

## Effect of $\alpha$ -SiC seed on microstructure and fracture toughness of pressureless-sintered $\beta$ -SiC

Young-Wook Kim, Won-Joong Kim, Kyeong-Sik Cho\* and Heon-Jin Choi\*

Department of Materials Science and Engineering, Seoul City University, Seoul 130-743, Korea

\*Division of Ceramics, Korea Institute of Science and Technology, Seoul 130-650, Korea

### $\alpha$ -SiC seed의 첨가가 상압소결된 $\beta$ -SiC의 미세구조와 파괴인성에 미치는 영향

김영욱, 김원중, 조경식\*, 최헌진\*

서울시립대학교 재료공학과, 서울, 130-743

\*한국과학기술연구원 세라믹스연구부, 서울, 130-650

Abstract  $\beta$ -SiC powder with or without the addition of 1 wt% of  $\alpha$ -SiC particles (seeds) was pressureless-sintered at 1950°C for 0.5, 2 and 4 h using  $Y_3Al_5O_{12}$  (yttrium aluminum garnet, YAG) as a sintering aid. The introduction of  $\alpha$ -SiC seeds into  $\beta$ -SiC accelerated the grain growth of elongated large grains during sintering, resulting in the coarser microstructure. The fracture toughnesses of materials with  $\alpha$ -SiC seeds and without  $\alpha$ -SiC seeds sintered for 4 h were 7.5 and 6.1 MPa·m<sup>1/2</sup>, respectively. Higher fracture toughness of the material with seeds was due to the enhanced bridging by elongated grains, resulting from coarser microstructure.

요 약 소결조제로  $Y_3Al_5O_{12}$ 를 첨가한  $\beta$ -SiC 분말에 seed로서 1 wt%의  $\alpha$ -SiC 분말을 첨가한 시편과 첨가하지 않은 시편을 1950°C, argon 분위기에서 0.5~4시간 동안 소결하였다. Seed로써 1 wt%  $\alpha$ -SiC 분말의 첨가는 소결 도중에 길게 자란 입자들의 성장을 가속시켰고,  $\alpha$ -SiC seed를 첨가한 시편에서 더 조대한 미세구조가 얻어졌다.  $\alpha$ -SiC seed를 첨가하여 4시간 동안 소결한 시편의 파괴인성은 7.5 MPa·m<sup>1/2</sup>이었고, seed를 첨가하지 않은 시편의 파괴인성은 6.1 MPa·m<sup>1/2</sup>이었다. Seed를 첨가한 시편의 높은 파괴인성은 조대한 미세구조에 포함된 길게

자란 입자들에 의한 균열가교 기구의 활발한 작용에 기인한다.

## 1. Introduction

Silicon carbide is a difficult material to sinter because of the covalent nature of its bond. The pressureless sintering of SiC through solid state sintering was pioneered by Prochazka [1], who found that small additions of B and C drastically improve the shrinkage kinetics of SiC. The resulting SiC materials consisted of fine, equiaxed grains (grain size 1~5  $\mu\text{m}$ ) and showed improved high-temperature strength and creep, wear, oxidation, and corrosion resistance [2,5]. However, the low fracture toughness (2.5~4  $\text{MPa}\cdot\text{m}^{1/2}$ ) limited their use in many potential structural applications, even though, in comparison to other ceramics, their superior other properties.

Omori and Takei's work [6] on the pressureless sintering of SiC opened the possibility of the liquid phase sintering of SiC. The interest in liquid phase sintered SiC has grown continually during past years, because such materials seem to superior to solid state sintered SiC in mechanical properties [7-10].

Several reports have been published on in situ-toughened SiC [11-15], akin to  $\text{Si}_3\text{N}_4$  [16-22]. The improvement of fracture toughness has been achieved through development of elongated  $\alpha$ -SiC grains; i.e., microstructural control for toughening was based on  $\beta \rightarrow \alpha$  phase transformation of

SiC [8,11-14]. Higher toughness of in situ-toughened materials was due to crack bridging [11] or crack deflection [14] by large elongated grains as evidenced by R-curve behavior [23]. A fracture toughness of 8  $\text{MPa}\cdot\text{m}^{1/2}$  has been reported in oxide-doped, liquid-phase-sintered SiC [11-15].

