

## Phase and microstructure of hot-pressed SiC - AlN solid solutions

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## 열간가압소결에 의한 SiC - AlN 고용체의 상 및 미세구조

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**Abstract** High-density SiC - AlN solid solutions were fabricated from powder mixtures of  $\beta$ -SiC and AlN by hot-pressing in the 1870 to 2030°C temperature range. The reaction of AlN and  $\beta$ -SiC (3C) powder transformed to the 2 H (wurzite) structure appeared to depend on the temperature and SiC/AlN ratio and seeds present. The crystalline phases consisted of a SiC-rich solid-solution phase and an AlN-rich solid-solution phase. At 2030°C for 1 h, for a composition of 50 % AlN/50 % SiC with a seeding of 5 wt%  $\alpha$ -SiC, the complete solid solution could be obtained and the microstructures are equiaxed with a relatively homogeneous grain size of 2 H phases. The variation of the seeding of  $\alpha$ -SiC in SiC - AlN solid solutions could be attributed to the transformation behaviour and differences in size and shape of the grains, as well as to other factors, such as grain size distributions, compositional inhomogeneity, and structural defects.

**요 약**  $\beta$ -SiC 와 AlN의 혼합분말로부터 열간가압소결에 의하여 고밀도의 SiC - AlN 고용체가 1870°C에서 2030°C 사이의 온도범위에서 제조되어졌다. 온도와 SiC/AlN의 비 및 seed의 존재에 따라 AlN과  $\beta$ -SiC(3C) 분말의 반응은 2 H(wurzite) 구조로의 전이를 나타내었다. 결정상들은 SiC-rich 및 AlN-rich 고용체로 구성되었다. 2030°C, 1시간에서 5 wt%의  $\alpha$ -SiC

seed를 첨가한 50 % AlN/50 % SiC의 조성에 대하여 완전한 고용체가 얻어졌으며, 미세구조가 비교적 균일한 2 H상의 결정립 크기를 가지고 균일한 성장경향을 나타내었다. SiC - AlN 고용체에 있어서  $\alpha$ -SiC seed의 변수가 전이기구 및 결정립의 크기와 모양을 비롯한 결정립 크기의 분포, 조성의 불균일성과 구조적 결합 등에 영향을 미칠 수 있었다.

## 1. Introduction

SiC and AlN become attractive materials with interesting mechanical and electronic properties. SiC is used as high strength and high temperature ceramics because of its excellent corrosion and erosion resistance in the field of promising candidates for structural materials at room as well as elevated temperatures. However, its low fracture toughness has to be overcome before promoting the application as engineering components. AlN has recently come into prominence as an electronic substrate material. SiC is a covalent compound which exists ei-

ther in a cubic structure (3C) or in various hexagonal or rhombohedral polytypes (2 H, 4 H, 6 H, 15 R and 21 R). The 2 H polymorph of SiC is isostructural with AlN and  $Al_2O_3$  with a strong covalent bond in Table 1 [1]. The similarity between two structures and their properties suggests that alloying of one with the other may provide the potential for property optimization.

Cutler et al. [2-6] reported the formation of a SiC - AlN solid solution in the range 2 - 100 % AlN has been formed at 1600°C by a vapor phase process using carbothermal reduction of amorphous silica and aluminium hydroxide in nitrogen. The 2 H SiC -

Table 1  
Compatibility of SiC with AlN and  $Al_2O_3$  [1]

	Molar weight (g/mol)	Lattice parameters(nm)	Mass density (g/cm <sup>3</sup> )	Length of covalent bond(nm)
SiC	40.10	a=0.3079 c=0.5048 c/a=1.641	3.21	0.194
AlN	40.99	a=0.3111 c=0.4978 c/a=1.600	3.26	0.196
$Al_2O_3$	40.99	a=0.3170 c=0.5060 c/a=1.596	2.99	Al - O=0.192 Al - C=0.203

AlN solution appears to form more easily when the starting SiC powders are cubic form, as opposed to hexagonal forms. Ruh and Zangvil [7] described the solid solution exists as a single phase above 2100°C over the composition range 35-100 mol% AlN. Their flexural strengths were quite low due to inhomogeneities in grain size and composition, and spinodal decomposition occurs on annealing below 1950°C. Recently, some studies of the phase relationship and microstructures of the SiC-AlN solid solutions have been reported by hot-pressing [8-20] and pressureless sintering with additives [21-23]. However, when all starting materials are in the powder form, the covalent nature of the atomic bonding in SiC and AlN makes diffusion extremely slow, so that pressures of several hundred bars and temperatures of up to 2300°C are required to obtain complete solid solutions with high-density bodies.

