Journal of the Korean Ceramic Society
Vol. 40, No. 9, pp. 832~836, 2003.

Effect of Silicon Nitride Whisker Content on the Flexural Strength of Silicon Nitride-Boron Nitride-Silicon Carbide Multi-Layer Composites

Dong-Soo Park† and Byung-Wook Cho

Ceramic Materials Group, Korea Institute of Machinery and Materials, Kyongnam 641-010, Korea

(Received July 31, 2003; Accepted August 13, 2003)

ABSTRACT

Multi-layer ceramic composites were prepared by tape casting followed by hot pressing using silicon nitride layer with silicon nitride whiskers, silicon nitride layer with silicon carbide particles and boron nitride-alumina layer. The whiskers were aligned during the casting. As the whisker content of the silicon nitride layer was increased up to 10 wt%, the flexural strength of the multi-layer composite was increased. However, further increase of the whisker content in the layer resulted in a rapid decrease of the strength of the composite. The results suggest that the strength of multi-layer ceramic composite showing non-catastrophic failure behavior can be significantly improved by incorporating the aligned whiskers in the layers.

Key words : ***β-silicon nitride whiskers, Alignment, Silicon nitride-boron nitride-silicon carbide, Multilayer composites, Flexural strength, Non-catastrophic failure***

1. Introduction

Introduction of weak interfaces to ceramics has been reported as a method to overcome their catastrophic failure.[1-3] Clegg *et al.* used graphite layer as the weak interface layer in SiC-C multi-layer composite that failed non-catastrophically.[1] Phillipps *et al.* built a model for fracture of ceramic laminates in order to find the optimum lamina thickness that is a function of interfacial toughness, lamina strength and Young's modulus.[2] Liu and Hsu prepared silicon nitride-boron nitride multi-layer composite that was conceptually similar to the above SiC-C multi-layer composite.[3] Since the above multi-layer composites failed gracefully, we can stop the fracture before complete failure if we can monitor the crack propagation by some means. Variation of electrical resistance has been employed for monitoring the fracture behavior of concrete.[4] In the previous reports, we also noticed that the electrical resistance of the multi-layer composite of silicon nitride-boron nitride-silicon carbide added silicon nitride was increased as the crack cuts the connectivity of silicon carbide particles during the fracture.[5,6] We also reported that the flexural strength of the multi-layer composite was improved by using silicon carbide whiskers instead of silicon carbide particles.[6]

Unlike silicon carbide whiskers, silicon nitride whiskers grew in silicon nitride matrix during sintering. In other words, we can increase the content of reinforcements by adding the silicon nitride whiskers instead of silicon carbide whiskers to silicon nitride matrix. In this study, we prepared multi-layer composites consisting of silicon nitride layer with silicon nitride whiskers, silicon nitride layer with silicon carbide particles and boron nitride-alumina layer. We examined the effect of the whisker content in the layer on the flexural strength of the multi-layer composite.

†Corresponding author : Dong-Soo Park
E-mail : pds1590@kmail.kimm.re.kr
Tel : +82-55-280-3345 Fax : +82-55-280-3399

2. Experimental Procedure

Fig. 1 shows the structures of the samples. Three kinds of samples were prepared by the same procedure as in the previous report.[6] Briefly, five kinds of slurries for tape casting were prepared with the ceramic ingredients shown in Table 1. Samples were prepared by stacking the tapes and were named according to the whisker content in the silicon nitride tape. In other words, sample 5W consisted of the repeated stacking unit of tape 5W-tape 20P-tape 5W-tape BN. In case of samples 10W and 20W, tapes 10W and 20W were used instead of tape 5W, respectively. The tapes were about 150 μm thick, and the sample thickness was 9 mm. There were about 60 layers in each sample. Both top and bottom layers of the samples were the layers with the aligned whiskers. Since the whiskers were aligned during the casting, we carefully stacked the tapes not to disturb the alignment of the whiskers between the tapes. Samples were hot pressed at 2073 K for 1.5 h under 30 MPa following binder removal procedure. The hot pressed samples were ground and cut parallel to the alignment directions to make the bend bars. Four large surfaces of the bend bars were polished to 1 μm diamond slurry and their four long edges were ground off using a diamond disc. The three point flexural strength was carried out using 20 mm span and the cross-head speed was 0.5 mm/min. During the flexure test,

