Effect of Additive Composition on Fracture Toughness of
In Situ-Toughened SiC-Si$_3$N$_4$ Composites

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ABSTRACT

Effect of additive composition on fracture toughness of in situ-toughened SiC-Si$_3$N$_4$ composites was investigated for five different additive compositions. The highest toughness (6.4 MPa·m$^{1/2}$) in SiC-Si$_3$N$_4$ composites investigated herein was obtained when an Y-Mg-Si-Al-O-N oxynitride glass was used as a sintering additive. The improvement in fracture toughness was produced by enhanced bridging and deflection by Si$_N$$_4$ grains.

Key words: Composite, Silicon carbide, Silicon nitride, Additive composition, Fracture toughness

1. Introduction

Both silicon carbide and silicon nitride are leading candidates for structural applications due to their superior properties in terms of wear, corrosion, strength, oxidation resistance and high-temperature creep, as well as their high-temperature strength retention characteristics. SiC has higher hardness and oxidation resistance, whereas Si$_3$N$_4$ has better strength and thermal-shock behavior. One approach for tailoring properties is to combine the properties of different materials. Several investigations on SiC-Si$_3$N$_4$ composites have been reported. Shaoming et al. investigated the mechanical properties of SiC-25-vol% Si$_3$N$_4$ composites that contained La$_2$O$_3$ and Y$_2$O$_3$ additives and were fabricated via hot isostatic pressing. They reported maximum flexural strength and fracture toughness values of 810 MPa and 5.5 MPa·m$^{1/2}$, respectively, in specimens with different additive compositions. Turan and Knowles reported the α→β reverse transformation of SiC in SiC-20-wt%Si$_3$N$_4$ composites that were fabricated via hot isostatic pressing. Kim and Mitomo fabricated SiC-Si$_3$N$_4$ nanocomposites using ultrafine starting powders and low-temperature sintering by hot-pressing. The resultant composites consisted of SiC grains with an average grain size of ~100 nm and Si$_3$N$_4$ grains with an average grain size of ~200 nm. The fracture toughness of 8-h annealed composites was 4.7 MPa·m$^{1/2}$ when 6 wt% Al$_2$O$_3$ and 4 wt% Y$_2$O$_3$ were added as sintering additives.

Due to the covalently bonded nature of SiC and Si$_3$N$_4$, densification of monolithic ceramics and their composites is very difficult without the aid of high pressure or sintering additives. Therefore, sintering additives such as metals, oxides, and non-oxide ceramics are usually added to densify the composites. The oxide reacts with SiO$_2$ which is always present on the surface of SiC and Si$_3$N$_4$ particles and forms an oxide melt and, with increasing temperature, an oxycarbide and oxynitride melt by dissolution of SiC and Si$_3$N$_4$, respectively. Additives for the sintering of nonoxide ceramic composites serve not only to aid densification but also as key elements for microstructure development. This is because the related properties of composites are affected by the microstructure and the chemistry of the grain-boundary phase, which is determined by the kinds and amounts of additives in the resulting ceramics.

Recently, using an Y-Mg-Si-Al-O-N oxynitride as a sintering additive, a microstructure consisting of uniformly distributed, elongated β-Si$_3$N$_4$, equiaxed β-SiC grains, and an amorphous grain boundary was obtained. The flexural strength and fracture toughness of the SiC-35 wt% Si$_3$N$_4$ composites were 1020 MPa and 5.1 MPa·m$^{1/2}$, respectively. Reduced defect size and enhanced bridging and deflection by the elongated β-Si$_3$N$_4$ grains have been identified as the principal factors underlying the improved mechanical properties. In a previous study, in situ-toughened SiC-Si$_3$N$_4$ composites were fabricated from β-SiC and α-Si$_3$N$_4$ powders containing 5-20 wt% oxynitride as a sintering additive. Introduction of a larger amount of the additive, within the range studied (5-20 wt%), accelerated the grain growth of elongated β-Si$_3$N$_4$ grains with higher aspect ratio and maintained weak interface boundaries after hot-pressing, resulting in improved fracture toughness and strength. Typical flexural strength and fracture toughness values of SiC-Si$_3$N$_4$ composites containing 15 wt% oxynitride glass were 800 MPa and 5.7 MPa·m$^{1/2}$, respectively. Previous studies showed
that the composition and the amount of sintering additives influence the properties of the resulting composites.

In this study, the effect of sintering-additive composition on the fracture toughness of SiC-Si₃N₄ composites was investigated for five different additive compositions; Al₂O₃, Y₂O₃-Al₂O₃, yttrium aluminum garnet (YAG), Al₂O₃-SiO₂-MgO, YAG-Al₂O₃, and Y-Mg-Si-Al-O-N oxynitride glass.

