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Effect of aluminum nitride on the properties of cordierite

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The low dielectric constant and thermal expansion coefficient of cordierite are two attractive properties for the material to be used in electronic applications. However, compared to some other materials such as alumina, aluminum nitride (AlN), and beryllium oxide, it has a much lower mechanical strength and thermal conductivity. In the present work, AlN-cordierite composite systems are fabricated using different AlN contents, and the effect of AlN content on the mechanical, thermal, and dielectric properties of the AlN-cordierite system are investigated. It was observed that there exists an optimum AlN content for the mechanical and thermal properties while the dielectric property decreases with an increase of AlN content. An explanation for the observed data trend is offered based on an effective void concept.

1. Introduction

Cordierite and cordierite-based composites have received much attention during the past decades. Its low dielectric constant has made it an attractive alternative to alumina in micro-electronic packaging. In addition, it offers a coefficient of thermal expansion (CTE) close to that of silicon. If used together with silicon in layered systems, thermal stresses associated with power cycling will be reduced. However, cordierite has a relatively low mechanical strength and thermal conductivity compared to other ceramics such as alumina, thus it has relatively shorter service life under thermal fatigue and its ability to dissipate heat is relatively low. On the other hand, in the demand for higher speed in electronics products nowadays, high thermal conductivity has become an important criterion for electronic materials to dissipate heat more efficiently. As a result, it will be of great advantage if the mechanical strength and thermal conductivity of cordierite can be improved.

Although a number of works [1–5] have shown that cordierite can be toughened to enhance its mechanical properties, little attention has been given to the effect of toughening on the thermal and dielectric properties [6]. It is noted that aluminum nitride (AlN) possesses very high thermal conductivity. However, the disadvantages of using AlN alone as a structural material are its high sintering temperature and cost. In the present work, the effects of adding different amount of AlN to cordierite on the mechanical, thermal, and dielectric properties of AlN-cordierite composites are studied. Some of the observed behavior is explained using a micro-mechanical model.

2. Experimental procedures

Cordierite powders containing 34.9 weight percent (wt%) of alumina, 13.7 wt% of magnesia and 51.4 wt% of silica were first formed by solid state reactions. The formed powders were then milled and sieved by a 45 μm ASTM mesh. X-ray diffraction (XRD) was used to confirm the cordierite powder produced. AlN powders of 10, 20, 30, 40 and 50 wt% were added to the cordierite powder by wet milling with 3 wt% of polyvinyl-acetate solution for 3 hours at 300 rpm. The mixture was then dried, crushed and sieve with a 38 μm mesh. The compaction of the AlN-cordierite composite powders with different weight percents of AlN were carried out by dry pressing at 18 tons in a 50 mm- diameter stainless steel die. Sintering of the compacts was finally performed in a vacuum furnace at 1400°C for 4 hours. The densities of the fired compacts were then measured.

Three-point-bend flexural tests of sintered samples of dimensions 3 mm × 4 mm × 45 mm were carried out on an Instron Tester. Fracture toughness of the sintered compact was obtained by micro-indentation method using Vickers hardness tester (HSV-20). Thermal diffusivity of sintered compacts with different weight percent of AlN were measured using a NETZSCH Laser Flash Analyzer. Thermal conductivity of the materials was calculated using the thermal diffusivity obtained and the specific heat capacity measured by a differential scanning calorimeter (NETZSCH DSC 404). The dielectric constants of the compacts were measured by using a Hewlett Packard Impedance Analyzer at 1 MHz.

3. Mechanical properties

3.1. Variation of flexural modulus with AlN content

The variation of the flexural modulus of the AlN reinforced cordierite composites with AlN content is shown in Fig. 1. The flexural modulus of the composite rises

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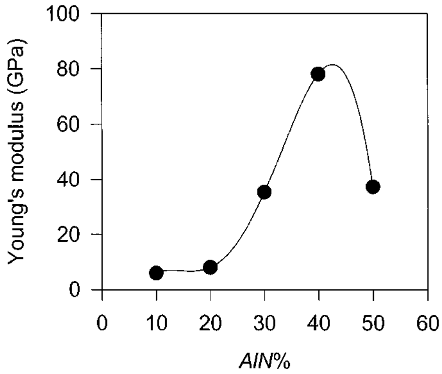


Figure 1 Variation of Young's modulus with AlN content, the line connecting data points showing possible trends.

non-linearly with an increase in the AlN content to a maximum of about 40 wt%. After which there is an abrupt drop of the modulus at 50 wt% of AlN. It is believed that this nonlinear rise-drop pattern is influenced by a number of factors such as interactions between particles, residual stress, dispersion of particles, and the sintering temperature.

