

Microstructure and toughening of SiC-AlN ceramics induced by seeding with α -SiC

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The microstructure and toughening of SiC-AlN ceramics from powder mixtures of β -SiC, AlN and α -SiC by hot-pressing were studied in the 1870 to 2030 °C temperature range. The reaction of AlN and β -SiC(3C) powders causing transformation to the 2H (wurtzite) structure appeared to depend on the hot-pressing temperature and the seeding with α -SiC. For the compositions of 49 wt% AlN/49 wt% SiC with 2 wt% α -SiC and 47.5 wt% AlN/47.5 wt% SiC with 5 wt% α -SiC heated at 2030 °C for 1 h, complete solid solutions with a single phase of 2H could be obtained. An appreciable amount of α -SiC seeding could develop columnar inter-grains of the 4H phase and the stable 2H phase with a relatively uniform composition and grain size distribution. The seeding effect of α -SiC on the phases present and compositional microstructures with columnar inter-grains was investigated in detail. The mechanical properties of the hot-pressed solid solutions were evaluated in terms of fracture toughness and Vickers hardness.

Key words: SiC-AlN, hot-press, α -SiC, seeding, microstructure, toughening.

Introduction

Silicon carbide(SiC) and aluminum nitride(AlN) from a solid solution which has received considerable attention owing to its high potential for application in chemically aggressive environments [1-4]. SiC is a covalent compound which exists either in a cubic structure (3C) of β -SiC or in various hexagonal or rhombohedral polytypes (2H, 4H, 6H, 15R and 21R) of α -SiC. However, there are few examples of the formation of solid solutions in the case of nonoxide ceramics with strong covalent bonds and low diffusion coefficients. The 2H polymorph of α -SiC is isostructural with AlN and Al₂O₃ with a strong covalent bond [5]. The similarities between the two structures and their properties suggest that alloying of one with the other may provide the potential for property optimization. During the past decade, it has been found that a series of solid solutions are formed between SiC and AlN over a wide composition range [2-26].

Cutler *et al.* [6] reported that a SiC-AlN solid solution in the range 2-100% AlN was formed at 1600 °C by a vapor phase process using the carbothermal reduction of amorphous silica and aluminum hydroxide in nitrogen, which was accompanied by increased mechanical properties due to their similar structures and high temperature properties. Ruh and Zangvil [7] described a solid solution that existed as a single phase above 2100 °C over the composition range 35-100 mol% AlN. The flexural strengths of these solid solution were quite low due to inhomogeneity in grain size

and composition and spinodal decomposition occurred on annealing below 1950 °C. Recently, some studies of the phase relationship and microstructures of SiC-AlN solid solutions have been reported by hot-pressing [7-13], pressureless sintering with additives [14-19], chemical vapor deposition [20] and combustion synthesis [21, 22]. In these cases, the covalent bonds in SiC and AlN are strong and the diffusion coefficients are low, when all starting materials are in powder form, so that pressures of several hundred bars and temperatures of up to 2300 °C are required in order to obtain complete solid solutions with uniform composition distributions. Furthermore, the low fracture toughnesses of the solid solutions have to be overcome before promoting their application in engineering components. Therefore, more detailed investigations to gain an improved understanding of the complete solid solutions with uniform composition distributions are required for the microstructure and toughening of SiC-AlN ceramics.

In this study, complete solid solutions with uniform composition distributions of SiC-AlN ceramics were induced by the seeding with α -SiC as an additive in powder mixtures of β -SiC and AlN by hot-pressing in the 1870 °C to 2030 °C temperature range. The seeding effect of α -SiC on the phases present and compositional microstructures with columnar inter-grains was investigated in detail. Subsequently, the mechanical properties of the hot-pressed solid solutions were evaluated in terms of fracture toughness and Vickers hardness.