In this paper, the fabrication of SiC-AlN solid solution is studied by the hot-pressing under 2030°C using seeds of  $\alpha$ -SiC to achieve the complete 2 H solid solutions with a lowering of the transformation temperatures. It is aimed at attaining a basic understanding of the effect of seeding in phase relationship and microstructural control.

## 2. Experimental

The materials used for this study were commercial  $\beta$ -SiC (Beta Randum, Ibiden Cimpany), AlN (Grade F. Tokuyama Soda

Company) and  $\alpha$ -SiC (Du A-1 Showa Denko) powders. As listed in Table 2, the major impurities in the  $\beta$ -SiC powders are 0.39 % SiO<sub>2</sub>, 0.64 % C, 0.02 % Al, and 0.03 % Fe, while AlN powders contain 0.89 % O and 360 ppm C. The average particle sizes of these two powders are 0.27 and 2  $\mu$ m, respectively. As a seeding process,  $\alpha$ -SiC powders are used. The major impurities in the  $\alpha$ -SiC powders are 0.46 % C, 0.27 % SiO<sub>2</sub>, 0.024 % Fe and 0.007 % Al, and the

Table 2  
Properties of raw powders

$\beta$ -SiC	Beta Randum. Ibiden Company Free SiO <sub>2</sub> (0.39 wt%) Free C (0.64 wt%) Al (0.02 wt%) Fe (0.03 wt%) Average particle size = 0.27 $\mu$ m Specific surface area = 20.4 m <sup>2</sup> /g
AlN	Type F. Tokuyama Soda Company O (0.89 wt%) C (360 ppm) Ca (65 ppm) Si (15 ppm) Fe (10 ppm) Average oparticle size = 2 $\mu$ m Specific surface area = 3.2 m <sup>2</sup> /g
$\alpha$ -SiC	Du A - 1 Showa Denko SiC (99.2 wt%) Free C (0.46 wt%) Free SiO <sub>2</sub> (0.27 wt%) Fe (0.024 wt%) Al (0.007 wt%) Average particle size = 0.47 $\mu$ m

average particle size of this powder is 0.47  $\mu\text{m}$ . Nominal compositions investigated ranged between 20 % AlN/80 % SiC and 90 % AlN/10 % SiC with seedings of 2, 5 and 8 wt%  $\alpha$ -SiC and without seeding (Table 3). Compositions were prepared by wet milling the appropriate amounts of powders for 24 h in isopropyl alcohol in a plastic jar with SiC balls. After milling, the specimens were evaporated to dryness, broken with a mortar and passed through a 50-mesh sieve.

Specimens (3 cm in diameter by 0.5 cm thick) were uniaxially hot-pressed in graphite dies lined with graphite washer. Hot-pressing was conducted under nitrogen at

1870°C for 4 h and 2030°C for 1 h at 22.5 MPa (Table 3). Cooling was sufficiently rapid for this study, so that the high-temperature phase was quenched to room temperature. After the specimens were removed from the die, the surfaces were ground, and the density was determined by measuring weights and dimensions. Near theoretical densities were obtained in all cases. The specimens were then polished with a diamond disk using diamond pastes of 30, 15, 3, 1  $\mu\text{m}$ . The samples were ultrasonically cleaned in ethanol, rinsed with water and dried. All of the samples were examined using X-ray diffraction (XRD) with  $\text{CuK}\alpha$

Table 3  
Compositions and hot-pressing conditions of powder mixtures

Sample name	SiC/AlN mole ratio	Composition (wt%)			Hot-press conditions		
		SiC	AlN	$\alpha$ -SiC	Temp.(°C)	Time(h)	Pressure(MPa)
A20	80/20	79.6	20.4	0	1870	4	22.5
					2030	1	22.5
A50	50/50	49.5	50.5	0	1870	4	22.5
					2030	1	22.5
A70	30/70	29.6	70.4	0	1870	4	22.5
					2030	1	22.5
A90	90/10	9.8	90.2	0	1870	4	22.5
					2030	1	22.5
2W50A	50/50	49.0	49.0	2	1870	4	22.5
					2030	1	22.5
5W50A	50/50	47.5	47.5	5	1870	4	22.5
					2030	1	22.5
8W50A	50/50	46.0	46.0	8	1870	4	22.5
					2030	1	22.5

Polished samples were etched using Murakami's etch to reveal the microstructure. The etched sections were investigated using optical microscopy and scanning electron microscopy (SEM).