Recently, silicon carbide nanoceramics (grain size~0.1  $\mu\text{m}$ ) were fabricated from very fine  $\beta$ -SiC powders by hot-pressing [24]. In situ-toughened SiC with duplex microstructure has been fabricated by annealing the nanoceramics at a temperature as low as 1850°C without appreciable  $\beta \rightarrow \alpha$  phase transformation [23]. Previous study also have shown that a wide particle size distribution in starting  $\alpha$ -SiC powder gives enough driving force for abnormal grain growth of some  $\alpha$ -SiC grains and result in a duplex microstructure [25]. Further microstructural control and optimization in SiC is crucially dependent on an increased knowledge of how  $\alpha$ -SiC seeds affect the microstructure and fracture toughness in  $\beta$ -SiC.

In the present work, fine-grained  $\beta$ -SiC was selected as the matrix for in situ-toughened microstructure, and the effect of  $\alpha$ -SiC seeds addition on microstructure and fracture toughness of pressureless sintered  $\beta$ -SiC was investigated.

## 2. Experimental procedure

Commercially available fine  $\beta$ -SiC powder (Ibiden Co., Ogaki, Japan, Ultrafine grade) and relatively coarse  $\alpha$ -SiC powder (Showa Denko K.K., Tokyo, Japan, A-1 grade) were used as starting powders. For higher sintered density,  $\beta$ -SiC and  $\alpha$ -SiC powders were oxidized at 550°C for 0.5 h under air. It was recognized that oxidation of SiC powders, prior to liquid phase sintering, increased the oxygen content and decreased carbon content, resulting in the higher sintered density [26]. The powder characteristics of starting powders and oxidized powders are shown in Table 1.

To prepare a powder composition without seeds, 88 wt%  $\beta$ -SiC (oxidized powder) and 12 wt%  $Y_3Al_5O_{12}$  (yttrium-aluminum garnet, YAG, 99.9 % pure, High Purity Chemicals, Chiyoda Sakado, Japan)

were ball milled in ethanol with SiC grinding balls for 24 h. To prepare a powder composition containing seeds, 87 wt%  $\beta$ -SiC (oxidized powder) and 12 wt%  $Y_3Al_5O_{12}$  were ball milled in ethanol for 22 h, and then 1 wt%  $\alpha$ -SiC seeds (oxidized powder) were added, followed by additional milling for 2 h. The milled slurry was dried, uniaxially pressed at 20 MPa, and isostatically pressed at 140 MPa. Sintering was performed in a graphite resistance furnace. The specimens were sintered at a heating rate of 600°C/h and maintained at 1950°C for 0.5, 2, and 4 h in argon. A powder bed with the same composition as the specimens was used to suppress the weight loss of the specimens [27].

The relative density was determined by the Archimedes method. X-ray diffraction using  $CuK\alpha$  radiation was performed on all the ground specimens. The sintered speci-

Table 1  
Characteristics of SiC powders

No.	Powder	Specific surface area (m <sup>2</sup> /g)	Impurities		Phase
			SiO <sub>2</sub> (wt%)	Free C (wt%)	
1	$\beta$ -SiC powder* (Ibiden Co., Ultrafine grade)	16.7	1.55	0.75	$\beta$
2	Powder 1 was oxidized at 550°C for 0.5 h under air	15.7	5.06	0.06	$\beta$
3	$\alpha$ -SiC powder* (Showa Denko K.K., A-1 grade)	11.7	1.23	0.46	$\alpha$
4	Powder 3 was oxidized at 550°C for 0.5 h under air	11.3	4.50	0.04	$\alpha$

\*Data were supplied from manufacturers.