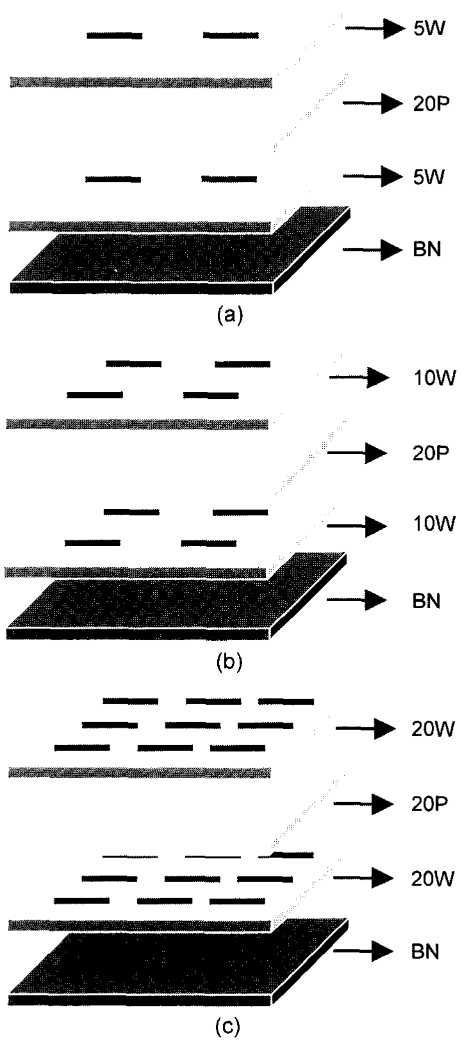

Fig. 1. Structure of the sample; the difference among the samples was the silicon nitride whisker content in the silicon nitride layer; (a) sample 5W, (b) sample 10W, and (c) sample 20W.

Table 1. Compositions of Ceramic Ingredients of the Tapes (wt%)

	α-Si_3N_4 powder[1]	Y_2O_3 powder[2]	Al_2O_3 powder[3]	β-Si_3N_4 whisker[4]	β-SiC powder[5]	BN powder[6]
Tape 5W	87	6	2	5	–	
Tape 10W	82	6	2	10		
Tape 20W	72	6	2	20		
Tape 20P	72	6	2	–	20	
Tape BN	–	–	88	–	–	12

[1]SN-E10, Ube Industries Ltd., Yamaguchi, Japan.
[2]Grade C, H.C.Starck Co., Berlin, Germany.
[3]AKP-30, Sumitomo Chemical Co., Osaka, Japan.
[4]SN-WB, Ube Industries Ltd., Yamaguchi, Japan.
[5]UF, Ibiden Do, Tokyo, Japan.
[6]A01, H.C.Starck Co., Berlin, Germany.

the load-displacement data were acquired for examining the fracture behavior. Surface of the sample parallel to both the casting direction and the lamination force direction was examined after plasma etching with 95% O_2-5% CF_4.

3. Results and Discussion

Fig. 2(a)-(c) clearly demonstrate that the sample consisted of three kinds of layers. Bright contrast layers were BN-Al_2O_3 layers. The layer next to BN-Al_2O_3 layer was silicon nitride layer with the silicon nitride whiskers. The other layer in uniform gray contrast was silicon nitride layer with silicon carbide particles. Tape casting aligned the whiskers and silicon nitride with the aligned whiskers was reported to exhibit higher strength than that of silicon nitride without the whisker.[7,8] Fig. 2(a)-(c) show that the amount of the aligned grains in silicon nitride layer with the silicon nitride whiskers was increased as the whisker content of the layer was increased. A closer examination of the layer with the whiskers revealed that some of the grains had "core-rim" structure in Fig. 2(d). The core was reported to correspond to the whisker and the rim was sialon that represented growth of the grains around the whiskers.[9] Fig. 3(a) shows the XRD patterns from the surface normal to the whisker alignment direction. Although there were small peaks for BN and β-SiC, all the major peaks correspond to β-Si_3N_4. The strong (002) peaks of β-Si_3N_4 in the XRD patterns of Fig. 3(a) resulted in part from the grains growing from the aligned whiskers. Fig. 3(b) shows the ratio of (002) peak intensity to the sum of (210) peak intensity and (200) peak intensity. As the volume fraction of the elongated grains parallel to the casting direction was increased, the above intensity ratio of the peaks was increased. Volume fraction of the grains parallel to the alignment direction was increased as the whisker content of the sample was increased. However, Fig. 3(b) also shows that the peak intensity ratio was not proportional to the whisker content. In other words, the fraction of the whiskers lying exactly parallel to the casting direction was decreased as the whisker content was increased. It seemed that perfect alignment of individual whisker was hindered by entanglement with the other whiskers at high whisker concentration.