Experimental

The materials used for this study were commercial β -SiC (Beta Random, Ividen Company), AlN (Grade F. Tokuyama Soda Company) and α -SiC (Du A-1 Showa Denko)

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powders. The major impurities in the β -SiC powder were 0.39% SiO₂, 0.64% C, 0.02% Al and 0.03% Fe, while the AlN powder contained 0.89% O and 360 ppm C. The average particle sizes of the two powders were 0.27 μ m and 2 μ m, respectively. As an additive for seeding, α -SiC powders were used. The major impurities in the α -SiC powder were 0.46% C, 0.27% SiO₂, 0.024% Fe and 0.007% Al and the average particle size of the powder was 0.47 μ m. As listed in Table 1, nominal compositions investigated ranged from the composition 20 mol% AlN/80 mol% SiC (sample A20) to 90 mol% AlN/10 mol% SiC (sample A90) without the additive, and 49 wt% AlN/49 wt% SiC with the addition of 2 wt% α -SiC (sample 2W50A), 47.5 wt% AlN/47.5 wt% SiC with the addition of 5 wt% α -SiC (sample 5W50A) and 46 wt% AlN/46 wt% SiC with the addition of 8 wt% α -SiC (sample 8W50A). The compositions of appropriate amounts of the powders were prepared by wet milling for 24 h in a plastic jar with isopropyl alcohol and SiC balls. After milling, the mixed powders were evaporated to dryness, crushed in 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 a graphite washer. Hot-pressing was conducted under nitrogen at 1870 °C for 4 h and at 2030 °C for 1 h at 22.5 MPa (Table 1). Cooling was sufficiently rapid, so that the high-temperature phase was quenched to room temperature. After removing the specimens from the graphite dies, the surfaces were ground. The density was determined by measuring weights and dimensions. The ground surfaces were then polished using diamond pastes of 30, 15, 3, 1 μ m. The polished specimens were ultrasonically cleaned in ethanol, rinsed with distilled water and dried. All of the specimens were examined using X-ray diffraction (XRD) with CuK α . The polished specimens were etched using Murakami's etch

to reveal the microstructure. The etched sections were investigated using optical microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The indentation fracture test method was used with a load of 10 kgf, a loading speed of 0.1 mms⁻¹ and a load time of 20 s on the finished surfaces of the specimens for measurements of fracture toughness and Vickers hardness.

Results and Discussion

In Table 2, the phases present in the solid solutions under the various hot-press conditions were determined by XRD analysis. The phases are listed in the order of the amounts present. At 1870 °C for 4 h, for the samples A20, A50 and A70, the hexagonal 2H phase is the strongest with hexagonal 4H and 6H present and possibly some rhombohedral 15R and 3C, whereas for the sample A90 the 2H with 4H and 6H are the observed phases. At 2030 °C for 1 h, for the sample A20 the 2H phase is the strongest with 4H and 6H present and possibly some 15R and 3C, while for the sample A50 and A70 the 3C phase was transformed to the hexagonal and rhombohedral phases, and for the sample A90 the 2H, 4H and 6H are present.

Results for the samples 2W50A, 5W50A and 8W50A at 1870 °C for 4 h were similar to the result for the sample A50 at 1870 °C for 4 h. On the other hand, when these compositions were hot-pressed at 2030 °C for 1 h, a single solid solution of 2H was obtained for the sample 2W50A and 5W50A and 2H with some 4H for the sample 8W50A. These results indicate that the reaction of AlN and β -SiC powders causing the transformation to the 2H phase appeared to depend on the hot-pressing temperature and the addition of α -SiC seeding. The reason why the α -SiC seeding affects the transformation to the 2H phase of SiC-AlN solid solutions may be attributed to the isostructure of α -SiC and AlN. The lattice parameters of the two structures are $a = 0.3079$ and $c = 0.5058$ nm for α -SiC and $a = 0.3111$ and $c = 0.4978$ nm for AlN [5].