### 3. Results and discussion

The phase presents in experimental samples were determined by XRD analysis. As given in Table 4, the phases were listed in the order of the amount present. For the compositions of A20, A50 and A70 hot-pressed at 1870°C for 4 h, the hexagonal 2 H phase is the strongest with hexagonal 4 H

and 6 H present and possibly some rhombohedral 15 R and 3 C, whereas for composition of A90 the 2 H with 4 H and 6 H are the observed phases. For the composition of A20 hot-pressed at 2030°C for 1 h, the 2 H phase is the strongest with 4 H and 6 H present and possibly some rhombohedral 15 R and 3 C, while for the compositions of A50 and A70 the 3 C phase was transformed to the hexagonal and rhombohedral phases and for the composition of A90 the hexagonal phases of 2 H, 4 H (6 H) are present.

Results on the compositions of 2W50A, 5W50A and 8W50A as hot-pressed at 1870°C for 4 h were similar to those obtained on

Table 4  
Phase present in SiC-AlN solid solutions

Sample name	Hot - press conditions		Phases present
	Temp.(°C)	Time(h)	
A20	1870	4	2H, 4H(6H),15R,3C
A50	1870	4	2H, 4H(6H), 15R, 3C
A70	1870	4	2H, 4H(6H), 15R, 3C
A90	1870	4	2H, 4H(6H)
A20	2030	1	2H, 4H(6H), 15R, 3C
A50	2030	1	2H, 4H(6H), 15R
A70	2030	1	2H, 4H(6H), 15R
A90	2030	1	2H, 4H(6H)
2W50A	1870	4	2H, 4H(6H), 15R, 3C
5W50A	1870	4	2H, 4H(6H), 15R, 3C
8W50A	1870	4	2H, 4H(6H), 15R, 3C
2W50A	2030	1	2H
5W50A	2030	1	2H
8W50A	2030	1	2H, 4H(6H)

the compositions of A50 hot-pressed at 1870°C for 4 h. When these compositions were hot-pressed at 2030°C for 1 h, a single 2 H solid solution was obtained for the compositions of 2W50A and 5W50A and with some 4 H and 6 H for the composition of 8W50A. These results indicate that the reaction of AlN and  $\beta$ -SiC powder transformed to the 2 H structure appeared to depend on the temperature and amount of AlN and seeds present. The phase transformation is influenced by the seeding resulting in a lowering of the transformation temperature.

The typical XRD patterns on the SiC-AlN solid solutions of the sample A50 and 5W50A pressed at 2030°C for 1 h are shown in Fig. 1. The hexagonal lines with various

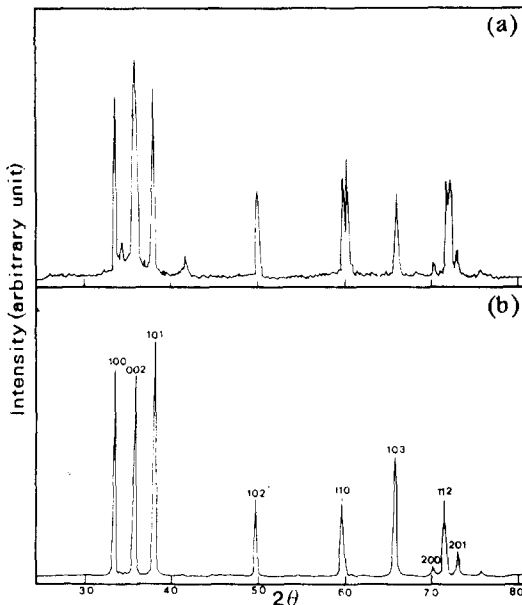


Fig. 1. XRD patterns of the SiC-AlN solid solutions of the sample (a) A50 and (b) 5W50A hot-pressed at 2030°C for 1 h.

splittings on the sample A50 in Fig. 1 (a) indicate the 2 H solid solution with various polytypes, whereas the strong hexagonal lines with the absence of any splitting indicates that the sample 5W50A is a single SiC-AlN solid solution of 2 H in Fig. 1 (b). For this solid solution, the  $2\theta$  value for the (100) plane is 33.3°, while that for AlN would be 33.2° and that for SiC (2 H) would be 33.7°.

