Journal of the Korean Ceramic Society
Vol. 39, No. 8, pp. 715~720, 2002.

# Effect of the Amount of the Sintering Additives on the Microstructural Development and the Mechanical Properties of Silicon Nitride with Aligned Whisker Seeds

**Byoung-Chan Bae**, Dong-Soo Park,†* Hai-Doo Kim*, Byung-Dong Han*, Chan Park** and Linhua Zou*****

**Ceramic Materials Group, Korea Institute of Machinery and Materials, Kyong-Nam 641-010, Korea*
***Department of Materials Science and Engineering, Pukyong National University, Pusan 608-739, Korea*
****Department of MSE, Tsinghua University, Beijing, China*
(Received July 22, 2002; Accepted August 7, 2002)

**ABSTRACT**

Silicon nitride samples with aligned whisker seeds were prepared with different amounts of yttria and alumina as the sintering additives. Their sintering behaviors and the microstructural developments between 2123 K and 2323 K were examined. The sample with larger amount of the sintering additives showed faster densification and grain growth. Even though addition of the aligned whisker seeds slightly retarded densification of silicon nitride, it improved the flexural strength and the fracture tou ghness. Both the flexural strength and the fracture toughness of silicon nitride with the aligned whisker seeds were increased as the amount of the sintering additives was increased.

***Key words*** **: Silicon nitride, Sintering additives, Microstructural development, Mechanical properties**

## 1. Introduction

Silicon nitride has been widely studied mainly due to the excellent mechanical properties including high strength, high fracture toughness, high thermal shock resistance and others. Recently, it was found that silicon nitride exhibited high thermal conductivity if it was specially prepared.[1-5] In order to make silicon nitride with high thermal conductivity, it is important to let the grains grow to an extremely large size. Growing the extremely large grains usually requires the heat treatment at high temperature for a long time. Hayashi *et al.* grew the grain with the width as large as 18 μm by sintering silicon nitride doped with 2 wt% $Yb_2O_3$ and 5 wt% $MgSiN_2$ at 2173 K for 48 h.[1] Extremely large grains were also found in silicon nitride doped with very small amount of the sintering additives. Park *et al.* reported that grains with the width as large as 28 μm grew in silicon nitride doped with 0.375 mol % $Y_2O_3$ and 0.5 mol % $HfO_2$.[6] Lee *et al.* also found that the widths of some grains in silicon nitride doped with 4 wt% $Yb_2O_3$ were about 10 μm after sintering at 2223 K for 2 h.[7] Hirosaki *et al.* examined the microstructural change and thermal conductivity of silicon nitride according to the amount of the sintering additives.[2] They reported that the grains grew to larger sizes and the thermal conductivity was increased as the amount of the sintering additives was decreased. So, it seems beneficial to growing the grains to extremely large sizes to reduce the amount of the sintering additives. In this study, silicon nitride samples with aligned whisker seeds were prepared with different amounts of the sintering additives. Their sintering behaviors and microstructural developments were investigated. Also, the mechanical properties of the fully dense samples were measured.

†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

Four kinds of samples were prepared according to the amounts of the sintering additives. Table 1 shows the samples and their compositions. The samples were prepared by a modified tape casting method[8] for enhanced alignment of the whisker seeds. Details of the slurry preparation, tape casting, stacking, lamination, binder burn-out and cold isostatic pressing procedure were described in a previous report.[8] The samples were sintered under the conditions of 2123 K-1MPa $N_2$, 2223 K-2 MPa $N_2$, 2273 K-3 MPa $N_2$ and 2323 K-4 MPa $N_2$ for 2 h. Density of the sintered sample was measured using the water immersion method if the sample was dense enough not to absorb water. In case where the sample was not dense enough for the water immersion method, the density was obtained by measuring the dimensions and the weight. The samples except sample 0.8Y0.4A were sintered at 2273 K for 4 h for studying the mechanical properties.

