JOURNAL OF MATERIALS SCIENCE **17** (1982) 3611–3616

Carbon fibre-reinforced silicon nitride composite

JING-KUN GUO, ZHI-QIONG MAO, CUE-DI BAO, RONG-HUA WANG, DONG-SHENG YAN
Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China

The processing of silicon nitride reinforced with carbon fibre was studied. The problems of physical and chemical incompatibility between carbon fibre and the silicon nitride matrix were solved by addition of a small amount of zirconia to the matrix and by low-temperature hot-pressing. The composite material possesses a much higher toughness than hot-pressed silicon nitride. Its work of fracture increased from 19.3 J m^{-2} for unreinforced Si_3N_4, to 4770 J m^{-2}; its fracture toughness, K_{Ic}, increased from 3.7 MN m$^{-3/2}$ for unreinforced material, to 15.6 MN m$^{-3/2}$. The strength remains about the same as unreinforced Si_3N_4 and the thermal expansion coefficient is only 2.51×10^{-6} °C^{-1} (RT to 1000° C). It is anticipated that this composite may be promising because of its mechanical and good thermal shock-resistance properties.

1. Introduction

Ceramic materials with many attractive properties, e.g. good high-temperature mechanical strength, high resistance to creep, resistance to oxidation and chemical attack etc., have attracted attention. However, they have a drawback – brittleness – which is a great worry to users. Improving the toughness of ceramics and glasses has long concerned material scientists and engineers. The approach of fibre reinforcement has obtained some delightful results. In the early sixties, several W or Mo filament-reinforced oxides [1–5] were developed in which the filaments were found to have the ability to impede crack propagation and thus enhance thermal shock and impact resistances of the materials. When carbon fibre became available in large quantities, it was frequently used for reinforcement. Crivelli-Visconti and Cooper [6] used carbon fibre-reinforced silica and obtained a composite sample with increased strength and work of fracture by wide margins. The work on carbon or graphite fibre-reinforced lithium aluminosilicate glass or borosilicate glass [7–10, [11] indicated that there exists a series of promising materials which not only have higher strength but also higher work of fracture and fracture toughness, and hence possess excellent anti-thermal and mechanical impact behaviour. SiC fibre-reinforced glassy matrix composites have been shown to be able to retain their strength up to 1000° C [12].

For Si_3N_4 matrix, Lindley and Godfrey [13] used SiC fibre with a W core as a reinforcement material and obtained a composite whose work of fracture could be up to 900 J m^{-2} with some increase in strength. Brennan and co-worker [14, 15] used W or Mo filament, and especially Ta filament, to reinforce Si_3N_4, and obtained a composite with a higher impact strength, which is 10 times better even at 1300° C.

This paper introduces a new composite – carbon fibre-reinforced Si_3N_4. In our preliminary work, it appeared that the fibre and matrix were incompatible with each other both physically and chemically. Various means were tried to solve these difficulties. It was found that an addition of zirconia to Si_3N_4 helped to alleviate the thermal expansion mismatch between carbon fibre and Si_3N_4 matrix; while by low-temperature hot-pressing, the chemical reaction between carbon fibre and Si_3N_4, could be avoided. Carbon fibre-reinforced Si_3N_4 composite with attractive properties can thus be fabricated.

0022–2461/82/123611–06$03.22/0 © *1982 Chapman and Hall Ltd.*

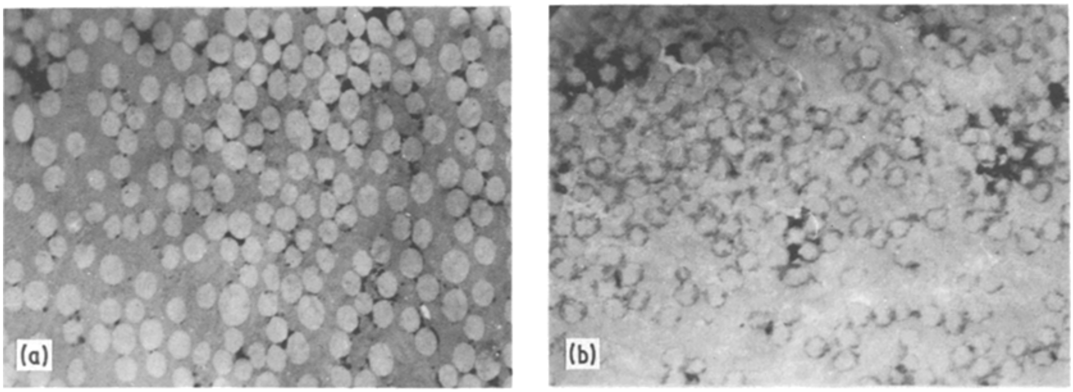

Figure 1 Carbon fibre embedded in Si_3N_4, (a) 1600° C; (b) 1650° C. × 200.