Table 2  
Characteristics of sintered SiC

No.	Composition (wt%)			Sintering time at 1950°C (h)	Relative density (%)	Crystalline phase	
	$\beta$ -SiC	$\alpha$ -SiC	Y <sub>3</sub> Al <sub>5</sub> O <sub>12</sub>			Major	Trace
1	88		12	0.5	99.0	$\beta$ -SiC	YAG*
2	88		12	2	98.3	$\alpha$ -SiC	YAG
3	88		12	4	94.3	$\alpha$ -SiC	YAG
4	87	1	12	0.5	99.0	$\beta$ -SiC	YAG, $\alpha$ -SiC
5	87	1	12	2	97.4	$\alpha$ -SiC	YAG
6	87	1	12	4	94.2	$\alpha$ -SiC	YAG

\* Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub> (yttrium aluminum garnet).

mens were cut and polished, and then plasma etched by CF<sub>4</sub> containing 7.8 % O<sub>2</sub>. The microstructures were observed by scanning electron microscopy (SEM). The fracture toughness was estimated by measuring crack lengths generated by a Vickers indenter with a load of 196 N [28].

### 3. Results and discussion

The characteristics of SiC materials obtained with  $\alpha$ -SiC seeds and without  $\alpha$ -SiC seeds are summarized in Table 2. The relative densities of >99 % were achieved by pressureless-sintering with a holding time of 0.5 h at 1950°C. The sintered densities were found to decrease with increasing the sintering time. It may be due to the reactions between SiC and YAG at sintering temperature (1950°C) [29]. These reactions probably result in the formation of volatile components such

as AlO, Al<sub>2</sub>O, and CO [27-30], which form isolated pores inside the specimen, and make the substantial weight loss and the reduction of liquid content, leading to the decrease in the sintered density.

Figure 1 shows the microstructural change of SiC materials with sintering time. The microstructures of 0.5-h sintered materials with or without  $\alpha$ -SiC seeds composed of equiaxed grains and the polytype of the materials was found to be composed primarily of 3C ( $\beta$ -SiC) by XRD. When the holding time was increased, the shape of the grains changed from equiaxed to elongated and the grain size and aspect ratio increased, as shown in Figs. 1 (b), (c), (e), and (f), which indicate, referring to the phase analysis in Table 1, the marked growth of  $\alpha$ -SiC. It is recognized that the  $\beta \rightarrow \alpha$  phase transformation of SiC takes place at high temperatures ( $\geq 1950^\circ\text{C}$ ), especially in the presence of proper liquids. The 2- and 4-h sintered materials with  $\alpha$ -SiC seeds (Figs. 1(e)

