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$_3$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.[1-4] 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.*[5] 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 flexible 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[6] reported the $\alpha \rightarrow \beta$ reverse transformation of SiC in SiC-20-wt%-Si$_3$N$_4$ composites that were fabricated via hot isostatic pressing. Kim and Mitomo[7] 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$_4$,

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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.[3-5] The oxide reacts with SiO$_2$, which is always present on the surface of SiC and Si$_3$N$_4$ particles, to form 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.[8-10]

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.[11] 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,[12] *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 860 MPa and 5.7 MPa·m$^{1/2}$, respectively. Previous studies[4,8-10,12] 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-Si_3N_4 composites was investigated for five different additive compositions; Al_2O_3-Y_2O_3-AlN, yttrium aluminum garnet (YAG), Al_2O_3-SiO_2-MgO, YAG-AlN, and Y-Mg-Si-Al-O-N oxynitride glass.

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 (99.9% pure, High Purity Chemicals, Osaka, Japan), MgO (99.99% pure, High Purity Chemicals, Osaka, Japan), Al_2O_3 (AKP-30, Sumitomo Chemicals, Tokyo, Japan), Y_2O_3 (99.9% pure, Shin-Etsu Chemical Co., Ltd, Tokyo, Japan), and AlN (Grade F, Tokuyama Soda Co., Tokyo, Japan) powders was prepared by ball milling the powders 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 good potential for crystallization control.[14] For other compositions, Al_2O_3, Y_2O_3, YAG (99.99% pure, High Purity Chemicals, Osaka, Japan), SiO_2, MgO, and AlN 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 N_2 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 Si_3N_4 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).[15] 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-Si_3N_4 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-Si_3N_4. These results show that α→β phase transformation of Si_3N_4, 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-Si_3N_4 composites with additives of different composition. SiC and Si_3N_4 grains are etched away, and consequently the microstructure is delineated by the grain boundary glass phase. The microstructure of SiC-Si_3N_4 composites consisted of randomly distributed, elongated β-Si_3N_4 grains and relatively equiaxed β-SiC grains. The Si_3N_4 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 Si_3N_4 led to the in situ growth of elongated β-Si_3N_4 grains. The β→α transformation of SiC was nearly suppressed, owing to the nitrogen-containing liquid.[16,17] The grain growth of SiC, which occurs via a solution-precipitation process (as evidenced by the core/rim structure in Fig. 1(e)),[18] appears to be hindered by the Si_3N_4 particles. In turn, the grain growth of Si_3N_4, which occurs via a solution-precipitation process,[19] is also hindered by the SiC particles.

Fig. 1 shows that relatively small (30-200 nm) SiC particles were trapped in the Si_3N_4 grains, which indicates Si_3N_4 has a faster growth rate than SiC. This result is similar to that obtained for the SiC-Si_3N_4 nanocomposites.[7,20] For the

Table 1. Batch Composition and Relative Density of Hot-pressed and Annealed SiC-Si_3N_4 Composites

| Sample designation | Batch composition (wt%) | | | | | | | | | Relative density (%) |
	β-SiC	α-Si_3N_4	Oxynitride†	Al_2O_3	Y_2O_3	YAG	SiO_2	MgO	AlN	
SCN1	53	35	12							99.6
SCN2	53	35				12				98.8
SCN3	53	35		3			7.2	1.8		98.2
SCN4	53	35				9			3	99.7
SCN5	53	35		1.81	8.01				2.18	99.8