2. Experimental details

2.1. Materials

Si_3N_4 powder was prepared by nitriding silicon powder, over 99.5% pure, finally at 1450° C, and by milling it for 48 h with WC balls and distilled water in a nylon cylinder. It was then dried. The Si_3N_4 powder had a specific surface area of 4.31 $m^2 g^{-1}$ measured by N_2 absorption. The average grain size of this powder was 3.2 μm measured by particle size analysis apparatus*. This Si_3N_4 powder contained about 92% α-phase. Carbon fibre, made by Shanghai Carbon Factory or Liou-yuen Factory of Petroleum Chemical Engineering from PAN precursor, was used which has a tensile strength $\geqslant 1800\,MN\,m^{-2}$ and an elastic modulus $\geqslant 180\,GN\,m^{-2}$.

2.2. Experimental procedure

Si_3N_4 powder was mixed with additives for 2 h in a nylon cylinder with WC balls in water medium, the slurry containing about 40% water. Then a tow of carbon fibre was released through a rolling apparatus and was guided to pass through a Si_3N_4 slurry bath and wound onto a square board in an aligned arrangement. After drying, the samples were cut into 60 mm × 60 mm squares, and put in graphite moulds coated with BN paint. Finally, they were sintered by hot-pressing in a furnace with a graphite heating element. Samples were cut into 3 mm × 5 mm × 50 mm bars for three-point bending strength measurement, 4 mm × 4 mm × 45 mm bars with a triangular gap in the centre for the measurement of work of fracture, and 2.5 mm × 5 mm × 30 mm bars with a half slot at the central position for fracture toughness, K_{Ic}, measurements. These samples were also used for microstructure and other physical property studies after mechanical property measurements.

3. Approach to solve the incompatibility problem between carbon fibre and silicon nitride

In our earlier work [16], we found that there are severe reactions at high temperature between carbon fibre and Si_3N_4. The attack is obvious at 1650° C where a reaction layer appears around the carbon fibre (see Fig. 1). As is known, the hot-pressing of Si_3N_4 usually requires a temperature of 1750° C and above, with additives such as MgO or Y_2O_3 and Al_2O_3. It is obvious, therefore, that carbon fibre will be damaged by hot-pressing at such temperatures and will lose its ability to reinforce. On the other hand, the thermal expansion coefficient of carbon fibre is reported to be 0.67×10^{-6}° C from RT to 900° C in the axial direction [17]. However, the thermal expansion coefficient of SMZ–Si_3N_4 is 4.62×10^{-6}° C (RT to 1000° C) measured in our laboratory. The thermal expansion mismatch will certainly result in a large tensile stress along the length of the fibre. Rough calculation shows that the tensile stress build up ($\sim 400\,MN\,m^{-2}$) will surpass the strength of the matrix and transverse cracks do appear in the matrix perpendicular to the fibres (see Fig. 2) after hot-pressing at various temperatures. With certain sintering additives, which will be described later, Si_3N_4 has been found to be sintered to a considerable extent at and above 1400° C. It is not surprising, therefore, that at and above 1400° C, large cracks perpendicular to the fibre occur together

---

*Micromeritics Instrument Corporation Product, USA.

