SCN4, with increasing the amount of an additive, probably due to the reduced impingement of grains at higher amount of an additive. The diameter of Si_3N_4 grains were almost constant and irrespective of the amount of an additive. Si_3N_4 grains in SCN4 therefore were longer than those of SCN1-3. Fig. 1 shows that relatively small (30–200 nm) SiC particles were trapped in the Si_3N_4 grains (marked by arrows), which indicates the faster growth rate of Si_3N_4, compared to SiC. This result is similar to the SiC-Si_3N_4 nanocomposites [19].

The fracture mode of SiC-Si_3N_4 composites with an Y-Mg-Al-Si-O-N oxynitride was mostly intergranular, which was a result of a weak interface created by the difference between the coefficients of thermal expansion of the liquid and the SiC and/or Si_3N_4 grains on cooling after hot-pressing. A large addition of additive amount leads to an increased tendency of intergranular fracture (Fig. 2) because of relatively large amount of liquid. Present results suggest that the oxynitride glass that has been selected in this research is one of the effective additives for the *in situ*-toughened SiC-Si_3N_4 composites, which results in intergranular fracture of the composites and a tortuous crack path.

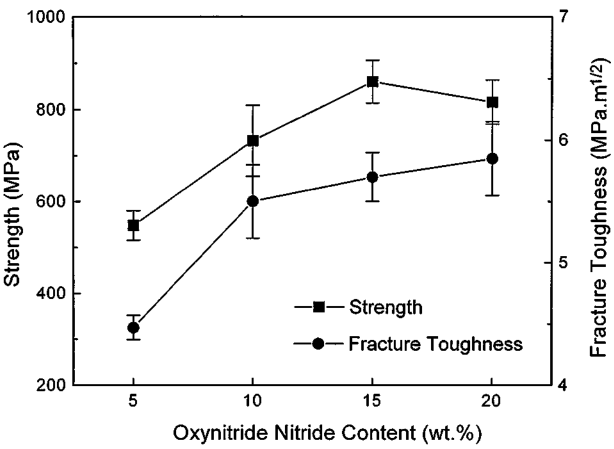

Figure 3 Flexural strength and fracture toughness of SiC-Si_3N_4 composites, as a function of oxynitride content.

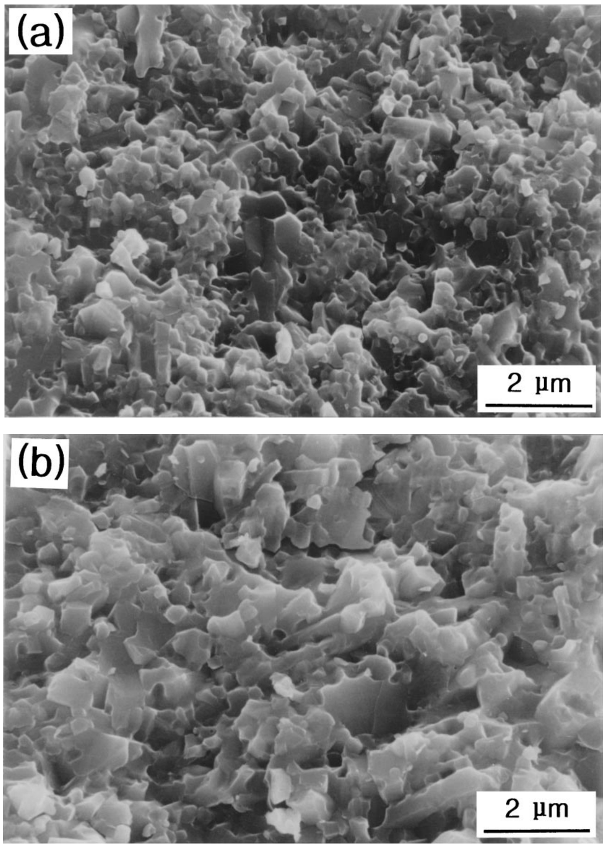

Figure 2 SEM micrographs of the fracture surfaces of hot-pressed specimens: (a) SCN1 and (b) SCN3 (refer to Table I).

The mechanical properties of the hot-pressed SiC-Si_3N_4 composites were dependent on the amount of additive, as shown in Fig. 3. The fracture toughness increased as the additive amount increased and showed a maximum value of 5.9 $MPa \cdot m^{1/2}$ at an additive amount of 20 wt%. The increase in fracture toughness with increasing the additive amount might be related to the following two factors: (1) microstructure of the composites; when relatively high amount of additives were added, the shape of Si_3N_4 grains was more acicular, because the oxynitride glass accelerated the growth of acicular grains. The acicular morphology of Si_3N_4 grains is beneficial for toughening via crack deflection and bridging, which are believed to be operating in this system [12]; (2) the increased tendency of intergranular fracture in specimens containing higher amount of additive; when relatively high amount of additives were added, weak interface boundaries due to thermal expansion mismatch between the second-phase (Y-Si-Mg-Al-O-N glass) and SiC and/or Si_3N_4 were maintained after 3-h hot pressing because of the sufficient amount of additives, leading to the enhanced crack bridging and deflection, as observed in Fig. 4b. In contrast, when small amount of an additive was added, the glass phase-insufficient regions might be introduced due to the evaporation of additives during hot-pressing, leading to the increased tendency of transgranular fracture, as observed in Fig. 4a.