Fig. 1 and Fig. 2 show typical microstructures of the

Table 1. Compositions and hot-pressing conditions of powder mixtures

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

Table 2. Phases 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

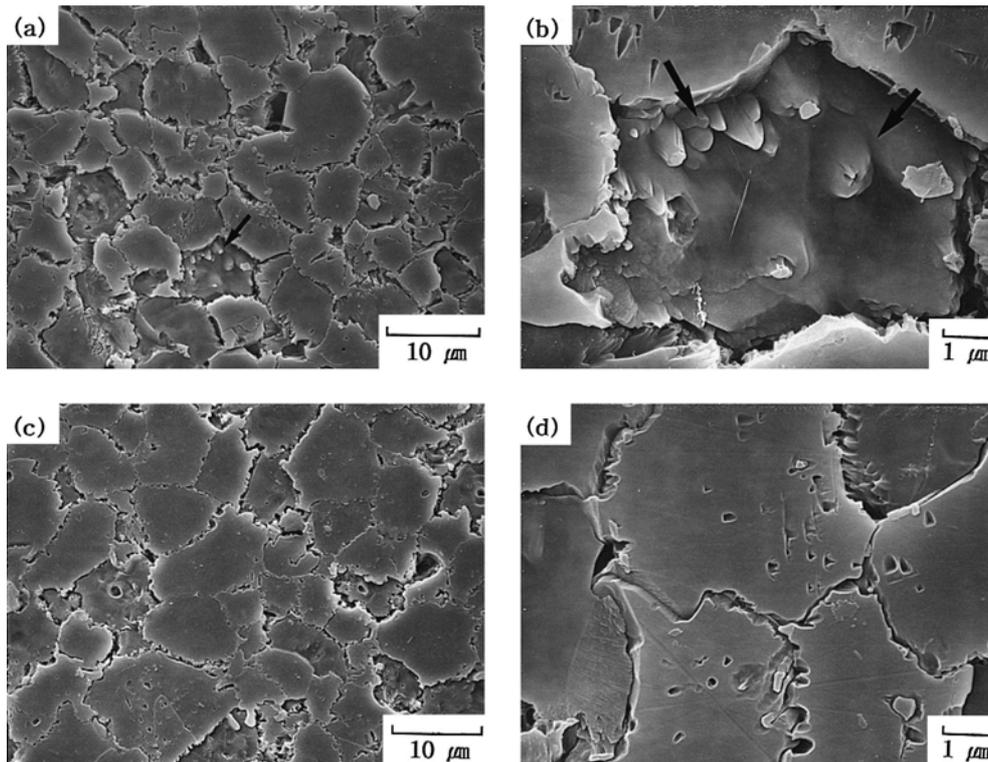


Fig. 1. SEM micrographs and high magnification images of SiC-AlN solid solutions for the sample 2W50A ((a), (b)) and 5W50A((c), (d)) as hot-pressed at 2030 °C for 1 h. The arrows on (a) and (b) indicate a small amount of columnar inter-grains.