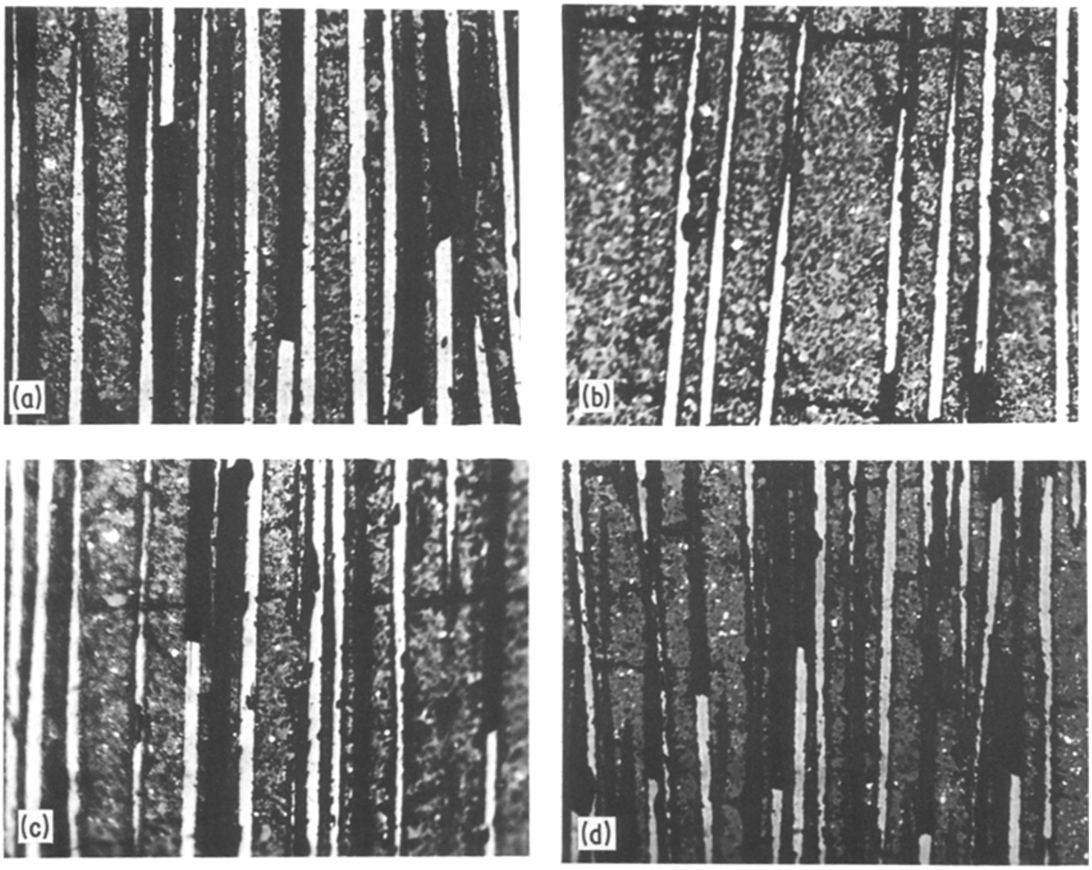

Figure 2 C fibre–Si_3N_4 composite hot-pressed at various temperatures, showing the appearance of cracks in the Si_3N_4 matrix (a) 135° C; (b) 1400° C; (c) 1450° C; (d) 1550° C. × 313.

with an increase in Si_3N_4 densification. However, at 1350° C, sintering of Si_3N_4 has not yet occurred to complete densification. Thus stress relaxation in the matrix is easily realized without crack initiation. It is pertinent, therefore, to tackle these two incompatibility problems, both physical and chemical, before any sound carbon fibre–Si_3N_4 composite can be fabricated.

3.1. Hot-pressing silicon nitride at low temperatures

In order to avoid the chemical reaction of carbon fibre with Si_3N_4, the most realistic approach is probably to lower the sintering temperature during the fabrication process. As mentioned above, the hot-pressing temperature of Si_3N_4 is usually about 1750° C. The thermal treatment temperature of the composite should now be lowered to below 1550° C. This was realized through the introduction of new additive systems of lower fusion temperature. Two such systems were found to be effective. One set of additives was found in the LiF–MgO–SiO_2 system by which Si_3N_4 can be hot-pressed to 99% theoretical density at 1450° C and 25 MN m^{-2} pressure [18]. Its sintering mechanism was found to be controlled by liquid-phase diffusion through grain boundaries [19]. The Si_3N_4 sample containing 5% additives of LiF–MgO–SiO_2 system is referred to as SML-5. Another set of additives is from the Al_2O_3–MgO–SiO_2 system with which Si_3N_4 can be hot-pressed to 99% densification at 1550° C. The mechanical properties, fracture behaviour and sintering mechanism of such samples were studied [20, 21].

With carbon fibre in SML-5 Si_3N_4 matrix hot-pressed at 1450 to 1500° C and 25 MN m^{-2} pressure, composite samples with undamaged carbon fibres can be fabricated.