The crystalline phases consist of two main phases: one is a SiC-rich solid-solution

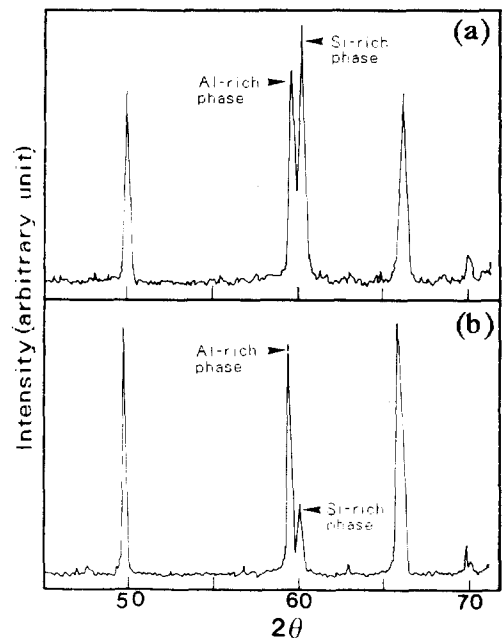


Fig. 2. XRD patterns of the SiC-AlN solid solutions of the sample (a) A50 and (b) A70 hot-pressed at 2030°C for 1 h showing the typical splitting of the (110) reflection at  $2\theta = 59.6^\circ$ : (a) sample A50 indicates the splitting at  $2\theta = 59.530^\circ$  and  $60.205^\circ$  and (b) sample A70 indicates the splitting at  $2\theta = 59.455^\circ$  and  $60.055^\circ$ .

phase and the other is an AlN-rich solid-solution phase. The (110) reflection at  $2\theta = 59.6^\circ$  provides the maximum possibility of observing splitting (two phases of identical structure with slightly different lattice parameters) since it has largest  $2\theta$  difference between SiC and AlN of the major diffraction peaks. Figure 2 shows the typical splitting of the (110) reflection of the SiC-AlN solid solution of the sample A50 and A70 hot-pressed at  $2030^\circ\text{C}$  for 1 h. Fig. 2 (a) shows the splitting at  $2\theta = 59.530^\circ$  and  $60.205^\circ$  in the sample A50, which indicates the high intensity value of Si-rich phase. Fig. 2 (b) shows the splitting at  $2\theta = 59.455^\circ$  and  $60.066^\circ$  in the sample A50, which indicates the high intensity value of Al-rich phase. This phase separation was presumed to be of spinodal or binodal decomposition, considering the peak splitting behaviour [13-15,20].

Results of SEM studies were in good agreement with XRD results. Figure 3 shows typical microstructures of the SiC-AlN solid solutions of 2W50A, 5W50A and 8W50A as hot-pressed at  $2030^\circ\text{C}$  for 1 h, which previously were etched using Murakami's etch. All of the samples had densities in excess of 99 % of theoretical value. According to the XRD results, for a composition of 50 % AlN / 50 % SiC with a seeding of 2 wt% and 5 wt%  $\alpha$ -SiC, the complete solid solution with a single phase of 2H could be obtained by hot pressing at  $2030^\circ\text{C}$  for 1 h. The microstructures of the samples of 2W50A and 5W50A are equiaxed with a relatively homogeneous grain size of 2H phases (Fig. 1 (a) and (b)). Sample 2W50A presents a micro-

structure similar to that of 5W50A, with somewhat smaller grains. However, the sample of 8W50A exhibits an inhomogeneous size distribution (Fig. 3 (c)), which suggests either untransformed or in the process of transformation from  $\beta$ - to  $\alpha$ -SiC.