Fig. 4 shows the three point flexural strength of the samples. For comparison, the three point flexural strength of the previously reported sample without the whisker addition is also shown in Fig. 4.[6] The low strength of the comparison sample in Fig. 4 was similar to the strength values of the silicon nitride/boron nitride multiplayer composite reported by Liu and Hsu.[3] It seemed that non-catastrophic failure of silicon nitride/boron nitride multiplayer composite occurred at the expense of the strength of monolithic silicon nitride. Although there were three different layers in each sample and the layer with silicon nitride whiskers occupied about a half of the total volume of the sample, the flexural strength of the sample was dependent on the whisker content of the layer. By incorporation of the whiskers, the flex-

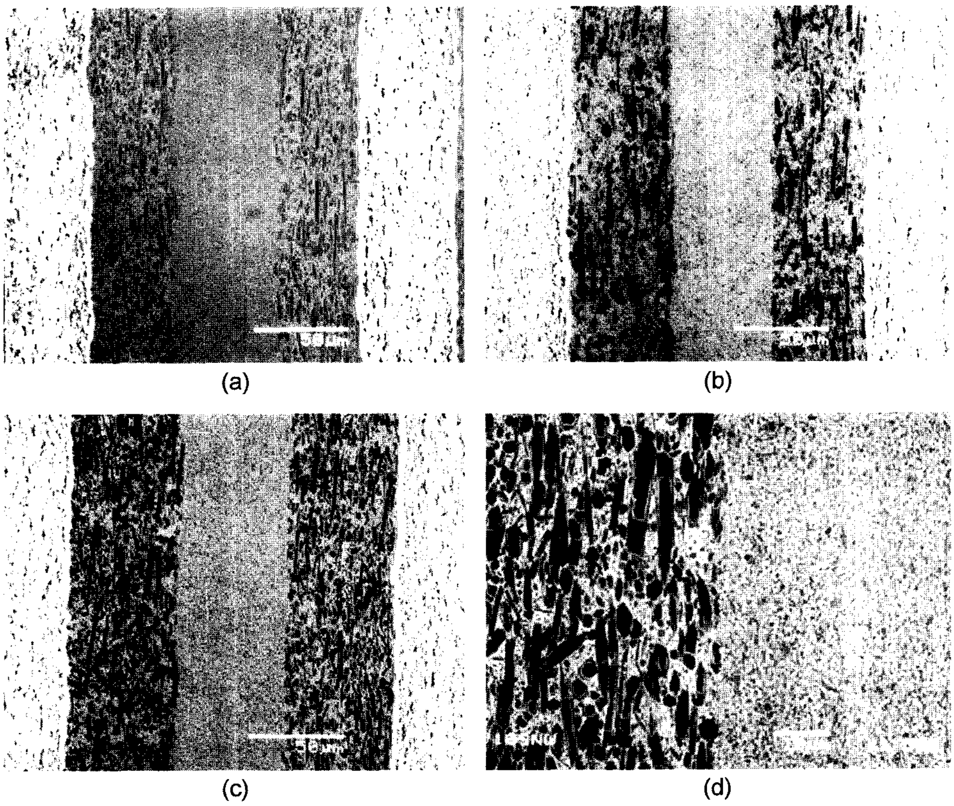

Fig. 2. SEM micrographs of the samples; (a) sample 5W, (b) sample 10W, (c) sample 20W, and (d) boundary region between silicon nitride with silicon nitride whiskers and silicon nitride with silicon carbide particles of sample 10W.