3.2. Zirconia-phase transformation for stress relaxation

The use of ZrO_2 to toughen ceramics has produced encouraging effects [22–24] in which stress-induced ZrO_2 martensitic-phase transformation is

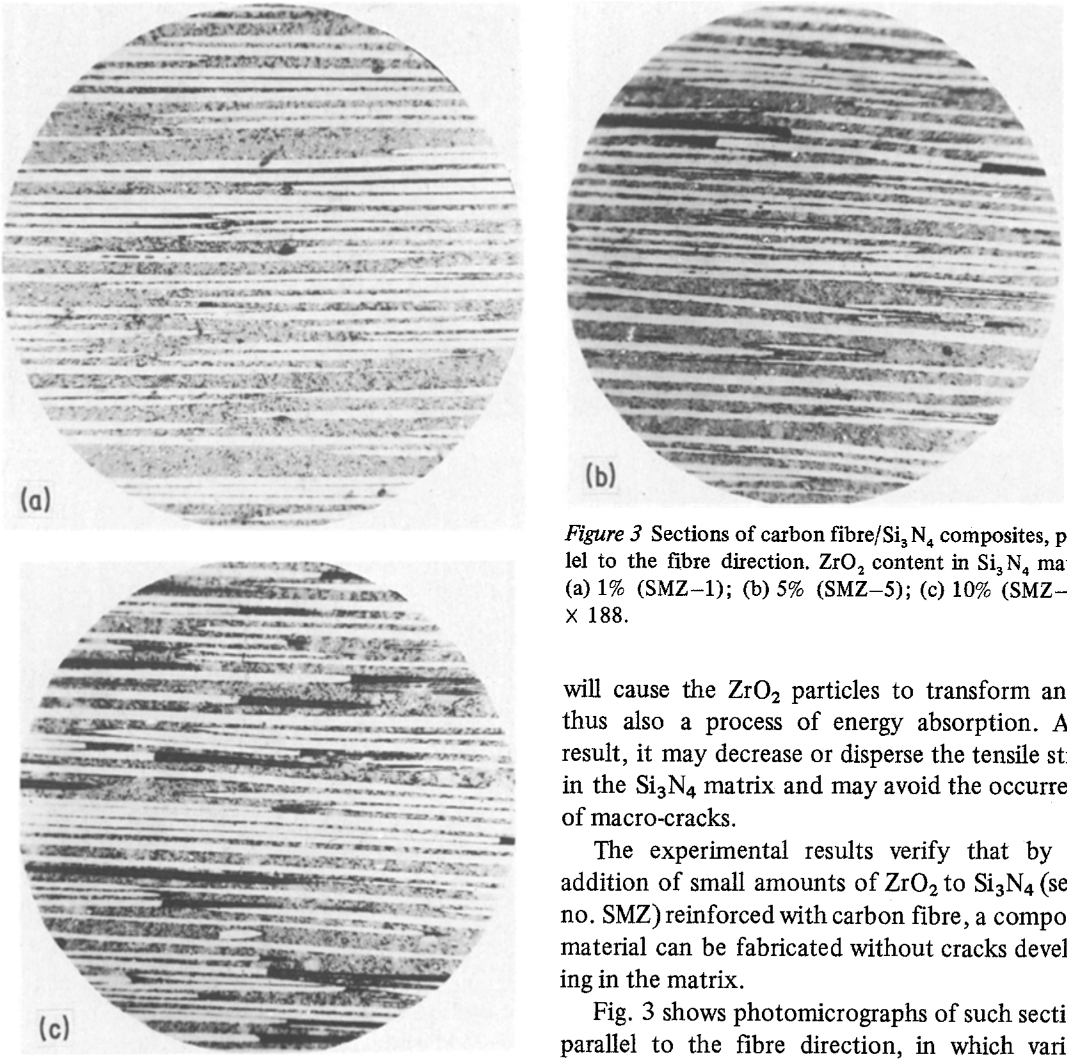

Figure 3 Sections of carbon fibre/Si_3N_4 composites, parallel to the fibre direction. ZrO_2 content in Si_3N_4 matrix: (a) 1% (SMZ–1); (b) 5% (SMZ–5); (c) 10% (SMZ–10). × 188.

one of the principle mechanisms. The difference in thermal expansion coefficients between carbon fibre and Si_3N_4 will produce a tensile stress in the matrix during cooling after the composite is hot-pressed at high temperatures. With ZrO_2 particles incorporated in the Si_3N_4 matrix, this tensile stress will cause the ZrO_2 particles to transform and is thus also a process of energy absorption. As a result, it may decrease or disperse the tensile stress in the Si_3N_4 matrix and may avoid the occurrence of macro-cracks.