If a particle is only partially "bonded" (mechanically or chemically) to its neighbors, the unbonded portion is acting like a pseudo void because there is no interaction between itself and other particles. The pseudo voids of the partially bonded particles and the physical void between particles can be treated collectively as the *effective* void of the material.

The nonlinear increase in the modulus of the composite results from the reinforcing effect of the stiffer AlN particles (the modulus of pure phase AlN is 318 GPa, about 1.5 time that of the cordierite, which is about 140 GPa) and enhanced AlN-cordierite interaction. At lower AlN content (below 40 wt%), the enhanced AlN-cordierite interaction (as compared to cordierite-cordierite interaction) is attributed partly to the increased particle size of the AlN. Also, the possible presence of residual stress may also strengthen the AlN-cordierite interaction [4]. The enhanced AlN-cordierite interaction, mechanical interlocking the most part, results in a reduction of the effective void content of the material. Increasing the content of the stiffer AlN phase in the composite increases the stiffness of the composite so long as the AlN particles are well dispersed and bonded in the cordierite matrix. At 50 wt% AlN content, however, the AlN particles begin to aggregate. As a result of a lower sintering temperature (1400°C, compared to sintering of pure phase AlN, which is 1800°C), the AlN-AlN particle interaction in the aggregates is weaker than that of the AlN-cordierite particles. The effect of this reduction in particle interaction is equivalent to an increase in the effect void content of the composite.

No practical models accounting for the observed data trend are currently available. However, by using micromechanics models for effective modulus of multi-phased composite, the effective void contents can be estimated for composites with different reinforcement contents. This single parameter not only provides indications on the trend of the modulus of the composite, it also reveals the trends in strength, fracture toughness, and thermal conductivity, as will be discussed in subsequent paragraphs. Here we will illustrate the idea of evaluating the effective void content by using a micromechanics model by Ju and Chen [7]. The effective bulk modulus, k, of a two-phase composite with spherical, non-interacting, elastic isotropic inclusions is

$$k = k_o\left[1+\frac{3(1-\upsilon_o)(k_1-k_o)\phi_1}{3(1-\upsilon_o)k_o+(1-\phi_1)(1+\upsilon_o)(k_1-k_o)}\right] \tag{1}$$

where k_o, and υ_o are the bulk modulus and Poisson's ratio of the matrix; k_1 and ϕ_1 are the bulk modulus and volume fraction of the inclusion, respectively. If all inclusions are voids, we have k_m, the bulk modulus of the matrix with void:

$$k_m = k_o\left[1+\frac{3(1-\upsilon_o)\phi}{3(1-\upsilon_o)-(1-\phi)(1+\upsilon_o)}\right] \tag{2}$$

Now ϕ is the void content in the matrix. Knowing the bulk elastic modulus, k, the effective void content, ϕ, can be evaluated by substituting Equation 2 into 1. The calculated *relative* effective void content are 85%, 77%, 53%, 0%, and 90% for AlN composites with 10%, 20%, 30%, 40%, and 50% AlN contents, respectively. If the effective void model can reasonably explain the trend in the elastic modulus, it may also alluding to the trend of fracture toughness and strength of the composite, since these quantities are intimately linked.

3.2. Variation of K_{IC} and flexural strength with AlN content

The variation of fracture toughness of the AlN-cordierite composites with AlN content is shown in Fig. 2. Similar to that of the elastic modulus, the trend of fracture toughness also exhibits a rise-drop pattern with increasing AlN content.

Wadsworth *et al.* [4] reported a similar rise-and-drop trend for ZrO_2-2 mole % Y_2O_3 composites. The four-point bend fracture strength of the composite increased to a maximum at about 20% (by weight) of

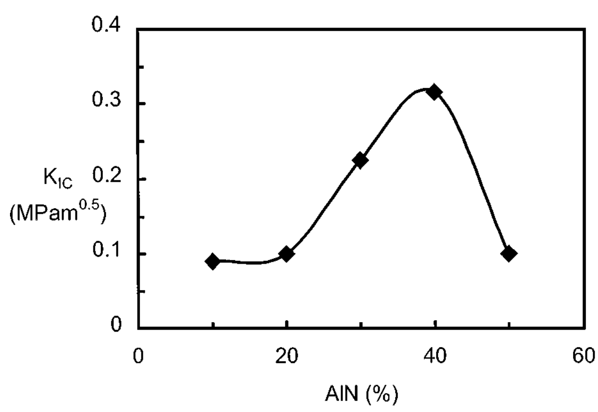


Figure 2 Variation of fracture toughness with the AlN content. The connecting line indicates data trend.

