JOURNAL OF MATERIALS SCIENCE 26 (1991) 957–962

A uniaxially reinforced zircon–silicon carbide composite

R. N. SINGH, A. R. GADDIPATI
General Electric Corporate Research and Development, Schenectady, New York 12301, USA

Zircon matrix composites uniaxially reinforced with as-supplied and BN-coated silicon carbide filaments were fabricated, and their mechanical properties were measured in flexure mode. A toughened-composite behaviour was displayed by the reinforced samples with strengths between 681 and 700 MPa and toughness between 24 and 41 kJ m^{-2}. In comparison, the monolithic zircon failed in a brittle manner, had an average strength of 280 MPa and toughness of 0.95 kJ m^{-2}. Influence of fibre-matrix interfacial shear stress on the first matrix cracking stress, ultimate failure strength and strain, toughness, and mode of failure were studied. The composite toughness was found to be dependent on the interfacial shear stress whereas the first matrix cracking stress was independent of the interfacial shear stress. These results on mechanical properties are compared with predictions from composite models.

1. Introduction

Ceramic–matrix composites with high-temperature capabilities are needed for a variety of structural applications in high-temperature engines. Most of these applications require thermomechanical and thermochemical stability of composite constituents at elevated temperatures in an oxidizing environment. Among the currently available fibres, only carbon- and silicon carbide-based materials appear promising as reinforcement candidates, but they need to be protected from oxidation at high temperatures. An oxide–ceramic matrix is a good choice for carbon or silicon carbide fibre-reinforced ceramic–matrix composites (CMC) because it offers oxidation protection for the fibres.

A mullite–ceramic composite uniaxially reinforced with silicon carbide filaments was fabricated [1]. Significant improvements in strength and toughness were observed for the composite when compared with monolithic mullite ceramic. However, as-fabricated composite samples showed matrix microcracking perpendicular to the filament as a consequence of tensile thermal stresses produced due to the higher thermal expansion coefficient of mullite than the silicon carbide filament. The zircon ($ZrO_2 \cdot SiO_2$) has somewhat lower thermal expansion coefficient than mullite and, therefore, was selected as a matrix material with the hope of preventing the matrix microcracking. Therefore, a zircon–ceramic composite uniaxially reinforced with silicon carbide filaments was developed. The influence of processing conditions and fibre–matrix interface properties on the room-temperature mechanical properties of zircon–silicon carbide composite is described.

2. Experimental procedure

Silicon carbide monofilaments (AVCO-SCS-6) were used as reinforcement in the zircon matrix. These filaments are made by a chemical vapour deposition process in which about 50 μm thick SiC is deposited on a 37 μm diameter carbon core, followed by depositions of about 3 μm thick carbon and carbon–silicon layers resulting in an overall filament diameter of 140 μm. Typical mechanical properties of these filaments at room temperature are: elastic modulus 400 GPa, strength 3.4 GPa, and failure strain between 0.8 and 1.0%.

Two types of fibre–matrix interfaces were created in the fully consolidated composites. In one case as-supplied filaments containing the carbon-rich surface were used, and in another case a boron nitride coating was deposited on the as-supplied filaments. The BN coating of about 1 μm thickness was deposited by a low-pressure chemical vapour deposition technique described elsewhere [2]. The interface between an as-supplied filament and surrounding zircon matrix is designated as interface A and that between a BN-coated filament and surrounding zircon matrix is designated as interface B.

The zircon matrix was prepared from a zircon powder (Zircon Flour, coarse-grained no. 51698, Remet Corporation, Chadwick, New York). X-ray diffraction analysis of the as-suppled zircon powder showed tetragonal zircon as the major phase. This powder was milled for 36 h to increase the surface area to about 4 m^2 g^{-1}. The composite was fabricated by uniaxially aligning the filaments and incorporating the zircon matrix around each of the filaments. The final consolidation of the matrix was done by hot-pressing between 1500 and 1650 °C. This produced fully dense composites with little porosity (< 1%). A typical fibre loading of 25% by volume was used in all the zircon–silicon carbide composites of this investigation.