Sintered samples were cut perpendicular to the casting direction. The cut surfaces were polished to 1 μm diamond slurry and then plasma etched using 95% $O_2$ 5% $CF_4$ gas

**Table 1.** Compositions of the Samples (wt%)

| | 0.8Y0.4A | 1.6Y0.7A | 2.4Y1.1A | 4.8Y2.2A | 1.6Y0.7AP | 4.8Y2.2AP |
|---|---|---|---|---|---|---|
| $Si_3N_4$[a] | 95.8 | 94.7 | 93.5 | 90 | 97.7 | 93 |
| $Y_2O_3$[b] | 0.8 | 1.6 | 2.4 | 4.8 | 1.6 | 4.8 |
| $Al_2O_3$[c] | 0.4 | 0.7 | 1.1 | 2.2 | 0.7 | 2.2 |
| β-$Si_3N_4$ whisker[d] | 3 | 3 | 3 | 3 | 0 | 0 |

[a]SN-E10, Ube Industries Co., Ltd., Tokyo, Japan (α: >95%).
[b]Grade C, H. C. Starck Co., Berlin, Germany.
[c]AKP-30, Sumitomo Chemical Co., Osaka, Japan.
[d]SN-WB, Ube Industries Co., Ltd.

mixture. The etched surfaces were observed using SEM. X-Ray Diffraction analysis (XRD) was performed on the surface perpendicular to the casting direction. The relative intensity of (002) peak of β-$Si_3N_4$ that was defined as (002) peak intensity divided by intensity sum of 11 major peaks of the XRD pattern was obtained. Vickers indentation using 196 N load was performed on the casting surface to obtain the fracture toughness according to Evans and Charles equation.[10] Ten indentations were performed for each sample and statistics of the ten data were used. The three point flexural strength was measured using the samples with 4 mm×3 mm×24 mm dimensions at room temperature. The length direction of the bend bar was parallel to the casting direction. The surfaces were polished to 1 μm diamond slurry and the edges were chamfered. The cross-head speed was 0.5 mm/min and the span was 20 mm. Five measurements of the flexural strength were carried out and their statistics was used. For comparison of the mechanical properties, two kinds of samples without addition of the whisker seeds were also prepared in the same way as the previous samples and were sintered at 2273 K for 4 h; the samples were sintered with 1.6 wt% $Y_2O_3$ and 0.7 wt% $Al_2O_3$ and with 4.8 wt% $Y_2O_3$ and 2.2 wt% $Al_2O_3$, respectively. The former comparative sample is named as 1.6Y0.7AP and the latter as 4.8Y2.2AP.

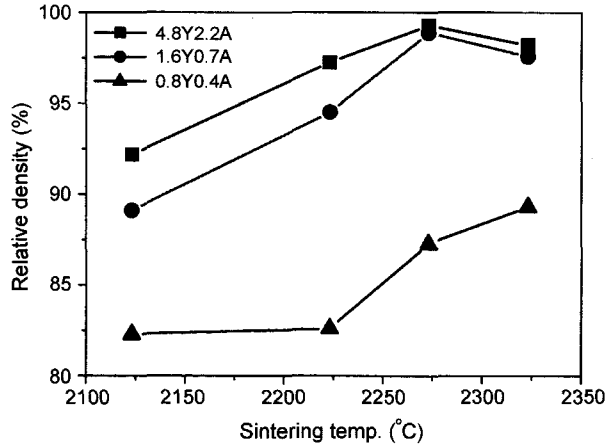


**Fig. 1.** Variations of the densities of the samples with aligned whisker seeds; sintering was performed for 2 h at the temperature.