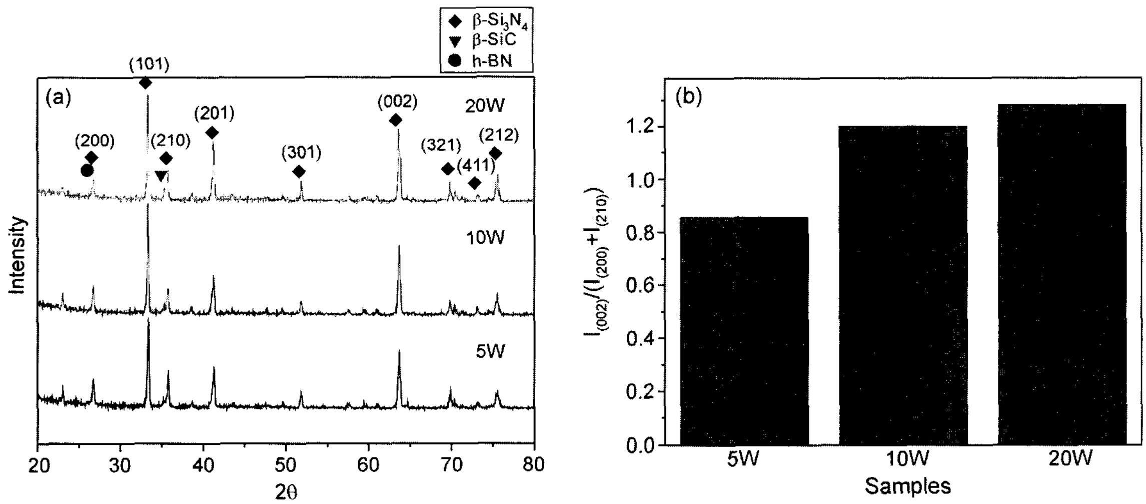

Fig. 3. XRD patterns from the surface normal to the whisker alignment direction (a) and variation of the ratio of the (002) peak intensity to sum of the (210) peak intensity and the (200) peak intensity (b).

ural strength was improved by up to 1.85 times. The flexural strength of the multi-layer composite was increased as the silicon nitride whisker content in the silicon nitride layer was increased up to 10 wt%. Then, it was decreased rapidly for further addition of the whiskers to the layer. One of the possible reasons for the strength decrease between sample 10W and sample 20W is entanglement of the large grains growing from the whiskers. Imamura *et al.* reported that the flexural strength of silicon nitride with aligned elongated grains was rapidly decreased when those large elongated grains occupied more than 50 vol% of the sample.[10] Fig. 2(b) shows that the large elongated grains already occupied more than 50 vol% of sample 10W. It seems that the critical volume fraction of the large elongated grains for the strength decrease depended on the degree of alignment of those grains among others. Both hot pressing and the whiskers for making our samples were suspected to improve the alignment of the large elongated

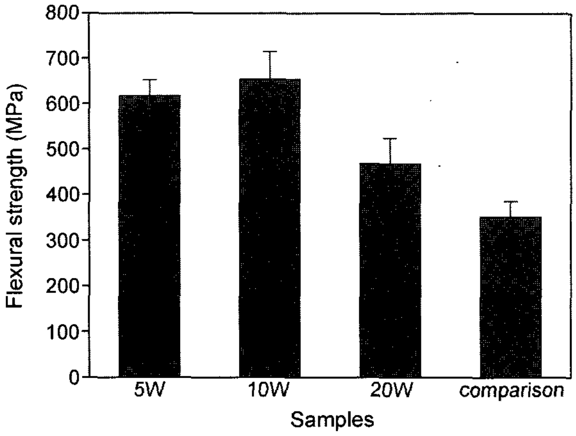

Fig. 4. The three point flexural strengths of the samples; the strength of the reference sample was from the previous report.[6]

grains growing from the seeds compared with Imamura *et al.*'s sample.[10]

Fig. 5(a)-(c) show fracture behaviors of samples 5W, 10W, 20W. Each sample exhibited multiple fractures to complete failure. In other words, the multi-layer ceramic composites were failed non-catastrophically. The main reason for the non-catastrophic failure was the weak BN-Al_2O_3 interface layer that deflected the crack propagation. However, the number of serrations of the load-displacement curve was less than that of BN-Al_2O_3 layers. Phillipps *et al.* described that a large load drop often involved failure of a number of layers at once.[2] That happened when the layer had substantially higher failure strength than the subsequent ones. Although the thickness and the composition of silicon nitride layers in the current samples were the same, the strengths of the layers were different from one another. That is basically due to the statistical nature of the flexural strength of ceramics. Fig. 6 shows the crack in sample 10W. The crack started from the top and deflected much at the interface between BN-Al_2O_3 layer and silicon nitride layer with silicon nitride whiskers. Then, the crack was deflected again at the interface between silicon nitride layer with silicon nitride whiskers and silicon nitride layer with silicon carbide particles. However, the crack was not deflected when it propagated from silicon nitride layer with silicon carbide particles to silicon nitride layer with silicon nitride whiskers. Choi *et al.* reported that a significant residual stress developed in the layers of a tri-layer composite consisting of silicon nitride layers and silicon nitride-silicon carbide particle layer.[11] The residual stress resulted from difference in the thermal expansion coefficients of the two layers in contact. Since the linear thermal expansion coefficient of silicon carbide was larger than that of silicon nitride, the silicon nitride layer with 20 wt% silicon carbide particles had tensile residual stress while silicon nitride layer with silicon nitride whiskers had compressive residual stress at their interface. Therefore, the crack approaching the interface between the two layers from silicon nitride