ZrO_2-2 mole % Y_2O_3. They attribute the toughening and strengthening mechanisms to stress-induced transformation toughening and the presence of residual stress between different particles, and the reduction in fracture strength to the heterogeneous dispersion of zirconia inclusions. Nieszery *et al.* [5] also showed that the flexural strength and fracture toughness of ZrO_2 or Y-TZP (Y_2O_3-stabilized tetragonal zirconia polycrystals) reinforced cordierite composites exhibit similar rise-and-drop pattern with increasing ZrO_2 or Y-TZP content to about 30 wt% of the reinforcement.

The toughened AlN-cordierite composites (up to 40 wt% AlN) can be explained by the reinforcing effect of the AlN phase [8]. If the density of the reinforcement is ρ, the frictional stress between the reinforcement and the matrix is τ, then the average surface force resisting crack propagation is $\tau A\rho$, where A is the surface area of contact between the matrix and the reinforcement. The stress intensity factor around a crack is

$$K_a = K_{IC} + K_p \tag{3}$$

where K_a is applied stress intensity factor, K_p is the stress intensity factor resulting from the crack processing zone (arise from the stress resisting crack propagation), and K_{IC} is the known fracture toughness of the matrix. It can be shown that [8] $K_p = \sigma(8d/\pi)^{1/2}$, where d is the length of the processing zone and σ is the stress resisting crack opening. The toughening effect is then given by [8]

$$K_p = \tau\rho A\left(\frac{8d}{\pi}\right)^{1/2} \tag{4}$$

Both the AlN-cordierite interaction term, τ, and the reinforcement density, ρ, increase with an increase of AlN content (below 50 wt% AlN), give rise to a non-linear increase in the fracture toughness. At 50 wt% AlN content, however, although ρ is increased, the interaction term (τ) has drastically dropped, resulting in a reduction of resistance to crack propagation.

The variation of the flexural strength with AlN content of the AlN-cordierite composite is shown in Fig. 3. The data trend is very similar to those presented in Figs 1 and 2. The flexural strength of the composite rises with an increase in the AlN content to a maximum of about 40 wt%. After which there is an abrupt drop of the strength at 50 wt% of AlN.

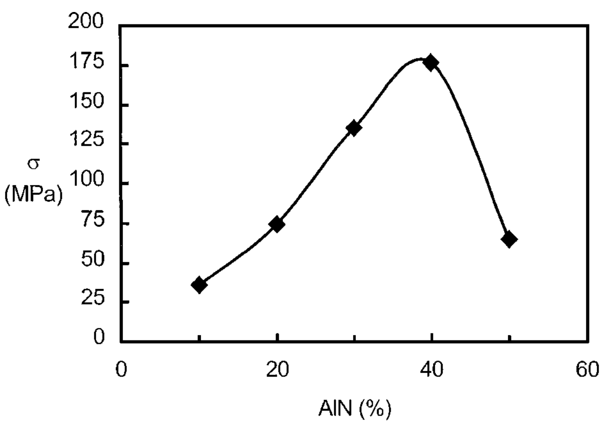


Figure 3 Variation of flexural strength with AlN content. Connecting line indicates data trend.

An explanation can be made along the same line as for the trend in the elastic modulus. The increased flexural strength may be attributed to the enhanced AlN-cordierite interaction and the strengthening effect of the AlN particles. The mismatch between the thermal and mechanical properties, as well as the geometry of the cordierite and AlN particles introduces residual stresses within the composite, thereby strengthen the AlN-cordierite interaction and thus enhances the strength of the composite.

