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Effect of pure-solvents without deflocculants for finer SiC particle dispersed MgO based composite

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The deagglomeration process and its effects on the microstructure have been investigated for fine MgO, SiC powders and SiC particle added MgO mixed powders which were ball-milled under both polar- and non-polar solvent without deflocculants. During the drying, exothermic reactions are observed at 300–450 °C in MgO and SiC powders ball-milled in alcohol. On the other hand, no chemical reaction could be observed for the powders ball-milled using acetone, and *n*-hexane. The observed exothermic reactions, then, are believed to be due to the oxide and/or oxide layer-alcohol reaction product formed during milling. This mechano-chemical reaction directly affects to deagglomerate during the drying process after wet-milling. Among the alcohol media, the well-dispersibility and deagglomeration of SiC powders as well as MgO powders seem to be reached by *n*-butyl alcohol, considering the balance between the steric effects and the dielectric constant of alcohol. These dispersion characteristics also effect on the microstructure of SiC particle dispersed MgO based composites. © *1999 Kluwer Academic Publishers*

1. Introduction

A stable powder dispersion is necessary to produce better ceramic based composites as well as uniformly dense monolithic ceramics. Two types of dispersion system may be used: pure solvent systems and solvent-deflocculant systems. Solvent-deflocculant systems are known to be more effective for dispersing fine powders than are pure solvent systems. In general, however, deflocculants are difficult to remove from the green body during binder burn-out, particularly for small-diameter powders.

Furthermore, mechanical comminution by ball milling is one of the most common operations in ceramic processing. Usually, milling is considered to be a simple comminution process resulting in changes in the particle size distribution. In this processes, however, it is reported that mechano-chemical reactions can occur between the powder and the liquid solvent media used in wet-milling operations. For example, Niesz and Bennett [1] observed the formation of aluminum monohydrate on alpha-alumina powders milled in water. Dynys and Halloran [2] showed that exothermic reactions were observed between 300 and 400 °C for alumina milled in alcohol. This communication reports evidence for mechano-chemical reactions experienced by alpha- and gamma-alumina milled in alcohol. Furthermore, heat-of-wetting studies showed that commercial SiC powders have acidic surfaces and were well dispersed in basic solvents [3]. SiC powders were more uniformly dispersed and both relative turbidity and packing density were increased when milled in alcohol with higher number of carbon atoms.

Recently, ceramic based nanocomposites fabricated by using ball-milling in pure solvent without deflocculants, were found to exhibit the high fracture strength at room and high temperatures and excellent creep resistance [4–7]. These significant improvement of mechanical properties, in special, fracture strength could be achieved for only the nanocomposites with homogeneously dispersed nano-sized second phases. This observation suggests that the homogeneous dispersion and narrow distribution of nano-sized second phase particles are most important factors to get the significantly improved mechanical properties for the ceramic nanocomposites.

In this paper, the effects of polar- and non-polar solvent media during ball-milling process and drying process on dispersibility and deagglomeration of powders were investigated for MgO and SiC powders. The SiC distribution in sintered MgO/SiC nanocomposites which were prepared from the powder mixtures milled under both polar- and non-polar solvent media was also observed. The effect of the kinds of solvent on the deagglomeration and the microstructure has been investigated using X-ray Photoelectron Spectroscopy (XPS), Particle Size Analyzer, Thermogravimetry/Differential

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Thermal Analyzers (TG/DTA), Scanning Electron Microscope, (SEM) and Transmission Electron Microscope (TEM).