## 3. Results and Discussion

Fig. 1 shows variations of the densities of the three samples according to the sintering temperature. Densities of samples 4.8Y2.2A and 1.6Y0.7A reached to 99% at 2273 K and then were decreased to about 98% at 2323 K. Sample 0.8Y0.4A showed very slow densification and did not reach to a full density even at 2323 K. Density of sample 0.8Y0.4A sintered at 2323 K was 89.3% and was close to that of sample 1.6Y0.7A sintered at 2123 K. Figs. 2 and 3 show the microstructures of the samples observed on the surfaces perpendicular to the casting direction. Even though total amount of the pores within sample 0.8Y0.4A was decreased as the sintering temperature was increased, the sample still contained a significant amount of pores after sintering at 2323 K. Figs. 2(b)-(d) show that there were well-defined hexagonal grains in the microstructures of the samples. Those hexagonal grains represent rod-like β-silicon nitride grains. Growth of the rod-like grains was reported to decrease sinterability.[10] Sizes of the pores in sample 0.8Y0.4A were decreased as the sintering temperature was increased to 2273 K, then were slightly increased between 2273 K and 2323 K. Even though the large grains exhibited a significant growth at high sintering temperatures, no such extra-large grain as reported in the literatures[6,7] was observed from the microstructure of sample 0.8Y0.4A. It is not clear at this point why the extra-large grains were not formed in sample 0.8Y0.4A although there was huge difference in the sizes of the starting powder and the whisker seeds. One possible explanation is that the liquid formed by the addition of the sintering additives, i.e. yttria and alumina and silica wetted the particles well. The extra-large grains were found only when the liquid did not wet the particles well and was inhomogeneously distributed within the sample.[6] Fig. 3(a) shows that many grains of sample 4.8Y2.2A had the cores representing the whisker seeds. In other words, the whisker grains grew even though there were many pores within the sample. Figs. 3(b)-(d) show almost no pore in the microstructures of the sample sintered at 2223 K and above. The large grains grew while the matrix grains did not show a significant growth between 2223 K and 2273 K as shown in Fig. 3(b) and (c). At 2323 K, both the large grains and the matrix grains grew significantly. Size of the large grains in sample 4.8Y2.2A was larger than

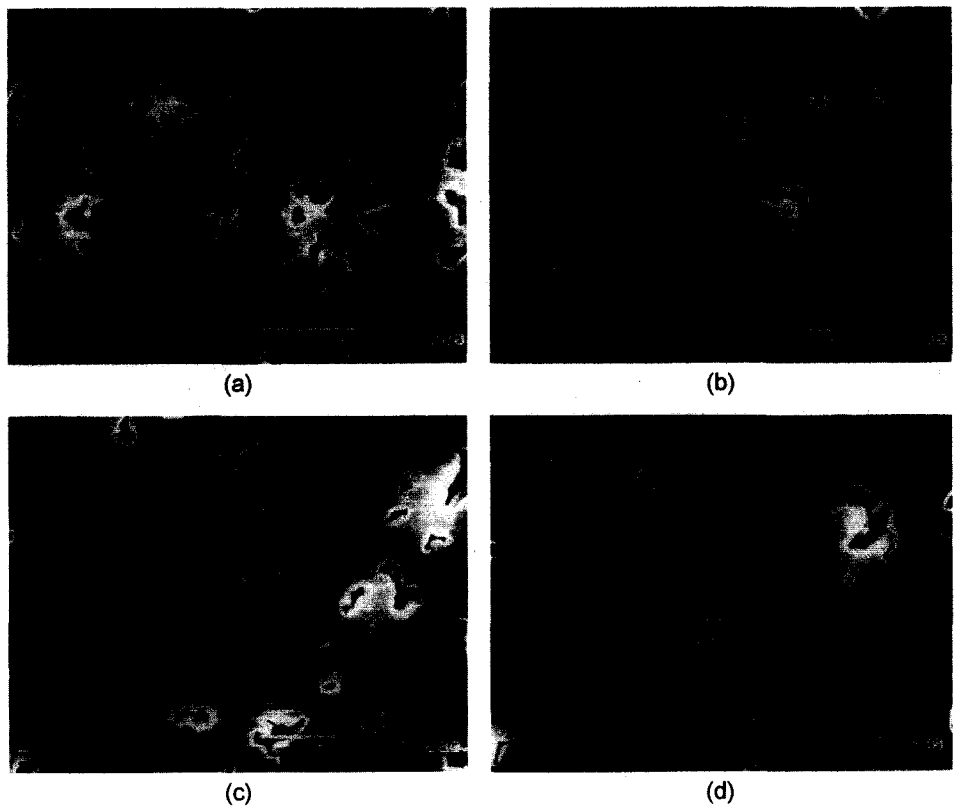


**Fig. 2.** SEM micrographs of sample 0.8Y0.4A after plasma etching; the sample sintered for 2 h at (a) 2123 K, (b) 2223 K, (c) 2273 K and (d) 2323 K.