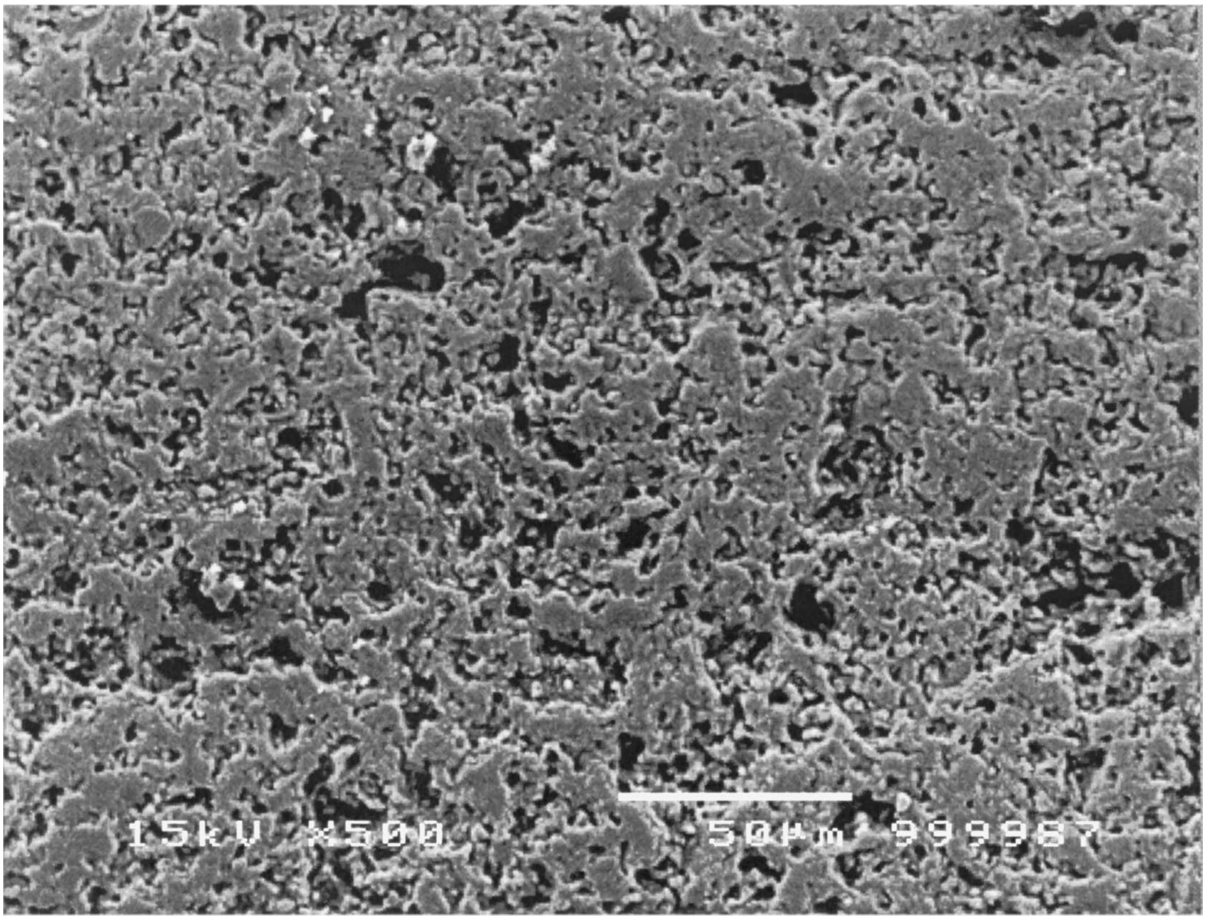
The strength enhancing effect continues until the content of AlN increased to 40 wt%. Beyond 40 wt% AlN content, however, larger aggregates of the AlN particles is seen (Fig. 3a and b), results in lowered flexural strength. As the sintering temperature (1400°C) is insufficient to promote significant sintering within the AlN aggregates, the densification within the aggregates is reduced, results in a weaker composite. In addition, it is seen from Fig. 4a and b that the composite with 50 wt% AlN has larger voids, resulting in lowering the fracture strength of the system.