2. Experimental

Silicon carbide powder with an average particle size of 100 nm (MSC20, Mitsui Touatsu Ltd., Japan) and MgO powder with an average particle size of 100 nm (Ube Industries Co., Japan) were used in this experiments. For SiC powder, the surface was characterized by XPS (Shimazu/Dupont 650B). Three kinds of prepared powders (each 100 g of MgO, SiC and 5 vol % SiC added MgO powders, respectively) were mixed in 400 ml of both polar-(acetone, ethyl-, *n*-butyl, and *n*-hexyl-alcohol) and non-polar (*n*-hexane) media by the conventional wet-ball milling in 120 rpm using zirconia balls with 100 ml of 5 mm ϕ and 50 ml of 10 mm ϕ in the plastic pot of 600 ml for 24 h. After wet-milling, each powder slurry was dried in evaporator at 50 °C. Centrifugal particle size analyzer (SA-CP3L, Shimazu Ltd.; measurement range is 0.02 to 500 μm) assisted with sedimentation and measured by semiconductor laser of 0.3 mW and wave length 780 nm, was used to determine the particle size and its distribution of dried MgO and SiC powders after milling in the various solvents. For these powders, DTA/TG (CN8078B2, Rigaku-denki) analyses were performed in air at a heating rate of 5 °C/min.

The 5 vol % SiC added MgO mixed powders were sintered using hot-pressing in a graphite die to measure the dispersibility of SiC particles in sintered bodies. After applying 30 MPa, the powder mixtures were heated to 1700 °C at the rising speed of 30 °C/min. After 60 min keeping at 1700 °C, the pressure was relaxed and the specimens were cooled. The sintered compacts were cut and ground into rectangular bar specimens. For microscopic observations, the samples were polished using diamond paste up to a 1/2 μm finished, and thermally etched in Ar at 1300 °C for 30 min. The microstructure was observed using SEM and TEM.

3. Results and discussion

TEM pictures in Fig. 1 reveal that the typical particle size of as-received MgO and SiC powders were approximately 100 nm. These powders include some agglomerates of particles of about 1 μm in diameter. The chemical analysis by the manufacture gave a free-SiO_2 of <0.12 wt %.

Fig. 2 shows the surface analysis of as-received β-SiC powders by XPS with Mg_{Ka} source. The O_{1s}, C_{1s}, and Si_{2p} peaks are detected, and then Si-O (534.5 eV) and O-Si-C (286.9 eV) bond peaks are suggested to exist. The peak in Fig. 2a well coincides with the Si-O bond peak on the SiC powder reported by Adair's results [8]. However, the reported Si-O bond peak in the pure-SiO_2 powder is 532.9 eV [9] which shifts by 1.6 eV compared with Si-O bond peak on the SiC powder. Therefore, this Si-O bond peak for the SiC powder is identified to be not pure Si-O bond peak. The O-Si-C bond peak as well as Si-O peak is also observed in the present experiment as shown in Fig. 2b. However, the Si-C bond peak (∼282 eV) is not observed in this work, in spite of being observed in the reference [9]. Therefore, it is clear that the surfaces of SiC powders are oxidized, and the oxidation layers are composed of Si, C and O elements. The dispersion characteristics of the SiC powder would be strongly dependent upon their oxidation layer [3].

Fig. 3 shows the differential graphs on the particle size distribution measured by particle size analyzer for the SiC powders dried after wet-ball milling for 24 h in various solvents. The powders milled in alcohol