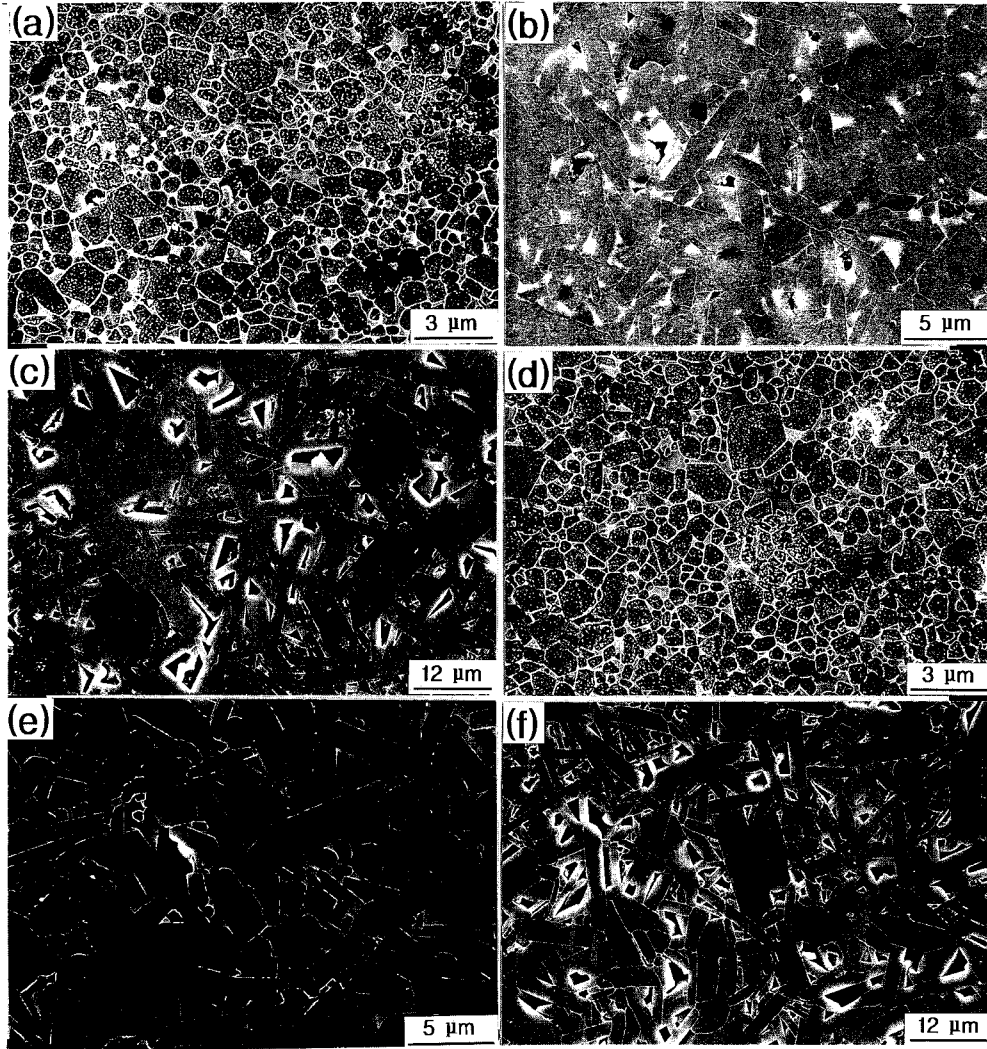


Fig. 1. SEM micrographs of SiC materials without seeds sintered at 1950°C for (a) 0.5 (b) 2 and (c) 4 h and SiC materials with seeds sintered at 1950°C for (d) 0.5, (e) 2 and (f) 4 h.

and (f)) have coarser microstructures than the equivalent materials without  $\alpha$ -SiC seeds (Figs. 1(b) and (c)). These results suggest that the addition of  $\alpha$ -SiC seeds into  $\beta$ -SiC accelerates the grain growth of elongated  $\alpha$ -SiC grains during sintering and resulted in the coarser mi-

crostructure. Alpha-SiC seeds are believed to act as nuclei for the grain growth of elongated large grains. The true shape of elongated grains is considered presumably as plate-shaped [23-31].