2. Experimental Procedure

Commercially available β-SiC (Ultrafine grade, Idbiden Co. Ltd., Nagoya, Japan) and α-Si₃N₄ (E10 grade, Ube Industries, Tokyo, Japan) powders were used as starting powders. A mixture of SiO₂ (99.9% pure, High Purity Chemicals, Osaka, Japan), MgO (99.99% pure, High Purity Chemicals, Osaka, Japan), Al₂O₃ (AKP-30, Sumitomo Chemicals, Tokyo, Japan), Y₂O₃ (99.9% pure, Shin-Etsu Chemical Co., Ltd., Tokyo, Japan), and Al₂O₃ (Grade F, Tokuyama Soda Co., Tokyo, Japan) powders was prepared by ball milling the powders in ethanol to form an oxynitride composition of Y₆₋₄ₓMgₓSi_1₋₄ₓOₓSi₁₋₄ₓOₓOₓ₁₋₄ₓ₁₋₄ₓNₓ. The oxynitride composition has an appreciable solubility of SiC at high temperatures⁸ and good potential for crystallization control.¹⁰ For other compositions, Al₂O₃, Y₂O₃, YAG (99.99% pure, High Purity Chemicals, Osaka, Japan), SiO₂, MgO, and Al₂O₃ powders were used as sintering additives. All individual batches were milled in ethanol for 24 h using a polyethylene jar and SiC balls. The milled slurry was dried, sieved, and hot-pressed at 1800°C for 4 h under a pressure of 25 MPa in a nitrogen atmosphere. The hot-pressed composites were further heated at 1900°C for 1 h in N₂ atmosphere.

Relative density of the sintered and annealed composites was measured by the Archimedes method using deionized water as an immersion medium. The microstructure was observed using scanning electron microscopy (SEM). Since toughness is mostly influenced by elongated grains, an image analysis of Si₃N₄ grains was conducted to quantitatively evaluate the microstructural features. The thickness (t), length (L), and aspect ratio (L/t) were measured using an image analyzer (Image-Pro Plus, Media Cybernetics, Silver Spring, MD, USA).¹⁰ The thickness of each grain was determined directly from the shortest grain diagonal in its two-dimensional image. The apparent length of each grain was obtained from the longest diagonal. The mean value of observed aspect ratio was taken to be the mean of the actual values. A total of 1000 to 1200 grains was used for the statistical analysis of each composite. X-ray diffraction (XRD) using CuKα radiation was performed on the ground powders. The fracture toughness was estimated using an indentation technique on the polished surfaces of the composites by measuring crack lengths generated by a Vickers indenter. The variation of fracture toughness with indentation load (R-curve-like behavior) was estimated by changing the indentation load over a range of 49-294 N, and the toughness values measured in the steady-state region are reported in this study.¹⁵

3. Results and Discussion

The composition and density of the hot-pressed and annealed SiC-Si₃N₄ composites are summarized in Table 1. All specimens have relative densities of ≥98% after annealing. Phase analysis of the composites by XRD showed that major phases of the specimens are β-SiC and β-Si₃N₄. These results show that α→β phase transformation of Si₃N₄, which usually accelerates the grain growth of elongated grains, took place during hot-pressing at 1800°C and subsequent annealing at 1900°C.

Fig. 1 shows the microstructure of the hot-pressed and annealed SiC-Si₃N₄ composites with additives of different composition. SiC and Si₃N₄ grains are etched away, and consequently the microstructure is delineated by the grain boundary glass phase. The microstructure of SiC-Si₃N₄ composites consisted of randomly distributed, elongated β-SiC and Si₃N₄ grains and relatively equiaxed β-SiC grains. The Si₃N₄ grains can be identified in the micrographs shown in Fig. 1 based on their concave nature, which results from their faster etching rate.¹¹ During hot-pressing, the α→β phase transformation of Si₃N₄ led to the in situ growth of elongated β-SiC grains. The β→α transformation of SiC, which usually occurs via a solution-precipitation process (as evidenced by the core/rim structure in Fig. 1(e)), appears to be hindered by the Si₃N₄ particles. In turn, the grain growth of Si₃N₄, which occurs via a solution-precipitation process, is also hindered by the SiC particles.