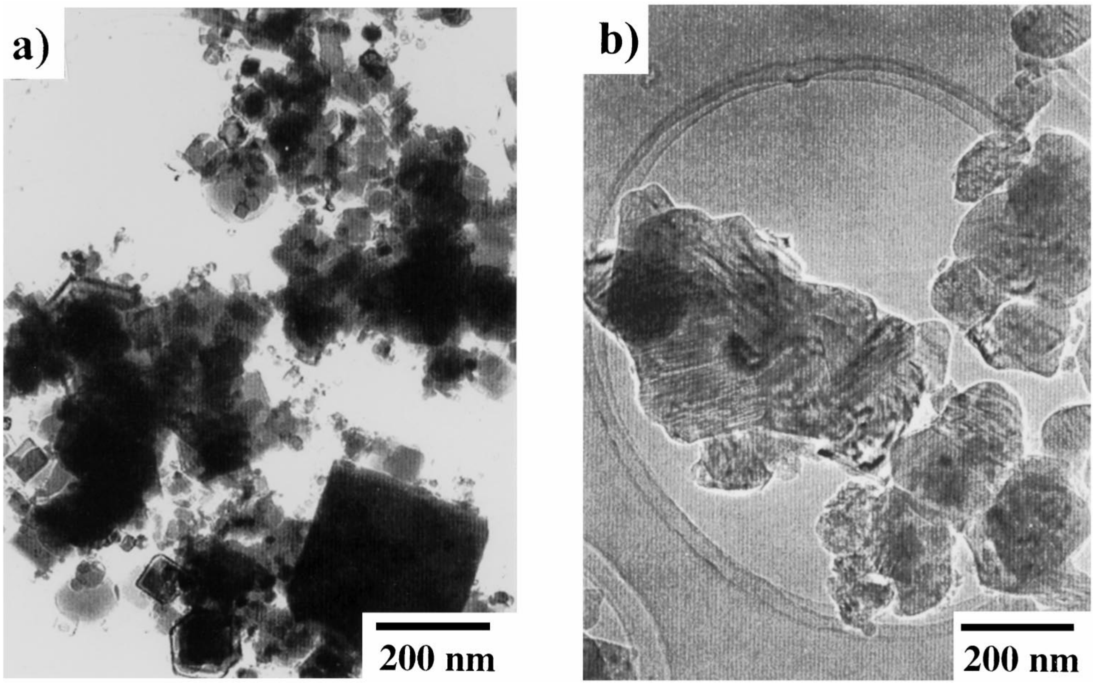


Figure 1 TEM micrographs of as-received (a) MgO and (b) SiC powders.

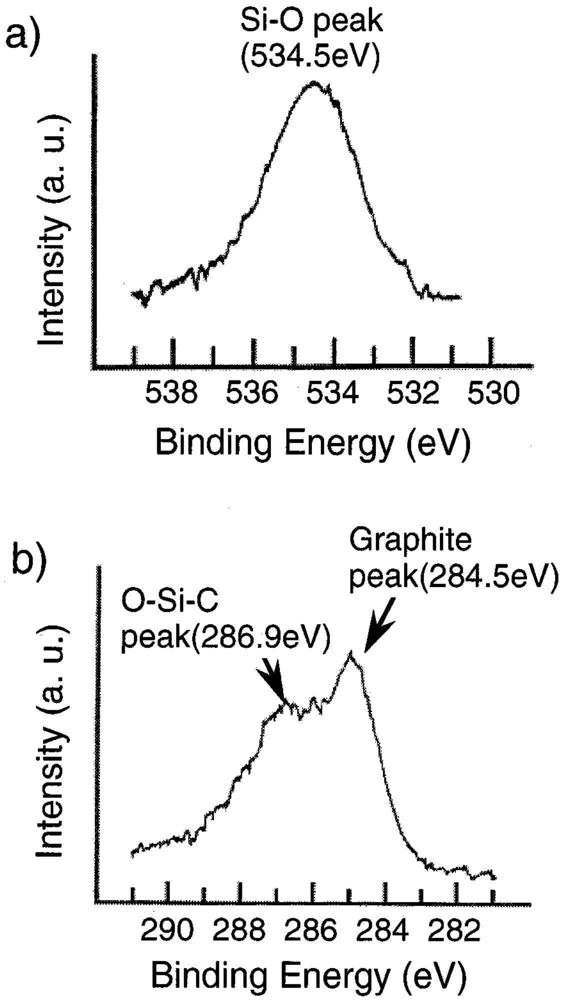


Figure 2 The oxygen 1s (a) and the carbon 1s (b) line spectrum for as-received SiC powder obtained by XPS.