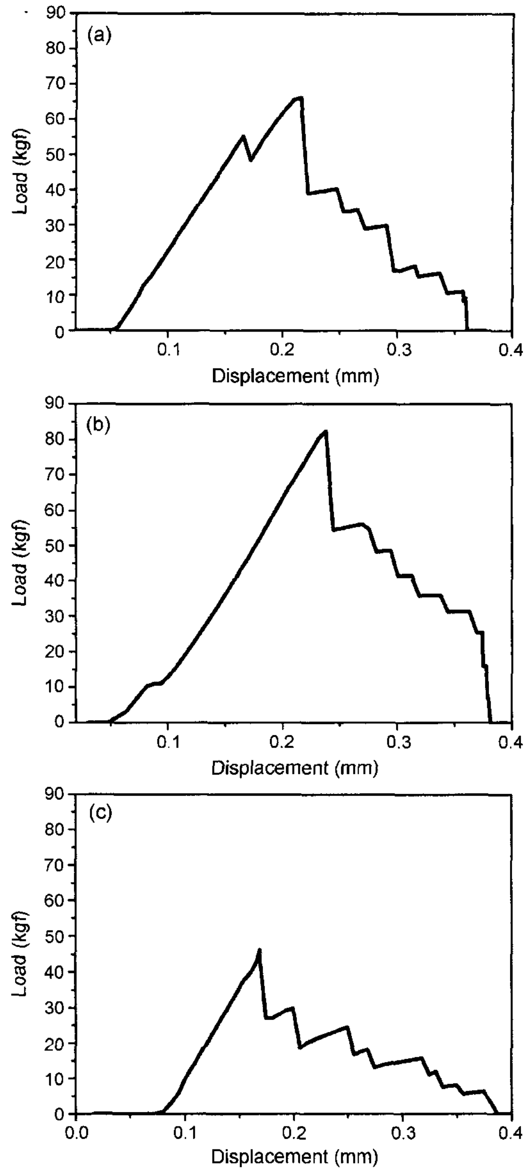

Fig. 5. Fracture behaviors of the samples; (a) sample 5W, (b) sample 10W, and (c) sample 20W.

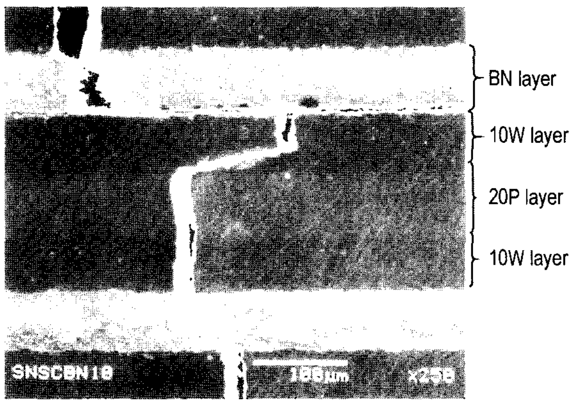

Fig. 6. The crack propagation through the sample during the flexure test; the top surface was under the tensile stress; the surface was not etched.

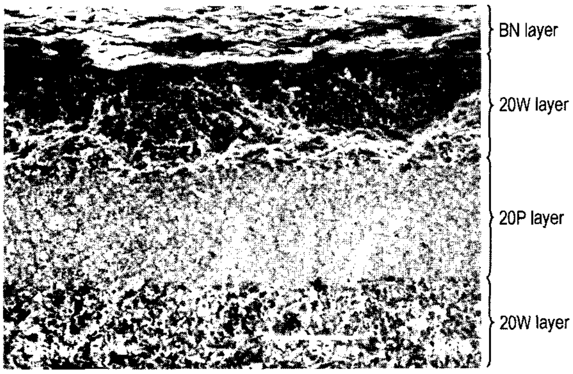

Fig. 7. Fracture surface of sample 20W showing the three kinds of layers.

layer with silicon nitride whiskers was deflected due to the residual compressive stress near the interface. On the other hand, the crack approaching the same interface from silicon nitride layer with silicon carbide particles cut the silicon nitride layer with silicon nitride whiskers due to the tensile residual stress. Fig. 7 shows the fracture surface of sample 20W. The top layer was $BN+Al_2O_3$ layer that contained many fine BN platelets. Those platelets appeared lying parallel to the casting surface. The second top layer was silicon nitride layer with silicon nitride whiskers. It appeared rough, suggesting the crack propagation was interfered with the large elongated grains. The third layer from the top was silicon nitride layer with silicon carbide particles. Unlike the second layer, the fracture surface of the third layer appeared smooth and there seemed little interaction between the crack and the microstructure.