The strength increased as the additive amount increased and showed a maximum of 860 MPa at an additive amount of 15 wt% (SCN3). This value is ∼55% higher than that of the specimen with a 5 wt% additive that was fabricated under the same conditions (548 MPa). However, additional additive loadings, up to 20 wt%, decreased the strength slightly, from 860 MPa to 816 MPa although the fracture toughness was increased. The critical defect size (c), calculated from the measured fracture-toughness (K_{IC}) and strength (σ) values (using the equation $K_{IC} = 1.35\sigma c^{1/2}$) [12], was ∼37 μm for the composites that contained 5 wt% additive and ∼24 μm for the composites that contained 15 wt% additive. The c values (24–37 μm) of these composites are equal to or smaller than those of typical monolithic SiC ceramics with a composite-type microstructure (30–150 μm) [20, 21]. The higher strength of SCN3 may be related to both reduction in c and the increase in fracture toughness. The lower strength of SCN1 may be partly due to the lower sintered density, compared to the other specimens because of insufficient

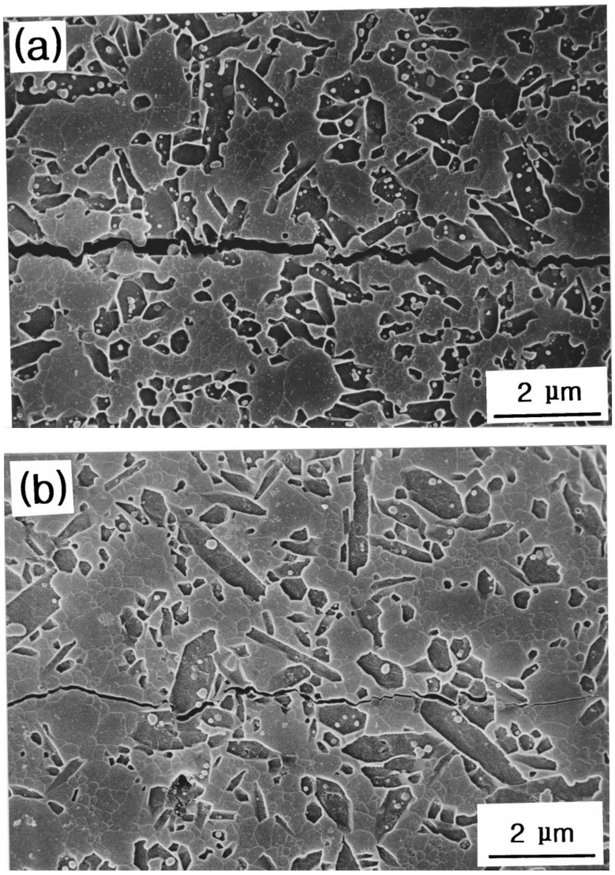

Figure 4 SEM micrographs of crack paths induced by a Vickers indentor for (a) SCN1 and (b) SCN3 (refer to Table I).

liquid amount during hot-pressing. This result suggest that 5 wt% loading of oxynitride glass is insufficient to densify the SiC-Si_3N_4 composites fully.

It was reported that there was a trade-off in improving both strength and toughness in SiC ceramics with self-reinforced microstructure: i.e., introducing large elongated grains in the microstructure has resulted in decreased strength [20, 21]. Both strength and fracture toughness of SiC-Si_3N_4 composites, however, have been improved by adding oxynitride glass, because of the reduced defect size and the enhanced bridging and crack deflection by the elongated β-Si_3N_4 grains. Further improvement in the mechanical properties of the SiC-Si_3N_4 composites may be possible by controlling and optimizing the microstructure.

4. Conclusions

In situ-toughened SiC-Si_3N_4 composites were fabricated from β-SiC and α-Si_3N_4 powders with an oxynitride glass. The microstructure consisted of uniformly distributed, elongated β-Si_3N_4 grains, equiaxed β-SiC grains, and an amorphous grain boundary phase. The introduction of larger amount of an additive, within the amount range studied (5–20 wt%), accelerated the grain growth of elongated β-Si_3N_4 grains with higher aspect ratio and maintained the weak interface boundaries after hot-pressing, resulting in the improved fracture toughness and strength. Typical flexural strength and fracture toughness values of SiC-Si_3N_4 composites that contained 15 wt% oxynitride glass were 860 MPa and 5.7 $\text{MPa} \cdot \text{m}^{1/2}$, respectively.

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