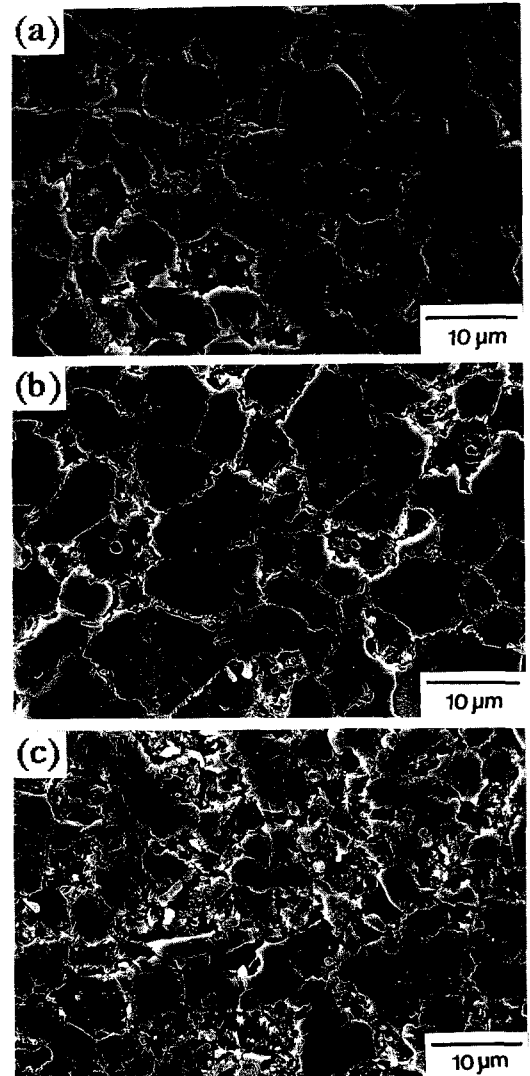


Fig. 3. Scanning electron micrographs of the SiC-AlN solid solutions as hot-pressed at  $2030^\circ\text{C}$  for 1 h: (a) 2W50A, (b) 5W50A and (c) 8W50A.

Figure 4 shows high magnification scanning electron micrographs of these samples of 2W50A, 5W50A and 8W50A. In Fig. 4 (a), small amount of the columnar growth was observed in equiaxed grains of the sample 2W50A. In Fig. 4 (b), the sample

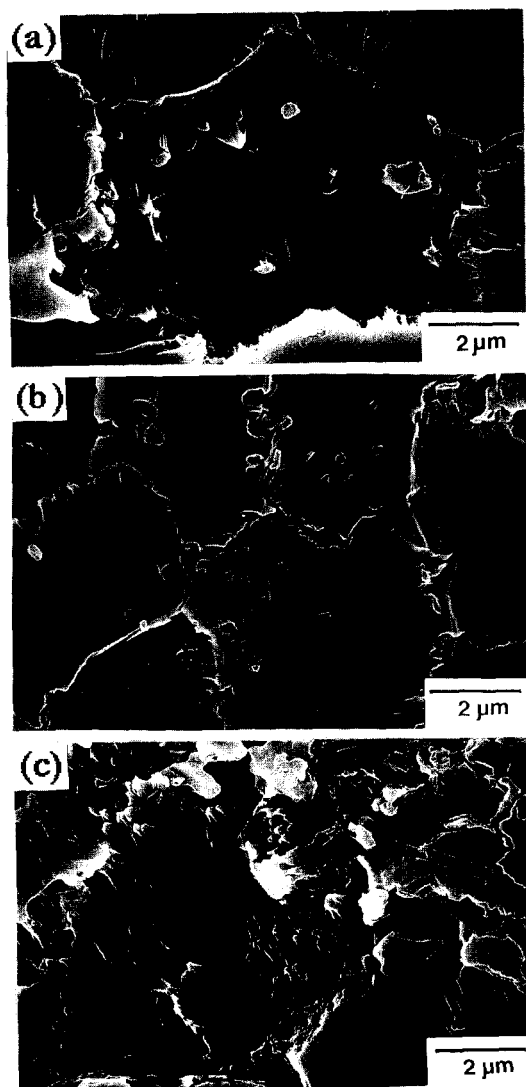


Fig. 4. High magnification scanning electron micrographs of the SiC-AlN solid solutions as hot-pressed at 2030°C for 1 h (a): 2W50A, (b) 5W50A and (c) 8W50A.

5W50A exhibits uniform grains, which consists of a single phase of the solid solution. In contrast, a large proportion of heavy strained and faulted grains with various columnar growths was observed in complicated grain mixtures of the sample 8W50A in Fig. 4 (c). It was reported that a material with high strength can be generated from SiC-AlN solid solution by controlling grain size and its distribution through proper compositional design and processing [18]. Therefore, the variation of the seeding of  $\alpha$ -SiC in SiC-AlN solid solutions could be attributed to the transformation behaviour and differences in size and shape of the grains, as well as to other factors, such as grain size distributions, compositional inhomogeneity, and structure defects.