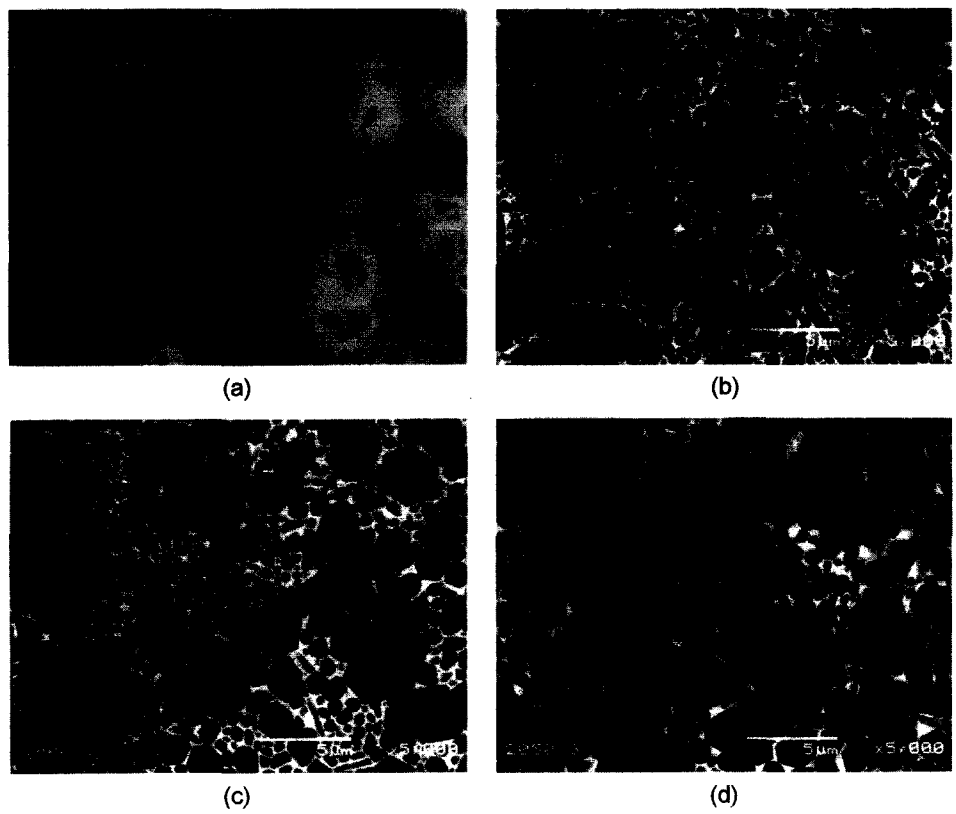


**Fig. 3.** SEM micrographs of sample 4.8Y2.2A after plasma etching; the sample sintered for 2 h at (a) 2123 K, (b) 2223 K, (c) 2273 K and (d) 2323 K.

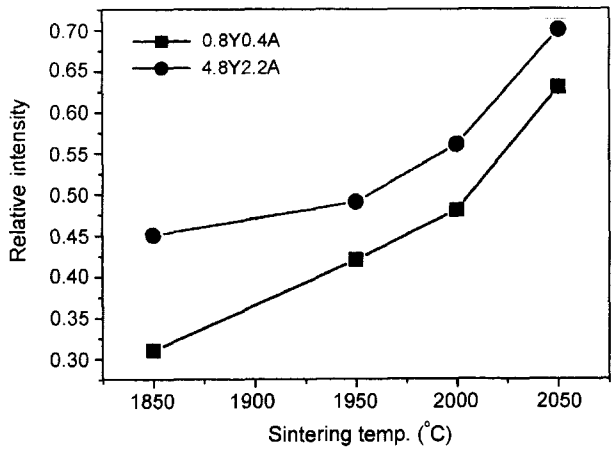


**Fig. 4.** Variations of the relative intensities of (002) peak of samples 1.6Y0.4A and 4.8Y2.2A according to the sintering temperature.