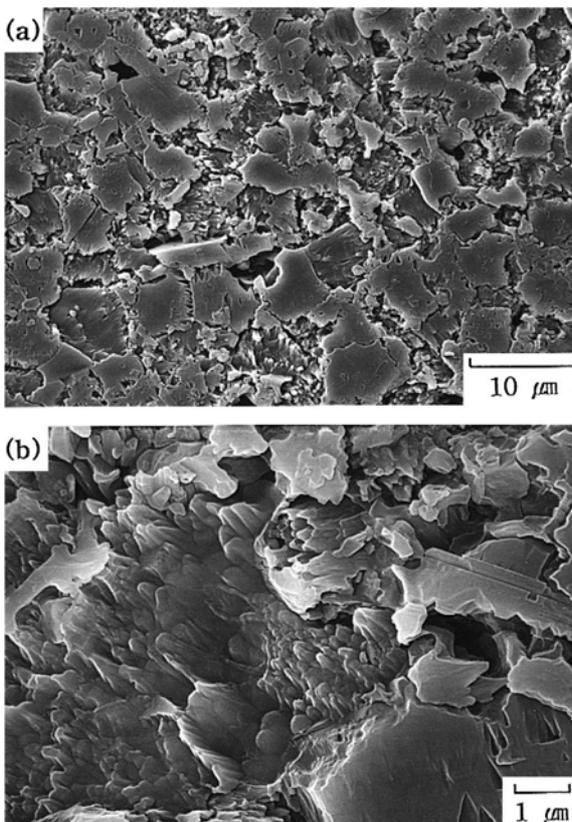


Fig. 2. SEM micrograph (a) and high magnification images (b) of a SiC-AlN solid solution for the sample 8W50A as hot-pressed at 2030 °C for 1 h.

SiC-AlN solid solutions for the samples 2W50A, 5W50A and 8W50A as hot-pressed at 2030 °C for 1 h, which previously were etched using Murakami's etch. All of the samples had densities in excess of 99% of theoretical density. According to the XRD results, for the composition of 49% AlN/49% SiC with an addition of 2wt% α -SiC (2W50A) or 47.5% AlN/47.5% SiC with an addition of 5 wt% α -SiC (5W50A), complete solid solutions with a single phase of 2H was obtained by hot pressing at 2030 °C for 1 h. The microstructures of the samples 2W50A and 5W50A in Fig. 1 show relatively uniform grain size distributions. The sample 2W50A exhibits a small amount of columnar inter-grains in the grain structure as indicated by the arrow in Fig. 1(a) and Fig. 1(b). In contrast, the sample 8W50A exhibits an inhomogeneous size distribution and a large proportion of heavily strained and faulted grains in Fig. 2(a) and with exaggerated columnar inter-grains in complicated grain mixtures in Fig. 2(b), which suggest either untransformed or in the process of the transformation from 4H to 2H. Fig. 3 shows a TEM micrograph (a) and diffraction patterns ((b) and (c)) of the columnar inter-grain in the 2H phases for the sample 2W50A. The columnar inter-grain was identified to be 4H (Fig. 3(c)) and the surrounded phase to be 2H (Fig. 3(b)). Therefore, it is noted that an appreciable amount of α -SiC seeding could develop the columnar inter-grains of the 4H phase and the stable 2H phase with a uniform composition and grain size distributions.

For the tentative SiC-AlN phase diagram [26], it is

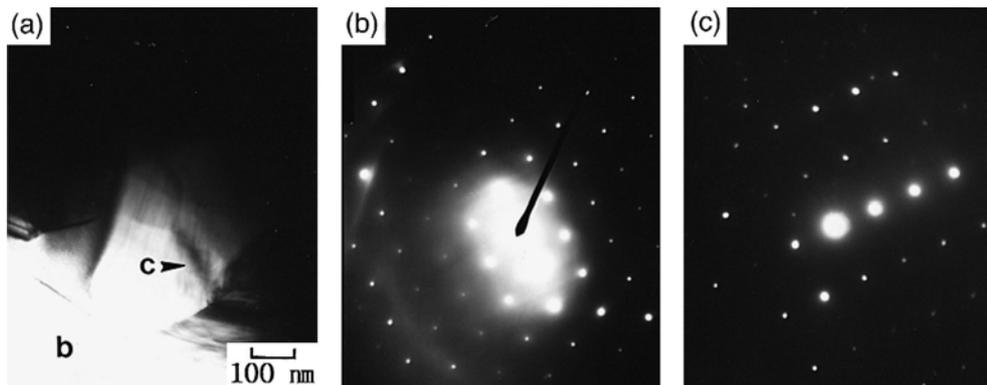


Fig. 3. TEM image (a) and diffraction patterns of 2H phase (b) and 4H phase (c) in a SiC-AlN solid solutions for the sample 2W50A.