SEM micrographs of the fracture surface of sintered materials are shown in

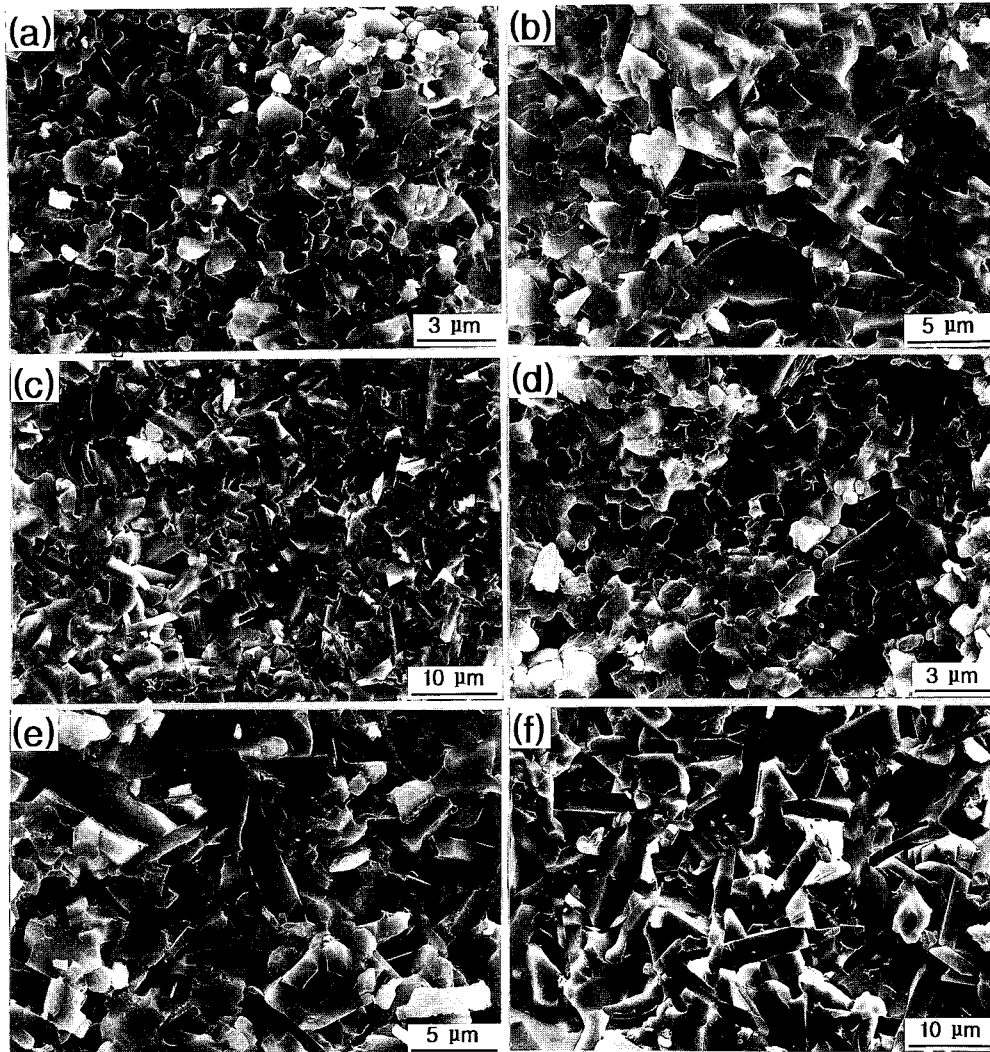


Fig. 2. SEM micrographs of fracture surfaces of SiC materials without seeds sintered at 1950°C for (a) 0.5, (b) 2 and (c) 4 h and SiC materials with seeds sintered at 1950°C for (d) 0.5, (e) 2 and (f) 4 h.

Fig. 2. As shown, the fracture mode of 0.5-h sintered materials was mostly intergranular. However, substantial transgranular fracture of the larger grains was observed in 4-h annealed materials. The microstructural development of Figs. 2 (c) and (f) is similar to the in situ formation

of elongated grains during sintering of  $\text{Si}_3\text{N}_4$  [16-20]. Such kind of an in situ-toughened microstructure is beneficial to the toughening of SiC. The microstructure of the 4-h annealed material with  $\alpha$ -SiC seeds was very similar to, but having more porosity than, the recently reported

high-toughness microstructure of SiC [11, 12].

The effect of isothermal holding time on the fracture toughness of sintered materials is shown in Fig. 3. The fracture toughness increased with increasing holding time and showed greater amount of increase in materials with  $\alpha$ -SiC seeds. The fracture toughness of 4-h sintered material ( $6.1 \text{ MPa}\cdot\text{m}^{1/2}$ ) for the material without  $\alpha$ -SiC seeds was 50 % higher than that of 0.5-h sintered material ( $4.0 \text{ MPa}\cdot\text{m}^{1/2}$ ), while the fracture toughness of 4-h sintered material ( $7.5 \text{ MPa}\cdot\text{m}^{1/2}$ ) for the material with  $\alpha$ -SiC seeds was 80 % higher than that of 0.5-h sintered material ( $4.1 \text{ MPa}\cdot\text{m}^{1/2}$ ). When the holding time was increased, the shape of grains changed from equiaxed (0.5-h sintered materials) to elongated grains (4-h sintered materials) and the average grain size and average aspect ratio of grains increased because of  $\alpha$ -SiC grain growth. The increased frac-