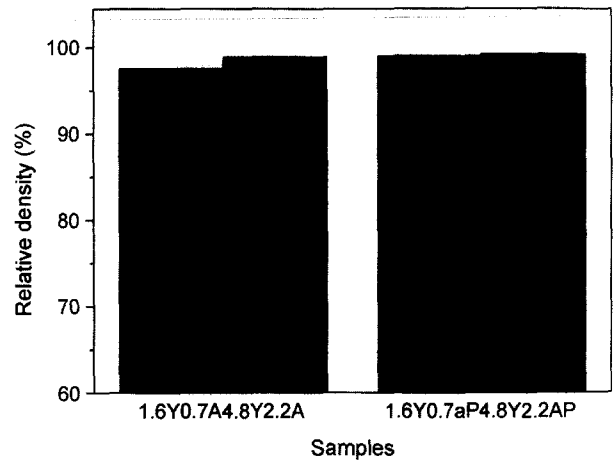


**Fig. 5.** Relative density of the samples sintered at 2273 K for 4 h.

that in sample 0.8Y0.4A when the two samples were sintered at the same temperature. When the extra-large grains were observed from silicon nitride, their number density and size were increased as the amount of the sintering additives was decreased.[6] Therefore, the microstructural development of the current sample is different from that of the previously reported silicon nitride with the extra-large grains.

Fig. 4 shows variations of the relative intensities of (002) peaks of samples 0.8Y0.4A and 4.8Y2.2A. Since the grains growing from the whisker seeds were aligned perpendicular to the diffracting surface, they were the major contributors to the strong (002) peak of the XRD pattern. In other words, variation of the relative intensity of (002) peak corresponded qualitatively to that of the volume fraction of the grains growing from the whisker seeds. Since the large grains grew at the expense of the small matrix grains, increase of the relative intensity of (002) peak was accelerated as they grew larger at higher sintering temperatures.

Densities of the samples sintered at 2273 K for 4 h are shown in Fig. 5. Samples 1.6Y0.7A and 4.8Y2.2A were sintered to 97.5% TD and 99% TD, respectively. Meanwhile, the comparative samples 1.6Y0.7AP and 4.8Y2.2AP were sintered to 99% TD and 99.2% TD, respectively. The above results show that the presence of the whisker seeds inhibited densification even though the whiskers were aligned during tape casting. Fig. 6 shows the linear sintering shrinkage anisotropy of the samples. The sample with the whisker seeds exhibited a strong anisotropy of the linear sintering shrinkage. The shrinkage along the lamination force direction was the highest among the three directions shown in Fig. 6. Comparison of the linear sinter shrinkage of the samples with and without the whisker seeds reveals that the sample with the whisker seeds exhibited much larger shrinkage in the lamination force direction than the comparative sample without the whiskers. The linear sintering shrinkage can be considered to result from removal of the pores in the direction of measurement during sintering. Since the two samples were prepared in the same way, there is no reason why the sample with the whisker seeds contained more pores between the laminated layers than that without the whisker seeds before sintering. As previously mentioned, some of the whisker seeds were not