4. Summary

Multi-layer ceramic composites containing silicon nitride layer with silicon nitride whiskers, silicon nitride layer with silicon carbide particles and boron nitride-alumina layer were prepared by tape casting and hot pressing. The multi-layer composites exhibited non-catastrophic failure behavior due to the presence of weak boundary phase, *i.e.* $BN-Al_2O_3$ layer. Silicon nitride whiskers were highly aligned in the casting direction. The aligned whiskers grew during sintering and were contributed to improving the flexural strength. The flexural strength of the multi-layer composite with silicon nitride layer with 10 wt% silicon nitride whiskers exhibited the highest strength. The crack was deflected within the weak $BN-Al_2O_3$ layer as well as the interface between silicon nitride layers with silicon nitride whiskers and with silicon carbide particles. The fracture surface showed that the crack propagation was interfered with the large elongated grains of silicon nitride layer with silicon nitride whiskers.

Acknowledgement

This work is supported by NRL program of Korean Ministry of Science and Technology.

REFERENCES

1. W. J. Clegg, K. Kendall, N. M. Alford, T. W. Button, and J. D. Birchall, "A Simple Way to Make Tough Ceramics," *Nature,* **347** 455-47 (1990).
2. A. J. Phillips, W. J. Clegg, and T. W. Clyne, "Fracture Behavior of Ceramic Laminates in Bending-I. Modelling of Creack Propagation," *Acta. Metall. Mater.*, **41** 805-17 (1993).
3. H. Liu and S. M. Hsu, "Fracture Behavior of Multilayer Silicon Nitride/Boron Nitride Ceramics," *Am. Ceram. Soc.*, **79** 2452-57 (1996).
4. N. Muto, H. Yanagida, T. Nakatsuji, M. Sugita, Y. Ohtsuka, Y. Arai, and C. Saito, "Materials Design of CFGFRP-reinforced Concretes with Diagnosing Function for Preventing Fatal Fracture," *Adv. Comp. Mater.*, **4** [4] 297-308 (1995).
5. D.-S. Park, H.-D. Kim, B.-D. Han, T.-W. Roh, C. Park, B.-W. Cho, and H.-C. Park, "Variation of Electrical Resistance during Fracture of Silicon Nitride-Silicon Carbide Whisker-Boron Nitride Laminate Composite," *J. Mater. Sci.*, **21** 1047-49 (2002).
6. B.-W. Cho, D.-S. Park, and H.-C. Park, "Fracture Behavior of Silicon Nitride-Silicon Carbide-Boron Nitride Multi-Layer Composites with Different Layer Thickness," *J. Kor. Ceram. Soc.*, **39** [7] 622-27 (2002).
7. D.-S. Park and C.-W. Kim, "A Modification of Tape Casting for Aligning the Whiskers," *J. Mater. Sci.*, **34** 5827-32 (1999).
8. D.-S. Park, M.-J. Choi, T.-W. Roh, H.-D. Kim, and B.-D. Han, "Orientation-dependent Properties of Silicon Nitride with Aligned Reinforcing Grains," *J. Mater. Res.*, **15** [1] 130-35 (2000).
9. D.-S. Park, T.-W. Roh, B. J. Hockey, Y. Takigawa, B.-D. Han, H.-D. Kim, and Y. Yasutomi, "Two Cores in One Grain in the Microstructure of Silicon Nitride Prepared with Aligned Whisker Seeds," *J. Euro. Ceram. Soc.*, **23** 555-60 (2003).
10. H. Imamura, K. Hirao, M. E. Brito, M. Toriyama, and S. Kanzaki, "Mechanical Properties of Silicon Nitride with Anisotropic Microstructures," *J. Ceram. Soc. Jpn.*, **104** [8] 748-51 (1996).
11. B.-J. Choi, Y.-H. Koh, and H.-E. Kim, "Mechanical Properties of Si_3N_4-SiC Three Layer Composite Materials," *J. Am. Ceram. Soc.*, **81** [10] 2725-28 (1998).