assumed that the sequence of stable polytypes with increasing temperature is b, 2H, 4H, 6H. This sequence is not clearly observed experimentally because of the very close thermodynamic stability of the polytypes. A mixture of hexagonal polytypes was observed between 1870 °C and 2030 °C temperature range in this study. It could be assumed that the AlN and β -SiC transformed to β -2H, 6H-4H and 4H-2H. The metastable β phase is shown above 1600 °C and may extend to around 2000 °C. Above 2000 °C a single solid solution with the 2H structure and a 2H + 4H two phase mixture are observed from 23% AlN to 100% AlN. The miscibility gap has been suggested by Toutanji *et al.* [3] who conducted annealing experiments on solid solutions obtained by carbothermal reduction reaction. They found that the solid solutions, which were obtained at low temperatures, were metastable and tended to separate to SiC-rich and AlN-rich phases. The crystalline structure of the SiC-AlN solid solutions consisted of two main phases: one was a SiC-rich solid solution phase and the other was a AlN-rich solid solution phase [23]. The SiC-AlN solid solution provides the maximum possibility of observing splitting with the two phases of identical structure due to the slightly different lattice parameters. This phase separation was presumed to be of a spinodal or binodal decomposition, considering the peak splitting behavior [13, 23, 26]. It seems certain that the location of the miscibility gap and the other phase boundaries in the diagram are dependent on the raw materials, additives and pressures. It was considered that the α -SiC seeding of the reaction of AlN and β -SiC affected the SiC-AlN phase relationships and the microstructures by stabilizing the 2H phase. An appreciable amount of α -SiC seeding could develop the stable 2H phase with the columnar inter-grains of 4H phase at 2030 °C.

Table 3 shows results from the fracture toughness and Vickers hardness measurements for the SiC-AlN solid solutions. The fracture toughness of the sample 5W50A was 5.4 MPa·m^{1/2} and the sample 2W50A and 8W50A were 5.3 and 5.1 MPa·m^{1/2}, respectively. These values of the fracture toughness are higher than other reported values [10, 17, 19] in SiC-AlN solid solutions, which presented values ranged between 3.7 and 4.6 MPa·m^{1/2}. The enhanced fracture toughnesses in this study are due to the reinforce-

Table 3. Fracture toughness and Vickers hardness of SiC-AlN solid solutions hot-pressed at 2030 for 1 h

Sample name	Fracture toughness (MPa·m ^{1/2})	Vickers hardness (GPa)
2W50A	5.29 ± 1.23	17.09 ± 0.15
5W50A	5.43 ± 1.11	18.81 ± 0.12
8W50A	5.05 ± 1.54	16.68 ± 1.34

ment by the columnar inter-grains of the 4H phase in the 2H phase induced by the appreciable amount of α -SiC seeding. The average hardness of samples 2W50A, 5W50A and 8W50A are 17.0, 18.8 and 16.7 GPa, which show no difference compared with other studies [19].

Conclusions

SiC-AlN solid solutions were prepared from powder mixtures of β -SiC, AlN and α -SiC by hot-pressing in the 1870 °C to 2030 °C temperature range. The reaction of AlN and β -SiC powders causing transformation to the 2H structure appeared to depend on the hot-pressing temperature and addition of α -SiC seeding. For the composition of 49 wt% AlN/49 wt% SiC with 2 wt% α -SiC (2W50A) and 47.5 wt% AlN/47.5 wt% SiC with 5 wt% α -SiC (5W50A) heated at 2030 °C for 1 h, complete solid solutions with a single phase of 2H could be obtained. An appreciable amount of α -SiC seeding could develop the columnar inter-grains of the 4H phase and the stable 2H phase with a relatively uniform composition and grain size distributions. The fracture toughness of the sample 5W50A was 5.4 MPa·m^{1/2} and the sample 2W50A and 8W50A were 5.3 and 5.1 MPa·m^{1/2}, respectively, which are higher than other reported values in SiC-AlN solid solutions. The enhanced fracture toughness is due to the reinforcement of the columnar inter-grains of the 4H phase in the 2H phase induced by the appreciable amount of α -SiC seeding.