†The composition of the oxynitride is $Y_{0.124}Mg_{0.160}Si_{0.414}Al_{0.302}O_{1.4}N_{0.151}$.
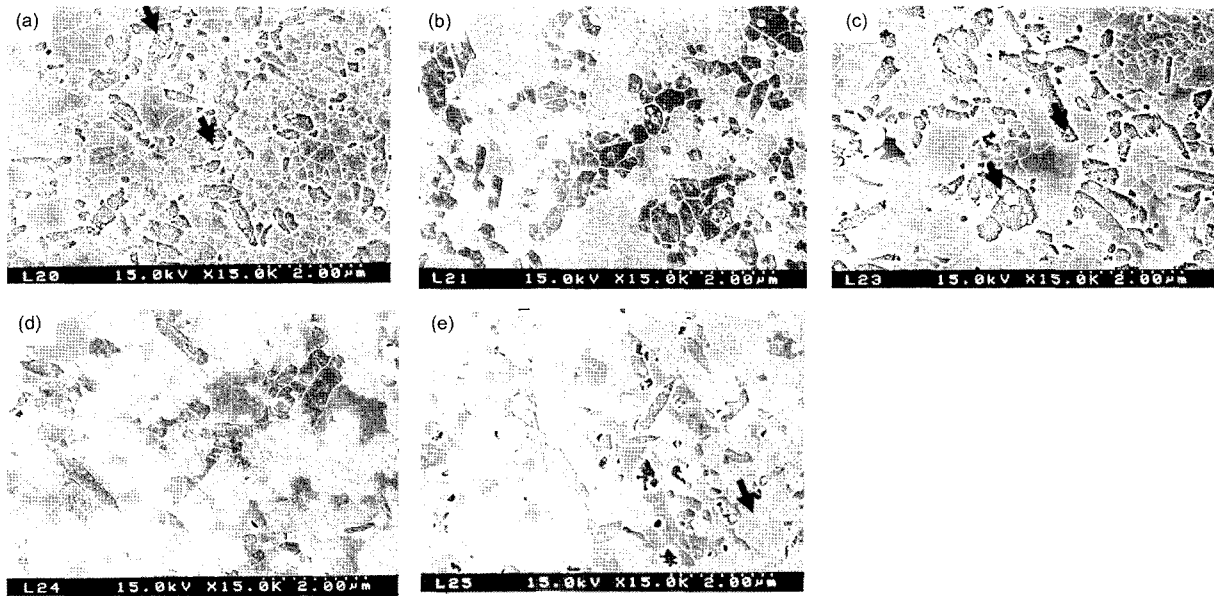
Fig. 1. Microstructures of the hot-pressed and annealed specimens: (a) SCN1, (b) SCN2, (c) SCN3, (d) SCN4, and (e) SCN5 (refer to Table I). Note the relative small (30-200 nm) SiC particles were trapped in the Si$_3$N$_4$ grains (marked by arrows in (a) and (c)). The arrow in (e) designates the core/rim structure in a SiC grain.

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-Si-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$^{1/2}$ and 4.4 MPa·m$^{1/2}$, respectively. A fracture toughness of 5.5 MPa·m$^{1/2}$ 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$^{1/2}$ 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.[7] A comparison of the toughness (6.4 MPa·m$^{1/2}$) of SCN1 with that of the specimens reveals that SiC-Si$_3$N$_4$ composite containing Y-Mg-Si-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$^{1/2}$, 3.8 MPa·m$^{1/2}$, and 4.4 MPa·m$^{1/2}$, respectively. Thus, the difference in fracture toughness between

Table 2. Grain Diameter and Aspect Ratio of Si$_3$N$_4$ Grains, and Fracture Toughness of the Hot-pressed and Annealed SiC-Si$_3$N$_4$ Composites

Sample designation	Diameter (μm)	Aspect ratio	Fracture toughness (MPa·m$^{1/2}$)
SCN1	0.23	1.9	6.4±0.2
SCN2	0.19	2.0	3.8±0.1
SCN3	0.21	2.2	5.3±0.3
SCN4	0.25	2.4	4.5±0.1
SCN5	0.18	2.3	4.4±0.2

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. 2(b) 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$^{1/2}$) than the others. The SiC-Si$_3$N$_4$ composite containing YAG (SCN2) showed the lowest fracture toughness of 3.8 MPa·m$^{1/2}$. 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.[16]