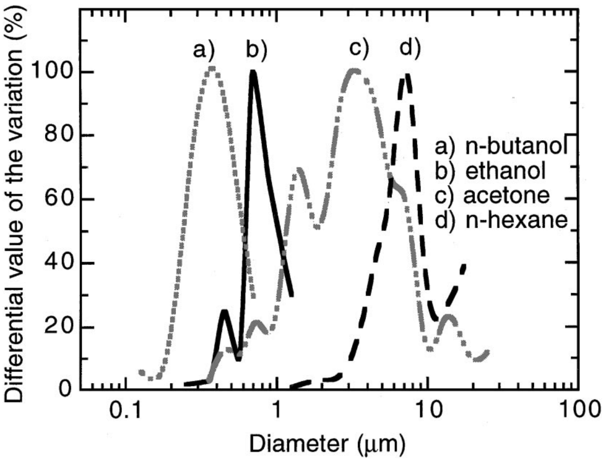


Figure 3 The differential graphs on paticle size distribution of SiC powder milled in *n*-butyl alcohol (a), ethyl alcohol (b), acetone (c), and *n*-hexane (d). (Maximum differential value of the variation is considered to be 100%.)

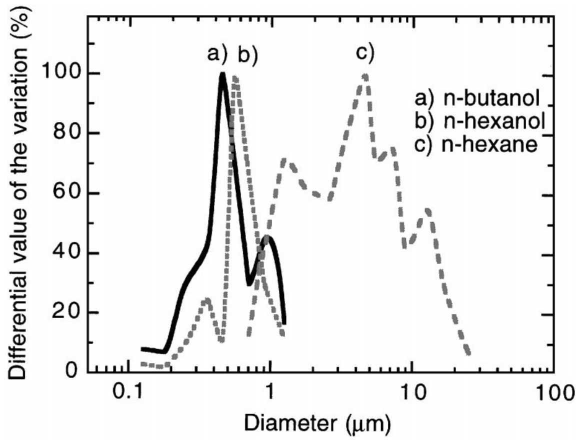
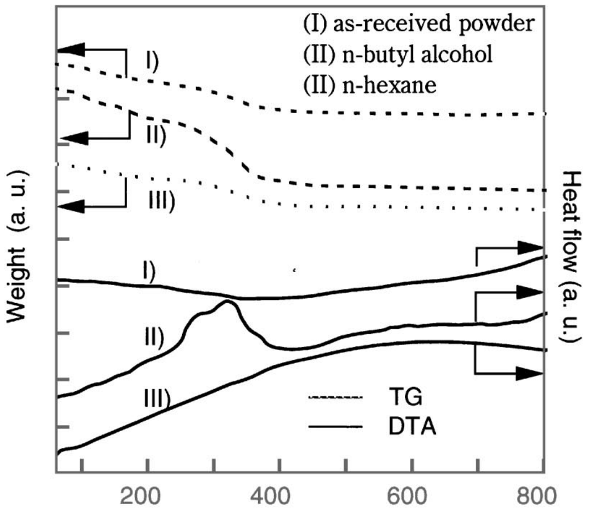


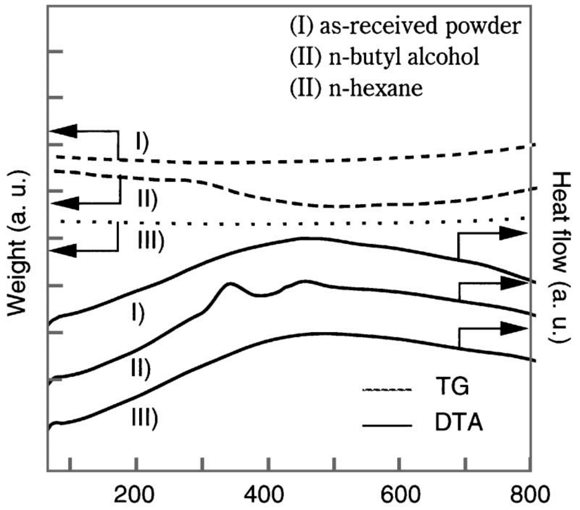
Figure 4 The differential graphs on paticle size distribution of MgO powder milled in *n*-butyl alcohol (a), *n*-hexyl alcohol (b), and *n*-hexane (c). (Maximum differential value of the variation is considered to be 100%.)