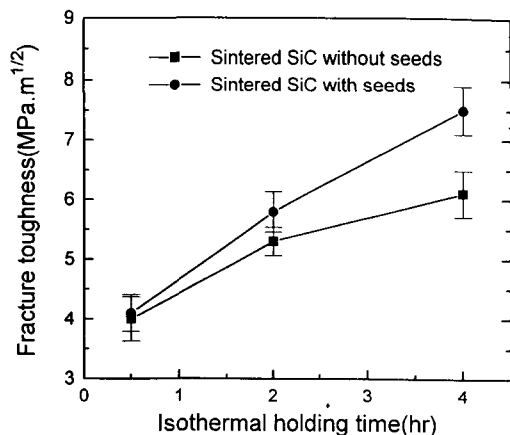


Fig. 3. Relation between fracture toughness of sintered SiC and holding time at  $1950^\circ\text{C}$ .

ture toughness, therefore, was related to the microstructure. Several toughening mechanisms have been reported for the liquid phase sintered SiC containing elongated grains, including crack bridging [11] or crack deflection [14]. Bridging by elongated grains (Fig. 4 (b)) behind the crack tip in 4-h sintered material and deflection by small equiaxed grains (Fig. 4 (a)) in 0.5-h sintered material were observed. Therefore, the improved fracture toughness of 4-h sintered material with seeds, comparing with the 4-h sintered material without seeds, was attributed to the en-

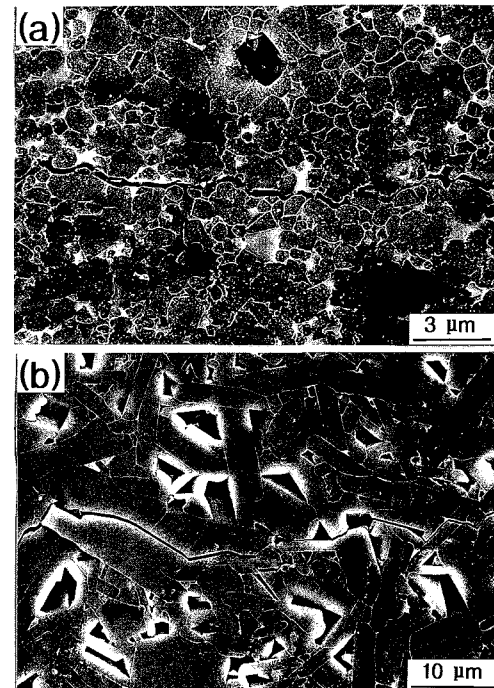


Fig. 4. SEM view of (a) crack deflection by equiaxed grains in 0.5-h sintered material with seeds and (b) crack bridging by elongated grains in 4-h sintered material with seeds.

hanced crack bridging by elongated grains, resulting from coarser microstructure.

#### 4. Conclusions

The introduction of  $\alpha$ -SiC seeds into  $\beta$ -SiC accelerated the grain growth of elongated large grains during sintering, resulting in the coarser microstructure. Alpha-SiC seeds acted as nuclei for the grain growth of elongated large grains. The fracture toughnesses of materials with  $\alpha$ -SiC seeds and without  $\alpha$ -SiC seeds sintered for 4 h were 7.5 and 6.1 MPa·m<sup>1/2</sup>, respectively. Higher fracture toughness of the material with seeds was due to the enhanced bridging by elongated grains, resulting from coarser microstructure.

#### Acknowledgment

This work was supported by Seoul City University's 1996 Research Program.