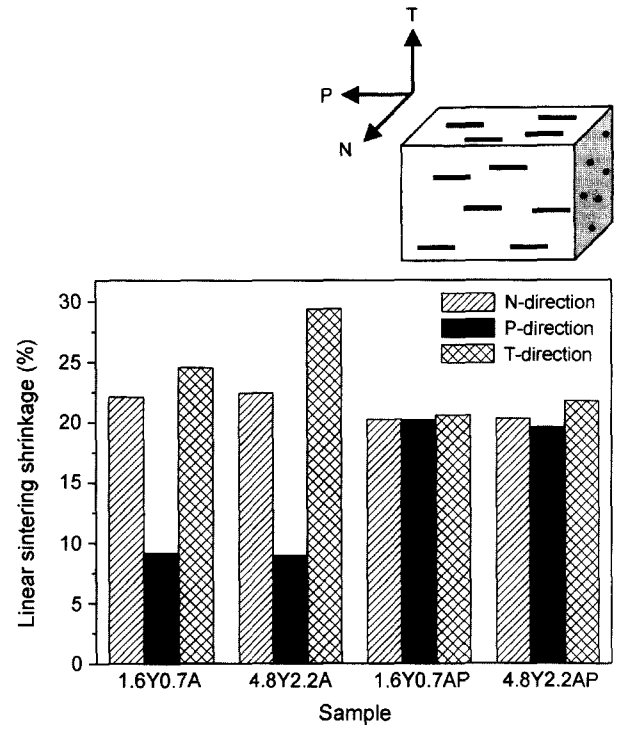


**Fig. 6.** The linear sintering shrinkage of the samples in the three directions; sintering was performed at 2273 K for 4 h; the diagram shows the three directions in which the shrinkage was measured; P-, N- and T-directions correspond to the casting direction, perpendicular to the casting direction and the lamination force direction, respectively.

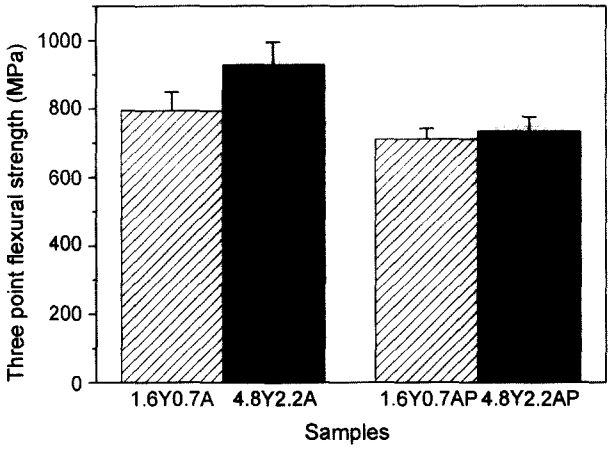


**Fig. 7.** The three point flexural strengths of the samples sintered at 2273 K for 4 h.

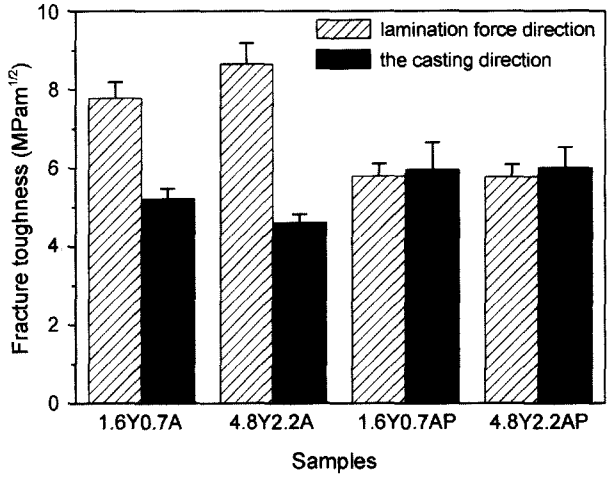


**Fig. 8.** The fracture toughness of the samples sintered at 2273 K for 4 h.

aligned and their entanglement within the casting plane interfered with the shrinkage within the plane. Meanwhile, almost all the whiskers were laid down on the casting plane during the casting and the entanglement among the whiskers in the different layers was greatly reduced. Therefore, densification of the samples with the whisker seeds was accomplished by a large shrinkage in the lamination direction.