#### 4. Conclusions

The fabrication of SiC-AlN solid solution is studied by the hot-pressing under 2030°C using seeds of  $\alpha$ -SiC to achieve the complete solid solutions. High-density SiC-AlN solid solutions were fabricated from powder mixtures by hot-pressing in the 1870°C to 2030°C temperature range. The reaction of AlN and  $\beta$ -SiC powder transformed to the 2H structure appeared to depend on the temperature and SiC/AlN ratio and seeds present. The phase transformation was influenced by the seeding resulting in a lowering of the transformation temperature. The crystalline phases consisted of a SiC-rich solid-solution phase and an AlN-rich solid-solu-



tion phase.

At 2030°C for 1 h, for a composition of 50 % AlN/50 % SiC with a seeding of 5 wt%  $\alpha$ -SiC, the complete solid solution could be obtained and the microstructures are equiaxed with a relatively homogeneous grain size of 2 H phase. The variation of the seeding of  $\alpha$ -SiC in SiC-AlN solid solutions could be attributed to the transformation behaviour and differences in size and shape of the grains, as well as to other factors, such as grain size distributions, compositional inhomogeneity, and structure defects.

#### References

- [ 1 ] D. Bloor, R.J. Brook, M.C. Flemings, S. Mahajan and R.W. Cahn, *The Encyclopedia of Advanced Materials*, Vol. 4 (1995) p. 2453.
- [ 2 ] I.B. Cutler, P.D. Miller, W. Rafaniello, H.K. Park, D.P. Thomson and K.H. Jack, *Nature* 275 (1978) 795.
- [ 3 ] W. Rafaniello, K. Cho and A.V. Virkar, *J. Mat. Sci.* 16 (1981) 3479.
- [ 4 ] Y. Sugahara, K.I. Sugimoto, H. Takagi, K. Kuroda and C. Kato, *J. Mat. Sci. Lett.* 7 (1988) 795.
- [ 5 ] K. Tsukuma, M. Shimada and M. Koizumi, *ibid.* 1 (1982) 9.
- [ 6 ] Y. Sugahara, K. Kuroda and C. Kato, *J. Am. Ceram. Soc.* 69 (1984) C247.
- [ 7 ] R. Ruh and A. Zangvil, *ibid.* 65 (1982) 260.
- [ 8 ] L.D. Bentsen, D.P.H. Hasselman and R. Ruh, *ibid.* 66 (1983) C40.
- [ 9 ] W. Rafaniello, M.R. Plichta and A.V. Virkar, *ibid.* 66 (1983) 272.
- [10] A. Zangvil and R. Ruh, *Mat. Sci. Eng.* 71 (1985) 159.
- [11] R. Ruh, A. Zangvil and J. Barlowe, *Am. Ceram. Soc. Bull.* 64 (1985) 1368.
- [12] Z.C. Jou, S.Y. Kuo and A.V. Virkar, *J. Am. Ceram. Soc.* 69 (1986) C279.
- [13] S.Y. Kuo, A.V. Virkar and W. Rafaniello, *J. Am. Ceram. Soc.* 70 (1987) C125.
- [14] A. Zangvil and R. Ruh, *ibid.* 71 (1988) 884.
- [15] S.Y. Kuo and A.V. Virkar, *J. Am. Ceram. Soc.* 73 (1990) 2640.
- [16] I. Teusel and C. Russel, *J. Mat. Sci.* 25 (1990) 3531.
- [17] J.F. Li and R. Watanabe, *ibid.* 26 (1991) 4813.
- [18] Y. Xu, A. Zangvil, M. Landon and F. Thevenot, *J. Am. Ceram. Soc.* 75 (1992) 325.
- [19] R. Sathyamoorthy, A.V. Virkar and R. A. Cutler, *ibid.* 75 (1992) 1136.
- [20] J. Chen, Q. Tian and A.V. Virkar, *ibid.* 75 (1992) 809.
- [21] R.R. Lee and W.C. Wei, *Ceram. Eng. Sci. Proc.* 11 (1990) 1094.
- [22] I. Teusel and C. Rüssel, *J. Mat. Sci. Lett.* 11 (1992) 205.
- [23] M. Miura, T. Yogo and S.I. Hirano, *J. Mat. Sci.* 28 (1993) 3859.