4. Thermal and dielectric properties

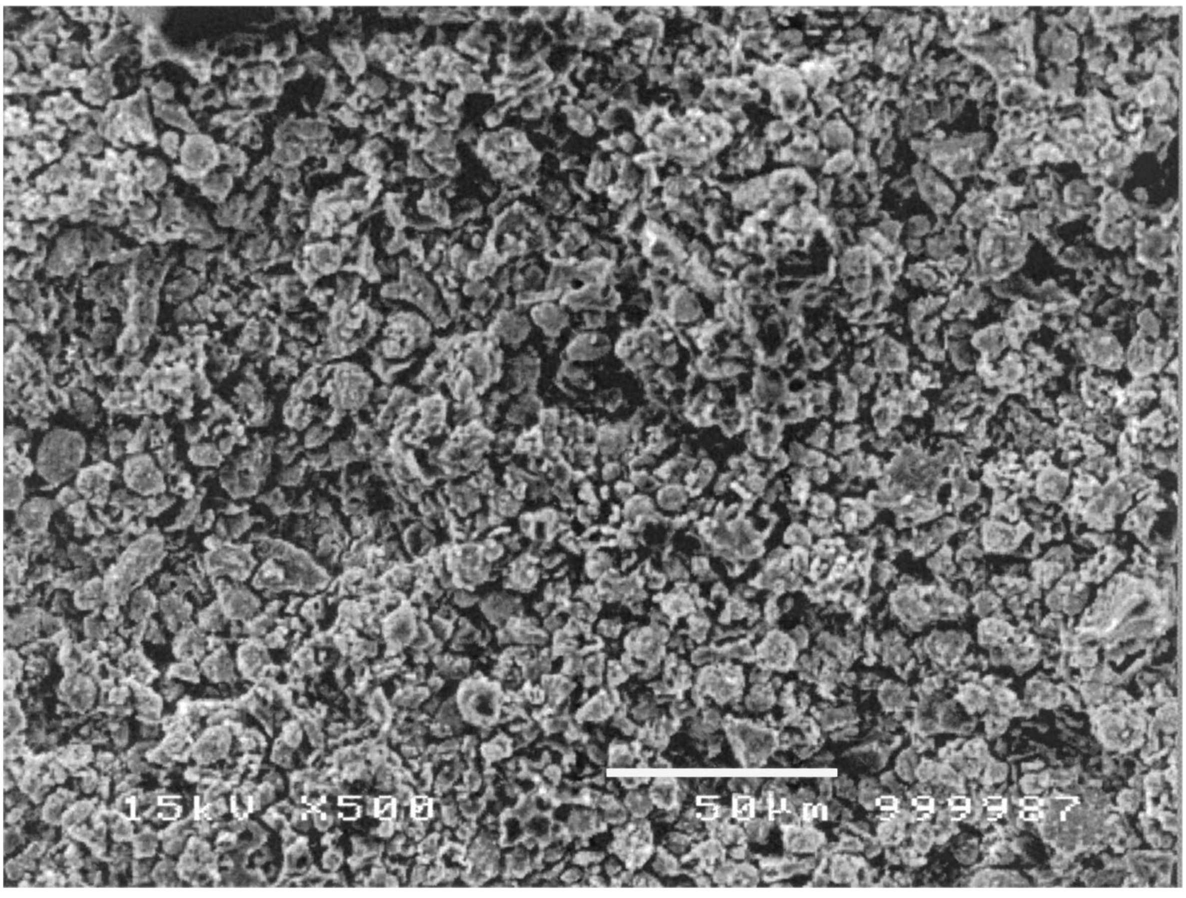
It is important that both the thermal and dielectric properties remain favourable as the mechanical property improves. The effect of AlN contents on both the thermal and dielectric properties of the AlN-cordierite system are shown in Figs 5 and 6.

It is noted that the thermal conductivity values increase almost 5 times as the percentage of AlN increases from 10 to 40 wt%. This increase in the thermal property of the composite is attributed to the higher thermal conductivity of AlN, where the heat dissipation network of the composite is enhanced as the AlN percentage increases. However, it is also noted that when the content of AlN increases to 50 wt%, an abrupt drop of the conductivity occurs. This phenomenon has been observed earlier in mechanical properties, where material properties were initially improved with an increase of a second phase, and then begin to decrease after a threshold percentage. In the case of thermal conductivity, this is attributed to the aggregation of AlN particles at high AlN content which results in a relatively poor dissipation network of the AlN, and hence a drop in the thermal conductivity of the composite.

The result on the dielectric constant measurement is shown in Fig. 6. It can be seen that the addition of AlN to the cordierite matrix does not increase the dielectric constant. In fact, the values dropped as the AlN additive increases from 10 to 50 wt%. It is noted that in the case of dielectric constant, the degradation in property of the composite is not observed when the AlN content increases from 40 to 50 wt%. This is attributed to the fact that increase in the effective void content benefits the dielectric property of the composite. As a result, for dielectric property, the abrupt drop in property is not observed.