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$_4$
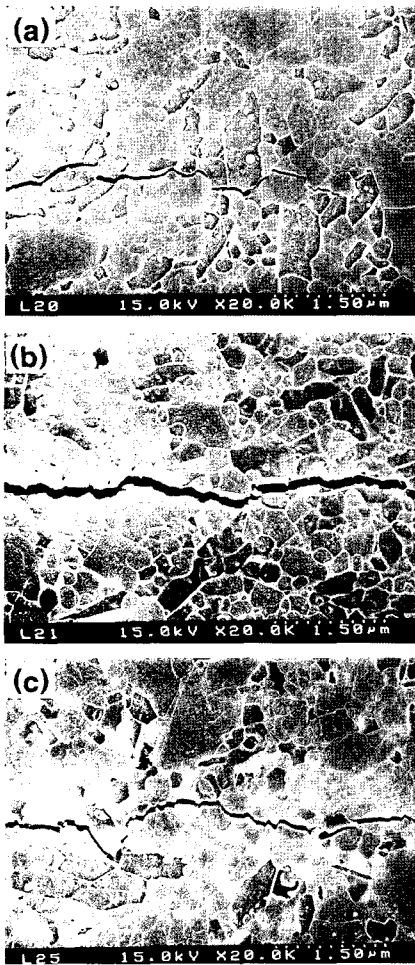
Fig. 2. SEM micrographs of crack paths induced by a Vickers indenter for (a) SC1, (b) SC2, and (c) SC5 (refer to Table 1).

grains with higher aspect ratio, resulting in improved fracture toughness. A maximal fracture toughness value of 5.7 MPa·m$^{1/2}$ was reported in a SiC-Si$_3$N$_4$ composite that contained 15 wt% oxynitride glass.[12] The toughness value (6.4 MPa·m$^{1/2}$) of the present SCN1 specimen containing 12 wt% oxynitride glass is higher than of previously reported data, although the amount of oxynitride glass is smaller than the composite. Note the difference in the fabrication procedure between the earlier and the present specimens. The earlier composite was fabricated by hot-pressing at 1800°C for 3 h with no further annealing. In contrast, the present composite was fabricated by hot-pressing at 1800°C for 4 h and subsequent annealing at 1900°C for 1 h. Thus, higher temperature annealing after hot-pressing was beneficial for improving the toughness in that it accelerated the grain growth of elongated β-Si$_3$N$_4$ grains with higher aspect ratio. The present results also suggest that the microstructural development and fracture toughness of the SiC-Si$_3$N$_4$ composites are strongly influenced by the sintering additive composition, which influences the chemistry of the glassy phase in the resulting ceramics.

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.[18]

Acknowledgement

REFERENCES

1. P. F. Becher, "Recent Advances in Microstructural Tailoring of Silicon Nitride Ceramics and the Effects on Thermal Conductivity and Fracture Properties," *J. Kor. Ceram. Soc.*, **42** [8] 525-31 (2005).
2. J. H. Kim, Y. G. Kim, and D. K. Kim, "Characterization of Subsurface Damage in Si$_3$N$_4$ Ceramics with Static and Dynamic Indentation," *J. Kor. Ceram. Soc.*, **42** [8] 537-41 (2005).
3. Y. S. Chun and Y.-W. Kim, "Possible Strategies for Micro-Structure Control of Liquid-Phase-Sintered Silicon Carbide Ceramics," *J. Kor. Ceram. Soc.*, **42** [8] 542-47 (2005).
4. Y.-W. Kim, S. H. Lee, T. Nishimura, and M. Mitomo, "Heat-Resistant Silicon Carbide with Aluminum Nitride and Scandium Oxide," *Acta Mater.*, **53** 4701-08 (2005).
5. D. Shaoming, J. Dongliang, T. Shouhong, and G. Jingkun, "Hot Isostatic Pressing of SiC/Si$_3$N$_4$ Composite with Rare Earth Oxide Additions," *Ceram. Int.*, **21** 451-55 (1995).
6. S. Turan and K. M. Knowles, "α→β Reverse Phase Transformation in Silicon Carbide in Silicon Nitride-Particulate-Reinforced Silicon Carbide Composites," *J. Am. Ceram. Soc.*, **79** [11] 2892-96 (1996).
7. Y.-W. Kim and M. Mitomo, "Fabrication and Mechanical Properties of Silicon Carbide-Silicon Nitride Nanocomposites," *J. Mater. Sci.*, **35** 5885-90 (2000).
8. J. Y. Kim, Y.-W. Kim, and J. G. Lee, "Effect of Grain Boundary Composition on Microstructure and Mechanical Properties of Silicon Carbide (in Korean)," *J. Kor. Ceram. Soc.*, **35** [9] 911-16 (1998).
9. S. H. Lee and Y.-W. Kim, "Effect of Additive Composition on Mechanical Properties of Silicon Carbide Sintered with Aluminum Nitride and Erbium Oxide," *J. Kor. Ceram. Soc.*, **42** [1] 16-21 (2005).
10. Y.-W. Kim, Y. S. Chun, T. Nishimura, M. Mitomo, and Y. H. Lee, "High-Temperature Strength of Silicon Carbide Ceramics Sintered with Rare-Earth Oxide and Aluminum Nitride," *Acta Mater.*, **55** 727-36 (2007).
11. Y.-W. Kim, Y. I. Lee, M. Mitomo, H. J. Choi, and J. G. Lee, "Fabrication and Mechanical Properties of Silicon Carbide-Silicon Nitride Composites with Oxynitride Glass," *J. Am.*