displayed finer average particle size and narrow distribution in size, whereas the larger particle size and the wide distribution were observed for powders milled in acetone and *n*-hexane. For powders milled in acetone and *n*-hexane, furthermore, large amount of agglomerated particles were remained, in special, for milling in *n*-hexane. To obtain finer and deagglomerated dispersion in the powder processing, therefore, it is desirable to use the alcohol as solvent media rather than acetone and *n*-hexane. Among powders milled in alcohol, the powders milled in *n*-butyl and *n*-hexyl-alcohol gave finer average particle size and narrow distribution, compared with the powders milled in ethylalcohol. However, there were little different for particle size and its distribution when used the *n*-butyl and *n*-hexyl-alcohol. The same results were also identified for the MgO powders milled in *n*-butyl alcohol, *n*-hexyl alcohol and *n*-hexane, as indicated in Fig. 4. This will be attributed to deagglomeration processes due to mechano-chemical reactions between solvent media and powders during the ball-milling [2, 14, 15].

The formation of alcohol-oxide layers by the mechano-chemical reaction is investigated by TG/DTA analysis [10–13]. Fig. 5a and b show TG/DTA results for the MgO and SiC powders milled in *n*-butyl alcohol and *n*-hexane for 24 h. The exotherms were observed in the DTA patterns for the MgO powder milled in *n*-butyl alcohol. Similar exothermic reaction was also observed for the SiC powder milled in *n*-butyl alcohol as shown in Fig. 5b. Notice the exothermic peaks at ∼330 and 420 °C. Clearly these peaks should correspond to the mechano-chemical reactions, since they closely correlate with the rate of weight loss determined by TG. This reaction, however, was not observed in the powders milled in acetone, in spite of polar-solvent. MgO and SiC powders milled in *n*-hexane for 24 h also exhibited quite different DTA patterns compared with those milled in *n*-butyl alcohol, and the exothermic reactions do not appear in the powders milled in *n*-hexane as well as those in as-received powders. It is apparent that the reactions involve oxidation of alcohol between the dispersed particle and solvent and also dehydration [14, 16, 17] which occurs during ball-milling in the alcohol solvents. These reactions must prevent the agglomeration between the particles. On the other hand, mechano-chemical reactions were not observed when milled in acetone and *n*-hexane, and then the agglomerates could be formed between the particles due to hydrogen bond during drying process. From these results, it is expected that both MgO and SiC powders will



(a) MgO powder



(b) SiC powder

Figure 5 TG/DTA patterns for MgO (a) and SiC (b) powders ball-milled in as-received powder(I), *n*-butyl alcohol(II), and *n*-hexane(III).

TABLE I Some properties of used solvent media

	Ethyl alcohol	*n*-butyl alcohol	*n*-hexyl alcohol	Acetone	*n*-hexane
Boling point (°C)	78.32	117.25	157.85	56.3	68.74
Density (g/cm^3)^a	0.7893	0.811	0.8158	0.7902	0.659
Viscosity (MPa · s)^a	1.20	2.948	—	0.322	0.313
Dielectric constant	24.3	17.30	13.2	20.7	1.89

^{a}At 20 °C.

be well deagglomerated and dispersed in alcohol than in acetone and *n*-hexane, as shown in Figs 3 and 4. The present results well coincide with the reported data of screening test and centrifugal casting tests for pure- and oxidized SiC powders [3]. Among powders milled in alcohol, the better deagglomeration and dispersibility observed for the powders milled in *n*-butyl, compared with the powder milled in ethyl-and *n*-hexyl-alcohol as shown in Figs 3 and 4, would be due to the dielectric constant of solvents as well as the steric effects.