Fig. 7 shows the flexural strengths of the samples sintered at 2273 K for 4 h. The samples with the whiskers exhibited higher strengths than the corresponding comparative samples even though they have lower densities than the comparative samples. The flexural strength of sample 4.8Y2.2A was 927 ± 68 MPa while that of sample 1.6Y0.7A was 794 ± 55 MPa. The latter sample exhibited lower strength than the former sample in part due to the lower density. Meanwhile, the comparative samples exhibited similar strength, about 720 MPa. The fracture toughness of the sample with the whiskers was highly anisotropic as shown in Fig. 8. The fracture toughness anisotropy was stronger for sample 4.8Y2.2A than for sample 1.6Y0.7A. Further study is needed to clarify the reason why the fracture toughness anisotropy was increased as the amount of the sintering additives was increased. Since the boundary among the aligned grains was reported to form a sub-grain boundary without the intergranular glassy film,[11] it will be interesting to study the high temperature strength of silicon nitride with the aligned whisker seeds.

## 4. Conclusions

Silicon nitride with aligned whisker seeds was sintered with various amounts of yttria and alumina as the sintering additives. Even though some samples contained only 0.8 wt% yttria and 0.4 wt% alumina, no extra-large grain was observed. The sample with smaller amount of the sintering additives showed slower densification and grain growth. Addition of the aligned whiskers to silicon nitride improved the flexural strength and the fracture toughness in the specific direction even though it hindered the densification. Both the flexural strength and the fracture toughness anisotropy were increased as the amount of the sintering additives was increased.

## Acknowledgement

This work has been in part supported by NRL program of Korea Ministry of Science and Technology.

## REFERENCES

1. H. Hayashi, K. Hirao, M. Toriyama and S. Kanzaki, "$MgSiN_2$ Addition as a Means of Increasing the Thermal Conductivity of β-Silicon Nitride," *J. Am. Ceram. Soc.*, **84** [12] 3060-62 (2001).
2. N. Hirosaki, Y. Okamoto, M. Ando, F. Munakata and Y. Akimune, "Thermal Conductivity of Gas-pressure-sintered Silicon Nitride," *J. Am. Ceram. Soc.*, **79** [11] 2878-82 (1996).
3. A. de Pablos, M. I. Osendi and P. Miranzo, "Effect of Microstructure on the Thermal Conductivity of Hot-pressed Silicon Nitride Materials," *J. Am. Ceram. Soc.*, **85** [1] 202-06 (2002).
4. K. Watari, K. Hirao, M. Toriyama and K. Ishizaki, "Effect of Grain Size on the Thermal Conductivity of $Si_3N_4$," *J. Am. Ceram. Soc.*, **82** [3] 777-79 (1999).
5. S. W. Lee, H. B. Chae, D. S. Park, Y. H. Choa, K. Niihara and B. J. Hockey, "Thermal Conductivity of Unidirectionally Oriented $Si_3N_4w/Si_3N_4$ Composites," *J. Mater. Sci.*, **35** [18] 4487-93 (2000).
6. D-S. Park, S-Y. Lee, H-D. Kim, B-J. Yoo and B-A. Kim, "Extra-large Grains in the Silicon Nitride Ceramics Doped with Yttria and Hafnia," *J. Am. Ceram. Soc.*, **81** [7] 1876-80 (1998).
7. K-M. Lee, W-H. Lee, Y-H. Koh, J-J. Choi and H-E. Kim, "Microstructural Evolution and Mechanical Properties of Gas-pressure-sintered $Si_3N_4$ with $Yb_2O_3$ as a Sintering

Aid," *J. Mater. Res.*, **14** [5] 1904-09 (1999).
8. D-S. Park and C-W. Kim, "A Modification of Tape Casting for Aligning the Whiskers," *J. Mater. Sci.*, **34** 5827-32 (1999).
9. M. Mitomo, N. Yang, Y. Kishi and Y. Bando, "Influence of Powder Characteristics on Gas Pressure Sintering of $Si_3N_4$," *J. Mater. Sci.*, **23** 3413-19 (1988).
10. A. G. Evans and E. A. Charles, "Fracture Toughness Determinations by Indentation," *J. Am. Ceram. Soc.*, **59** [7-8] 371 72 (1976).
11. 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.*, in press.