Fig. 1 shows that relatively small (30-200 nm) SiC particles were trapped in the Si₃N₄ grains, which indicates Si₃N₄ has a faster growth rate than SiC. This result is similar to that obtained for the SiC-Si₃N₄ nanocomposites.¹²⁵ For the

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Batch composition (wt%)</th>
<th>Relative density (%)</th>
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<tbody>
<tr>
<td></td>
<td>β-SiC</td>
<td>α-Si₃N₄</td>
</tr>
<tr>
<td>SCN1</td>
<td>53</td>
<td>35</td>
</tr>
<tr>
<td>SCN2</td>
<td>53</td>
<td>35</td>
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<td>SCN3</td>
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<td>SCN4</td>
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<td>35</td>
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<tr>
<td>SCN5</td>
<td>53</td>
<td>35</td>
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</tbody>
</table>

³The composition of the oxynitride is Y₆₋₄ₓMgₓSi₁₋₄ₓOₓSi₁₋₄ₓOₓOₓ₁₋₄ₓ₁₋₄ₓNₓ₁₋₄ₓ₁₋₄ₓ₁₋₄ₓ.
YAG-containing composites (SCN2 and SCN4), the addition of AlN into the YAG increased the average grain diameter of Si$_3$N$_4$ from 0.19 μm for SCN2 to 0.25 μm for SCN4. SCN4 containing YAG-AlN additives showed the largest grain length (0.74 μm) and the highest aspect ratio (2.4) among the samples investigated herein. This indicates that the addition of AlN into YAG enhances the grain growth of Si$_3$N$_4$ grains in SiC-Si$_3$N$_4$ composites.

As shown in Fig. 1, the morphology of Si$_3$N$_4$ grains changed from a well-faceted morphology in a composite containing Y-Mg$_{3}$Si$_2$Al-O-N oxynitride glass (SCN1) to a less-faceted morphology in composites containing YAG (SCN2 and SCN4) as a sintering additive. The microstructure of SCN4 containing YAG-AlN was similar to that of SCN5 containing Al$_2$O$_3$-Y$_2$O$_3$-AlN as a sintering additive; specifically, there was no appreciable difference in the aspect ratio of Si$_3$N$_4$ grains (see Table 2). Thus, they have similar toughness values; the fracture toughness of SCN4 and SCN5 were 4.5 MPa·m$^{0.5}$ and 4.4 MPa·m$^{0.5}$, respectively. A fracture toughness of 5.5 MPa·m$^{0.5}$ was reported in SiC-Si$_3$N$_4$ composites sintered with 6 wt% La$_2$O$_3$-Y$_2$O$_3$ additives$^5$ whereas a fracture toughness of 4.7 MPa·m$^{0.5}$ was reported in SiC-Si$_3$N$_4$ composites sintered with 6 wt% Al$_2$O$_3$ and 4 wt% Y$_2$O$_3$ additives.$^6$ A comparison of the toughness (6.4 MPa·m$^{0.5}$) of SCN1 with that of the specimens reveals that SiC-Si$_3$N$_4$ composite containing Y-Mg$_{3}$Si$_2$Al-O-N oxynitride glass as a sintering additive (SCN1) has superior fracture toughness to those containing other additives.

The aspect ratios of SCN1 and SCN2 were similar, i.e., 1.9 and 2.0, respectively, and the aspect ratio of SCN5 was 2.3. However, the fracture toughness of SCN1, SCN2, and SCN5 was 6.4 MPa·m$^{0.5}$, 3.8 MPa·m$^{0.5}$, and 4.4 MPa·m$^{0.5}$, respectively. Thus, the difference in fracture toughness between SCN1 and the others cannot be explained by the microstructure alone. As shown in Fig. 2, the crack path in SCN1 was mostly localized in the glass phase and mostly around Si$_3$N$_4$ grains; crack deflection and crack bridging were more pronounced in SCN1 than in the other specimens (Figs. 2b and c). Thus, the more tortuous crack path in SCN1 may be due to an optimum interface strength, which affects the crack propagation behavior in the case of intergranular fracture. The tortuous crack path in SCN1 resulted in higher fracture toughness (6.4 MPa·m$^{0.5}$) than the others. The SiC-Si$_3$N$_4$ composite containing YAG (SCN2) showed the lowest fracture toughness of 3.8 MPa·m$^{0.5}$. The present results suggest that oxynitride glass is more effective as a sintering additive for toughening than the other additives. This result agrees with previously reported findings for SiC ceramics: SiC ceramics sintered with an oxynitride glass showed superior toughness than those sintered with oxide glasses at an equivalent grain size.$^{10}$

In a previous study on a SiC-Si$_3$N$_4$ composite,$^{12}$ introduction of a larger amount of oxynitride glass as a sintering additive accelerated the grain growth of elongated β-Si$_3$N$_4$,
4. Conclusions

In SiC-Si$_3$N$_4$ composites, the ambient fracture toughness was maximized (6.4 MPa·m$^{1/2}$) when Y-Mg-Si-Al-O-N oxynitride glass was used as a sintering additive. The improvement in fracture toughness was produced by enhanced bridging and deflection by Si$_3$N$_4$ grains. The interface strength of SiC-Si$_3$N$_4$ composites can be controlled by manipulating the sintering additive composition, which influences the chemistry of the glassy phase in the resulting ceramics, as in Si$_3$N$_4$ [21] and SiC ceramics. [10]

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REFERENCES