Ceram. Soc. **82** [4] 1058-60 (1999).

12. Y. I. Lee, Y.-W. Kim, H. J. Choi, and J. G. Lee, "Effects of Additive Amount on Microstructure and Mechanical Properties of Silicon Carbide-Silicon Nitride Composites," *J. Mater. Sci.,* **36** 699-702 (2001).

13. T. Rouxel and P. Verdier, "SiC Particle Reinforced Oxynitride Glass and Glass-Ceramic Composites: Crystallization and Viscoplastic Forming Ranges," *Acta Mater.,* **44** [6] 2217-25 (1996).

14. B. Baron, T. Chartier, T. Rouxel, P. Verdier, and Y. Laurent, "SiC Particle Reinforced Oxynitride Glass: Processing and Mechanical Properties," *J. Eur. Ceram. Soc.,* **17** 773-80 (1997).

15. S. G. Lee, Y.-W. Kim, and M. Mitomo, "Relationship between Microstructure and Fracture Toughness of Toughened Silicon Carbide Ceramics," *J. Am. Ceram. Soc.,* **84** [6] 1347-53 (2001).

16. Y.-W. Kim and M. Mitomo, "Fine-Grained Silicon Carbide Ceramics with Oxynitride Glass," *J. Am. Ceram. Soc.,* **82**

[10] 2731-36 (1999).

17. Y.-W. Kim, M. Mitomo, and G. D. Zhan, "Mechanism of Grain Growth in Liquid-Phase-Sintered β-SiC," *J. Mater. Res.,* **14** [11] 4291-93 (1999).

18. J. Y. Kim, Y.-W. Kim, M. Mitomo, G. D. Zhan, and J. G. Lee, "Microstructure and Mechanical Properties of a-Silicon Carbide Sintered with Yttrium-Aluminum Garnet and Silica," *J. Am. Ceram. Soc.,* **82** [2] 441-44 (1999).

19. M. Mitomo, R. J. Xie, and N. Hirosaki, "Materials Development in α-Sialon Ceramics," *J. Kor. Ceram. Soc.,* **43** [8] 451-57 (2006).

20. H. J. Park, H. E. Kim and K. Niihara, "Microstructure and High-Temperature Strength of Si$_3$N$_4$-SiC Nanocomposite," *J. Eur. Ceram. Soc.,* **18** [7] 907-14 (1998).

21. R. L. Satet and M. J. Hoffmann, "Influence of the Rare-Earth Element on the Mechanical Properties of RE-Mg-Bearing Silicon Nitride," *J. Am. Ceram. Soc.,* **88** [9] 2485-90 (2005).