The experimental results verify that by the addition of small amounts of ZrO_2 to Si_3N_4 (serial no. SMZ) reinforced with carbon fibre, a composite material can be fabricated without cracks developing in the matrix.

Fig. 3 shows photomicrographs of such sections parallel to the fibre direction, in which various amounts of ZrO_2 were added to the Si_3N_4 matrix. It may be seen that cracks perpendicular to the fibres have disappeared, even with 1 wt% ZrO_2 addition, but according to results discussed below, it is appropriate to have a 5 wt% ZrO_2 addition. X-ray diffraction shows that all ZrO_2 particles are monoclinic.

TABLE I The properties of C fibre/Si_3N_4 composite

	SMZ–Si_3N_4	C fibre/SMZ–Si_3N_4
Bulk density (g cm^{-3})	3.44	2.7
Fibre content (vol %)		30
Bending strength (MN m^{-2})	473 ± 30	454 ± 42
Young's modulus (GN m^{-2})	247 ± 16	188 ± 18
Work of fracture (J m^{-2})	19.3 ± 0.2	4770 ± 770
Fracture toughness K_{Ic} (MN m$^{-3/2}$)	3.7 ± 0.7	15.6 ± 1.2
Thermal expansion coefficient, (RT to 1000° C) (× $10^{-6°}$ C^{-1})	4.62	2.51

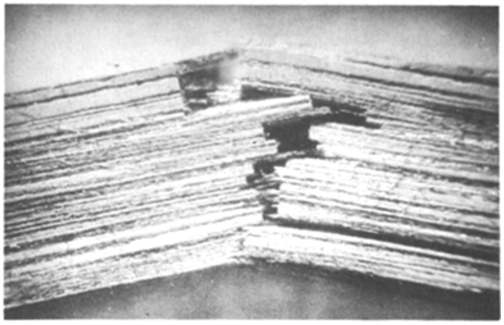

Figure 4 A micrograph of fractured C fibre/Si_3N_4 composite sample, × 8.8.

4. Properties of carbon fibre/Si_3N_4 composite

Table I shows the properties of a carbon fibre-reinforced Si_3N_4 composite. For comparison, the properties of Si_3N_4 with the same additives and ZrO_2 (SMZ–Si_3N_4) are also given in the same table. All samples were made by hot-pressing at 1450° C, 25 MN m^{-2} pressure and held for 1 h. It can be seen that there is no increase in strength of the composite. This may be attributed to the fact that the Young's modulus of Si_3N_4 is larger than that of the carbon fibre used (180 GN m^{-2}). It is also in accordance with Fitzer's analysis [25]. However, it may be noted that the work of fracture of the composite is about 200 times higher than that of the reinforced Si_3N_4. Its fracture toughness is also upgraded three times and its thermal expansion coefficient is considerably lower. Therefore, it should be a good material with high thermal shock and mechanical shock resistance.

Fig. 4 shows a micrograph of fractured C fibre/Si_3N_4 composite sample. It is typical of a fibre-reinforced brittle material showing delamination and fibre pull-out which is entirely different from a brittle ceramic material. The scanning electron micrograph of a fracture surface is shown in Fig. 5. It can be seen that the pull-out of fibres is obvious. The significant contribution of the work of pulling of the fibres to enhance the work of fracture and fracture toughness of the composite is as expected

5. Conclusions

The addition of a small amount of ZrO_2 to silicon nitride and low-temperature hot-pressing, enables the problems of physical and chemical incompatibilities between carbon fibre and silicon nitride matrix to be overcome, and a sound carbon fibre-reinforced silicon nitride composite with a much higher fracture toughness was fabricated. Its work of fracture is higher than unreinforced silicon nitride by two orders of magnitude; its fracture toughness increases three-fold and its strength generally retains the original level. The thermal expansion coefficient of the composite is also considerably lower. It is anticipated that the composite is a promising material with a potential for high thermal and mechanical shock resistance.