(a)



(b)

Figure 4 (a) SEM micrograph of cordierite with 10 wt% AlN; (b) SEM micrograph of cordierite with 50 wt% AlN.

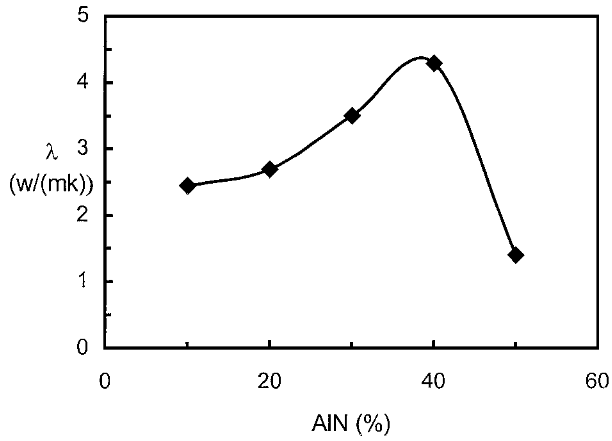


Figure 5 Variation of thermal conductivity with AlN content. Connecting line indicates data trend.

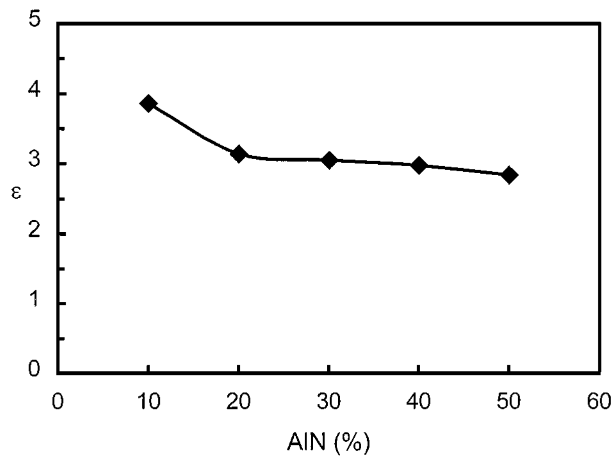


Figure 6 Variation of dielectric constant with AlN content, connecting line indicated data trend.

5. Concluding remarks

It is found that by adding appropriate amount of AlN to cordierite, the mechanical, thermal, as well as dielectric properties of the AlN-cordierite composite system are improved. In the present study, the optimum reinforcement content appears to be at 40 wt% AlN content. The dielectric constant of the cordierite-AlN composite has shown a 30% decrease as AlN was increased from 10 to 50 wt%. The thermal conductivity of the AlN-cordierite composite has also demonstrated a five-fold increase in magnitude as the percentage of AlN added increased from 10 to 40 wt%. It is observed that further addition of AlN to 50 wt% has resulted in lowering of the thermal conductivity and mechanical properties. This is attributed to the aggregation of AlN particles at high AlN content and the reduction of sintering. The rise-drop data trend in stiffness, fracture toughness, fracture strength, and thermal conductivity of the composite with varying reinforcement content may be explained using an effective void content concept. Qualitative trends in the mechanical and thermal properties of the composite can be estimated based on the effective void content. The effective void content is shown to be a critical parameter that is indicative of the mechanical and thermal properties of the AlN-cordierite composite.

References

1. M. A. MCCOY and A. H. HEUER, *J. Am. Ceram. Soc.* **71** (1988) 673.
2. M. HIRANO and H. INADA, *J. Mater. Sci.* **28** (1993) 74.
3. I. WADSWORTH and R. STEVENS, *ibid.* **26** (1991) 6800.
4. K. NIESZERY, K. L. WEIBKOPF, G. PETZOW and W. PANNHORST, "High Tech. Ceramics," edited by P. Vincenzini (Elsevier Science Publishers, Amsterdam, 1987) p. 841.
5. I. WADSWORTH and R. STEVENS, *Journal of Materials Science.* **25** (1990) 3982.
6. J. T. OH, Z. WEIDA, P. HING and H. S. FONG, in "Advanced Materials Development and Performance," edited by W. G. Ferguson and W. Gao (Auckland, 1997) p. 197.
7. J. W. JU and T. M. CHEN, *Acta Mechanica* **103** (1994) 123.
8. S. M. WIEDERHORN, *Annual Review of Materials Science* **14** (1984) 373.

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