The steric effect acts as to prevent close approach of individual particles, and the longer chain of carbon atoms induces the stronger steric repulsion. Furthermore, dielectric constant of alcohol affects dispersibility of ceramic powders [3, 18], and then the higher dielectric constant gave the better dispersibility of powders. As shown in Table I [19], the dielectric constant of alcohol is higher for the alcohol with lower carbon number.

Based on the results in this study, the optimum condition of the dispersibility for the SiC powders as well as the MgO powders should be reached by the *n*-butyl alcohol, considering the balance between the steric effect and the dielectric constant of alcohol as well as the mechano-chemical reaction.

Fig. 6 shows the SEM micrographs of thermally etched surfaces for 5 vol % SiC added MgO based sintered bodies prepared from the milled powders in

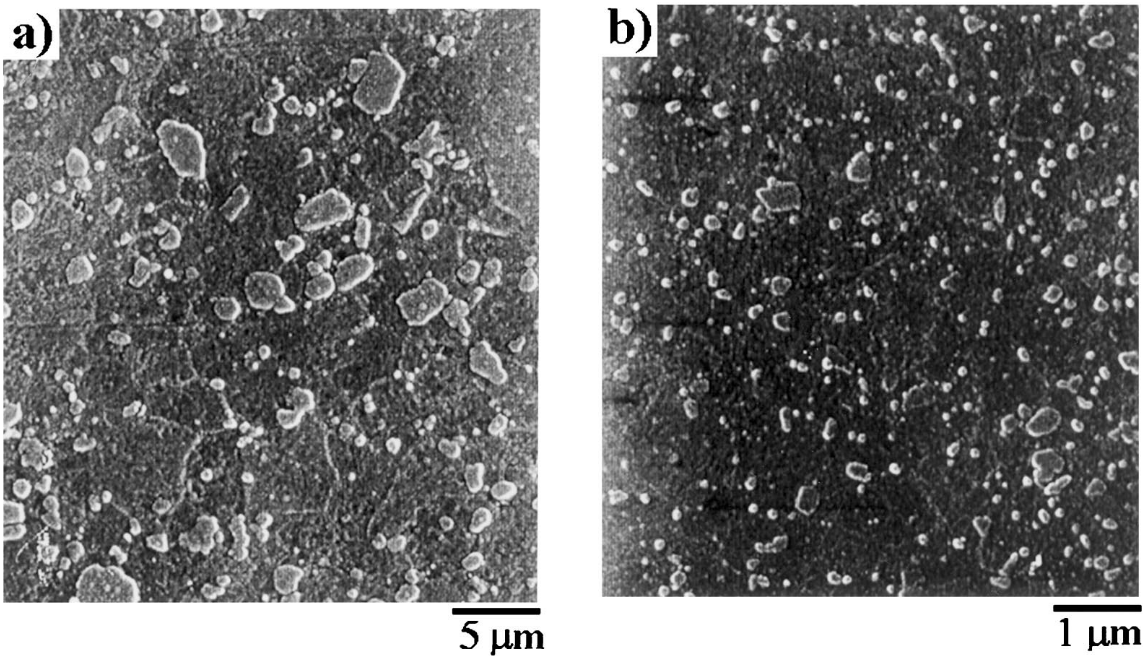


Figure 6 SEM micrographs of thermally etched surface for MgO/SiC composites fabricated from the powder mixtures milled in *n*-hexane (a) and *n*-butyl alcohol (b).

n-butyl-alcohol and *n*-hexane. From these pictures, it is concluded that the SiC particles milled in *n*-butyl-alcohol will give finer and better dispersion than those milled in *n*-hexane. These results clearly coincided with the particle size distribution data and the fact that the better dispersion as well as deagglomeration of SiC particulate was obtained for the sintered bodies prepared from the powder mixtures milled in *n*-butyl-alcohol.