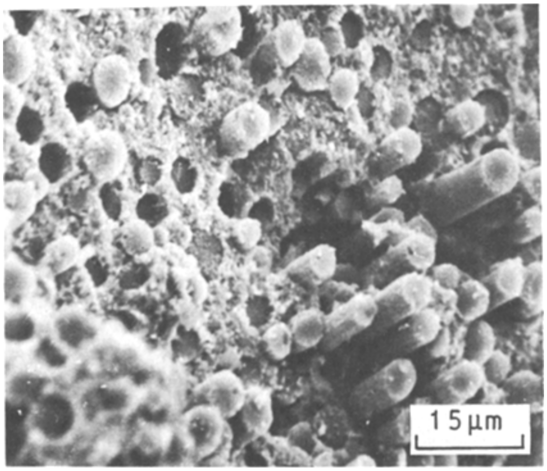

Figure 5 Fracture surface of C fibre/Si_3N_4 composite by SEM.

References

1. J. R. TINKLEPAUPH, B. R. GOSS, W. R. MOSKYNS, J. H. CONNOR and D. D. BUTTON, WADC-TR-58-452, Part III, Novermber (1960) PB-171550.
2. J. R. TINKLEPAUPH, "Strengthening Mechanisms", edited by J. J. Burke (Reed and Weiss, Syracuse University Press, New York, 1966) p. 579.
3. Y. BASKIN, Y. HARADA and J. H. HANDWERK, *J. Amer. Ceram. Soc.* **43** (1960) 489.
4. Y. BASKIN, C. A. ARENBERG and J. H. HANDWERK, *Amer. Ceram. Soc. Bull.* **38** (1959) 345.
5. L. A. NEIMARK, J. H. KITTEL and C. L. HOENIG, *J. Amer. Ceram. Soc.* **46** (1963) 219.
6. I. CRIVELLI-VISCONTI and G. A. COOPER, *Nature* **221** (5182) (1969) 754.
7. R. A. J. SAMBELL, D. H. BOWEN and D. C. PHILLIPS, *J. Mater. Sci.* **7** (1972) 663.
8. R. A. J. SAMBELL, A. BRIGGS, D. C. PHILIPS and D. H. BOWEN, *ibid.* **7** (1972) 676.
9. S. R. LIVITT, *ibid.* **8** (1973) 793.
10. K. M. PREWO, J. F. BACON and D. L. DICUS, *SAMPE Q.* **10** (4) (1979) 42.
11. D. C. PHILLIPS, *J. Mater. Sci.* **9** (1974) 1847.
12. J. J. BRENNAN, "Program to Study SiC Fiber Reinforced Glass Matrix Composites", AD-A077 638/5 (1979).
13. M. W. LINDLEY and D. J. GODFREY, *Nature* **229** (5281) (1971) 192.
14. J. J. BRENNAN and M. A. DE CRESCENTE, "Fiber

Reinforced Ceramic Matrix Composites", AD-757 063 (1973).

15. J. J. BRENNAN, in "Special Ceramics 6", edited by P. Popper (British Ceramics Research Association, London 1975) p. 123.
16. Composite Material Research Group, *New Ceram. Mater.* 4 (4) (1975) 1 (in Chinese).
17. Data Report, Sansi Institute of Coal Chemistry, The Chinese Academy of Sciences (1981).
18. Project Report, Shanghai Institute of Ceramics, The Chinese Academy of Sciences (1980).
19. J. K. GUO, C. D. BAO, R. H. WANG and D. S. YAN, *ibid.* December 1981, to be published.
20. H. Y. LIU, M.S. Thesis, Shanghai Institute of Ceramics, The Academy of Sciences, October (1981).
21. L. J. YUEN, M.S. Thesis, Shanghai Institute of Ceramics, The Academy of Sciences, October (1981).
22. R. C. GARVIE, R. H. HANNINK and R. T. PASCOE, *Nature* 258 (5537) (1975) 703.
23. N. CLAUSSEN, *J. Amer. Ceram. Soc.* 59 (1976) 49.
24. D. L. PORTER and A. H. HEUER, *ibid.* 60 (1977) 183.
25. E. FIZER, "Fiber Reinforced Ceramics and Glasses", International Symposium on Densification and Sintering of Oxides, Hakonne, Japan, October (1978).

Received 5 May
and accepted 12 May 1982