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References

1. S.H. Lee, S.Guo, H. Tanaka, K. Kurashima, T. Nishimura and Y. Kagawa, *J. Euro. Cer. Soc.* 28 (2008) 1715-1722.
2. W. Han, X. Zhang, W. Tai and J. Han, *Mat. Sci. Eng. A* 515 (2009) 146-151.
3. H.A. Toutanji, D. Friel, T.E. Korchi, R.N. katz, G. Wechsler and W. Rafaniello, *J. Euro. Cer. Soc.* 15 (1995) 425-434.
4. Y.B. Pan, J.H. Qiu and M. Morita, *Mat. Res. Bull.* 33 (1998) 133-139.
5. D. Bloor, R. J. Brook, M. C. Flemings, S. Mahajan and R.W. Cahn, *The Encyclopedia of Advanced Materials*, 4 (1995) 2452-2454.
6. I.B. Cutler, P.D. Miller, W. Rafaniello, H.K. Park, D.P. Thomson and K.H. Jack, *Nature*, 275 (1978) 434-435.
7. R. Ruh and A. Zangvil, *J. Am. Ceram. Soc.*, 65 (1982) 260-265.
8. S. Y. Kuo and A. V. Virkar, *J. Am. Ceram. Soc.*, 73 (1990) 2640-2646.
9. I. Teusel and C. Russel, *J. Mat. Sci.*, 25 (1990) 3531-3534.
10. J.F. Li and R. Watanabe, *J. Mat. Sci.*, 26 (1991) 4813-4817.
11. Y. Xu, A. Zangvil, M. Landon and F. Thevenot, *J. Am. Ceram. Soc.*, 75 (1992) 325-333.
12. R. Sathyamoorthy, A.V. Virkar and R.A. Cutler, *J. Am. Ceram. Soc.* 75 (1992) 1136-1139.
13. J. Chen, Q. Tian and A. V. Virkar, *J. Am. Ceram. Soc.* 75 (1992) 809-821.
14. G. magnani, F. Antolini, L. Beaulardi, E. Burrese, A. Coglitore and C. Mingazzini, *J. Euro. Cer. Soc.* 29 (2009) 2411-2417.
15. G. Magnani and L. Beaulardi, *J. Euro. Cer. Soc.* 26 (2006) 3407-3413.
16. J.K. Lee, H. Tanaka and H. Kim, *Mat. Lett.* 29 (1996) 1-6.
17. R.R. Lee and W.C. Wei, *Eng. Sci. Proc.*, 11 (1990) 1094-1121.
18. I. Teusel and C. Russel, *J. Mat. Sci. Lett.*, 11 (1992) 205-207.
19. M. Miura, T. Yogo and S. I. Hirano, *J. Mat. Sci.*, 28 (1993) 3859-3865.
20. Z. Qin, P. han, T.T. han, B. Yan, N. Jiang, S. Xu, J. Shi, J. Zhu, Z.L. Xie, X.Q. Xiu, S.L. Gu, R. Zhang and Y.D. Zhang, *Thin Solid Films*, 515 (2006) 580-582.
21. R.C. Juang, C.C. Chen, J.C. Kuo, T.Y. Huang and Y.Y. Li, *J. Alloys & Compounds*, 480 (2009) 928-933.
22. C. Kexin, J. Haibo, Z. Heping and J.M.F. Ferreira, *J. Euro. Cer. Soc.* 20 (2000) 2601-2606.
23. A. Zangvil and R. Ruh, *J. Am. Ceram. Soc.* 71 (1988) 884-890.
24. L. Zhou, X. Ni, U. Ozgur, H. Morkoc, R.P. Devaty, W.J. Choyke and D.J. Smith, *J. Cry. Growth*, 311 (2009) 1456-1459.
25. H. Okumura, M. Horita and T. Kimoto, J. Suda, *Appl. Surf. Sci.* 254 (2008) 7858-7860.
26. A. Zangvil and R. Ruh, *J. Am. Ceram. Soc.* 70 (1987) C125-128.