#### References

- [ 1 ] S. Prochazka, Special Ceramics 6, Ed., P. Popper (British Ceramic Research Assoc., Manchester, 1975) p. 171.
- [ 2 ] S.G. Seshadri, M. Srinivasan, and K. Y. Chia, Silicon Carbide '87, Ed., J. D. Cawley and C.E. Semler (The American Ceramic Society Inc., Westerville, 1989) p. 215.
- [ 3 ] S. Dutta, J. Mater. Sci. 19 (1984) 1307.
- [ 4 ] Y.W. Kim and J.G. Lee, J. Mater. Sci. 27 (1992) 4746.
- [ 5 ] Y.W. Kim and J.G. Lee, J. Mater. Sci. 30 (1995) 1005.
- [ 6 ] M. Omori and H. Takei, J. Am. Ceram. Soc. 65 (1982) C92.
- [ 7 ] H.J. Kleebe, J. Eur. Ceram. Soc. 10 (1992) 151.
- [ 8 ] S.K. Lee and C.H. Kim, J. Am. Ceram. Soc. 77 (1994) 1655.
- [ 9 ] W.J. Kim and Y.W. Kim, J. Kor. Ceram. Soc. 32 (1995) 1162.
- [ 10 ] W.J. Kim and Y.W. Kim, J. Kor. Asso. Crystal Growth 5 (1995) 343.
- [ 11 ] N.P. Padture, J. Am. Ceram. Soc. 77 (1994) 519.
- [ 12 ] M.A. Mulla and V.D. Krstic, J. Mater. Sci. 29 (1994) 934.
- [ 13 ] N.P. Padture and B.R. Lawn, J. Am. Ceram. Soc. 77 (1994) 2518.
- [ 14 ] M.A. Mulla and V.D. Krstic, Acta Metall. Mater. 42 (1994) 303.
- [ 15 ] V.D. Krstic, MRS Bulletin 20 (1995) (1995) 46.
- [ 16 ] M. Mitomo, M. Tsutsumi, H. Tanaka, S. Uenosono, and F. Saito, J. Am. Ceram. Soc. 73 (1990) 2441.
- [ 17 ] M. Mitomo and S. Uenosono, J. Am. Ceram. Soc. 75 (1992) 103.
- [ 18 ] M. Mitomo, H. Hirotsuru, H. Suematsu, and T. Nishimura, J. Am. Ceram. Soc. 78 (1995) 211.
- [ 19 ] Y.W. Kim, M. Mitomo, and N. Hirosaki, J. Mater. Sci. 30 (1995)



- 4043.
- [20] Y.W. Kim, M. Mitomo, and N. Hirosaki, *J. Mater. Sci.* 30 (1995) 5178.
- [21] H.J. Choi, Y.W. Kim, and J.G. Lee, *J. Mater. Sci. Lett.* 15 (1996) 282.
- [22] H.J. Choi, Y.W. Kim, and J.G. Lee, *J. Mater. Sci. Lett.* 15 (1996) 375.
- [23] Y.W. Kim, M. Mitomo, and H. Hirotsumu, *J. Am. Ceram. Soc.* 78 (1995) 3145.
- [24] M. Mitomo, Y.W. Kim, and H. Hirotsumu, *J. Mater. Res.* 11 (1996) 1601.
- [25] Y.W. Kim, K.S. Cho, and J.G. Lee, *Kor. J. Ceram.* 2 (1996) 39.
- [26] Y.W. Kim, M. Mitomo, and J.G. Lee, *J. Ceram. Soc. Japan* 104 (1996) 816.
- [27] Y.W. Kim and J.G. Lee, *J. Am. Ceram. Soc.* 72 (1989) 1333.
- [28] G.R. Anstis, P. Chantikul, B.R. Lawn, and D.B. Marshall, *J. Am. Ceram. Soc.* 64 (1981) 533.
- [29] K.S. Cho, Y.W. Kim, H.J. Choi, and J.G. Lee, *J. Am. Ceram. Soc.* 79 (1996) 1711.
- [30] Y.W. Kim, H. Tanaka, M. Mitomo, and S. Otani, *J. Ceram. Soc. Japan* 103 (1995) 257.
- [31] Y.W. Kim, M. Mitomo, and H. Hirotsumu, *J. Am. Ceram. Soc.*, in press.