4. Conclusions

The dispersibility and deagglomeration behaviors were investigated in acetone, alcohol and *n*-hexane as polar and non-polar media for MgO and SiC powders and their composite materials. The exothermic reaction is detected by TG/DTA analysis for the SiC and MgO powders wet-milled in alcohol solvents. This mechano-chemical reaction would prevent the agglomeration between the particles, while this reaction in acetone and *n*-hexane was not observed and the agglomerates were formed between the particles due to hydrogen bond during drying process. As expected, the better deagglomeration and homogeneity were obtained when alcohol solvents were used, compared with those used acetone and *n*-hexane. Among powders milled in alcohol, the better deagglomeration and dispersibility which were found for powders milled in *n*-butyl alcohol would be due to the balance between the steric effects and the dielectric constant of alcohol as well as the mechano-chemical reaction.

References

1. D. E. NIESZ and R. B. BENNETT, in "Ceramic Processing Before Firing," chapt. 7 edited by L. L. Hench and G. Y. Onoda (John Wiley & Sons, New York, 1978).
2. F. W. DYNYS and J. W. HALLORAN, *J. Amer. Ceram. Soc.* **64** (1981) C62–63.
3. M. OKUYAMA, G. J. GARVEY, T. A. RING and J. S. HAGGERTY, *ibid.* **72** (10) (1989) 1918–1924.
4. K. NIIHARA and A. NAKAHIRA, in Proceedings of the Third International Symposium on Ceramic Materials and Composites for Engines., edited by V. J. Tennery (American Ceramic Society, Westerville, OH, 1988) pp. 919–926.
5. K. NIIHARA, A. NAKAHIRA, G. SASAKI and M. HIRABAYASHI, in Proceeding of the First MRS. International Meeting on Advanced Materials, Vol. 4. edited by M. Doyama, S. Somiya, and R. P. H. Chang (Materials Research Society, Pittsburgh, PA, 1989) pp. 129–134.
6. K. NIHARA, *J. Ceram. Soc. Jp.*, 99 (10) (1991) 975–982.
7. T. OHJI, A. NAKAHIRA, T. HIRANO and K. NIIHARA, *J. Amer Ceram. Soc.* **77** (12) (1994) 3259–3262.
8. J. H. ADAIR, B. C. MUTSUDDY and E. J. DRAUGLIS, *Adv. Ceram. Mater.* **3** (1988) 231–234.
9. M. N. RAHAMAN, Y. BOITEUX and L. C. D. JONGHE, *Amer. Ceram. Soc. Bull.* **65** (8) (1986) 1171–1176.
10. R. GREENLNER, *Crit. Rev. Solid State Sci.* **4** (3) (1974) 415–428.
11. H. IMAI and M. SENNA, *J.Appl. Phys.* **49** (8) (1978) 4433–4437.
12. I. J. LIN, S. NADIV and D. J. M. GRODJIAN, *Miner. Sci. Eng.* **7** (4) (1975) 313–3136.
13. P. G. FOX, *J. Mater. Sci.* **10** (2) (1975) 340–369.
14. M. S. KALISZEWSKI and A. H. HEUER, *J. Amer. Ceram. Soc.* **73** (6) (1990) 1504–1509.
15. M. J. READEY, R. R. LEE, J. W. HALLORAN and A. H. HEUER, *ibid.* **73** (6) (1990) 1499–1503.
16. S. WADA, *J. Ceram. Soc. Jp.* **104** (11) (1996) 1085–1087.
17. T. HIRANO, J. YANG and K. NIIHARA, *ibid.* **104** (4) (1996) 348–353.
18. S. MITZUTA, W. R. CANON, A. BLEIER and J. S. HAGGERTY, *Amer. Ceram. Soc. Bull.* **61** (8) (1982) 872–875.
19. "Handbook of Chemistry, the Basic Part II," 3rd ed. (Maruzen, Japan, 1982) edited by Chem. Soc. Jap.

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