Mechanical testing of the uniaxially reinforced composite was performed in three-point flexure mode. All the samples were individually hot-pressed and ground to a finish of 60 μm. Typical dimensions of the bar-shaped specimens were 3.18 cm long, 0.79 cm wide, and 0.15 cm thick. The span of the lower support pins was 2.54 cm, which produced a span-to-thickness ratio of 16.9 in three-point flexure mode. The flexure tests were performed in a universal testing machine at a cross-head speed of 0.0127 cm min^{-1} (0.005 in. min^{-1}). Load–deflection data were obtained for monolithic zircon and the filament-reinforced composite until complete failure of the samples. The mode of failure was determined from visual observations during the test and scanning electron microscope (SEM) examinations of the failed samples subsequent to the test.

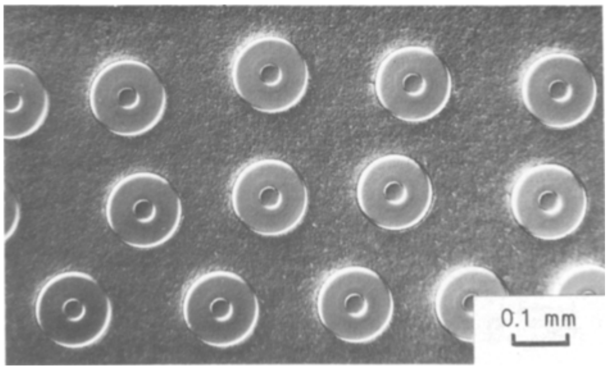

Figure 1 Optical micrograph showing cross-section of a fully consolidated zircon–silicon carbide composite.

3. Results and discussion

3.1. Physical characteristics

Physical properties of fully consolidated zircon and zircon–silicon carbide composite samples are summarized in Table I. It contains information on sample density, filament loading, and filament–matrix interface. The density of about 4.45 g cm^{-3} for monolithic zircon is close to its theoretical density of about 4.6 g cm^{-3}. Little or no porosity was found in the microstructure of zircon samples when examined by optical metallographic techniques. The X-ray diffraction analysis from an as-fabricated sample showed zircon as the major phase with a trace amount of the monoclinic zirconia phase.

The composite samples had densities between 4.12 and 4.29 g cm^{-3} which are close to the predicted density of 4.14 g cm^{-3} based on the zircon density of 4.45 g cm^{-3} and the silicon carbide filament density of 3.2 g cm^{-3}. All of the composite samples had 25 vol % filament loading. The densities of composite samples were similar in spite of the different types of filament–matrix interfaces, i.e. type A or B.

An optical micrograph showing the cross-section normal to the filaments of a fully consolidated composite is shown in Fig. 1. It shows uniform distribution of filaments in a fully dense zircon matrix, and filaments are completely surrounded by the zircon matrix. Cross-sections of a number of composites were examined in this way, and none of the samples showed filament-to-filament contact which can be deleterious to the composite properties. Sample-to-sample variations in density are small, which is indicative of excellent process reproducibility.

TABLE I Summary of physical characteristics of fully consolidated samples

Sample no.	Monolithic (M) or composite (C)	Density (g cm^{-3})	Fibre content (vol %)	Interface type
1	M	4.44	0	None
2	M	4.43	0	None
3	M	4.45	0	None
4	M	4.37	0	None
1-A	C	4.2	25	A
2-A	C	4.12	25	A
3-A	C	4.16	25	A
4-A	C	4.29	25	A
1-B	C	4.14	25	B
2-B	C	4.14	25	B
3-B	C	4.19	25	B
4-B	C	4.11	25	B

3.2. Mechanical properties

The load–deflection behaviour of monolithic zircon and zircon–matrix composites reinforced with the as-supplied and the BN-coated silicon carbide filaments were determined at room temperature in three-point flexure mode. The results are shown in Fig. 2. The data for a monolithic zircon sample shows elastic loading of the sample up to the onset of brittle failure. A failure strength of 267 MPa and corresponding failure strain of 0.15% were displayed by this sample. In contrast, the composite samples show elastic behaviour in the initial stages followed by an extended regime showing inelastic behaviour as the load increases. There is a sudden load drop at the transition point from elastic to inelastic regime which is characterized by the first evidence of matrix cracking. Beyond this point, in the inelastic region, the slope of the load–deflection curve progressively decreases as the sample deflects because of filament failure and matrix microcracking. The sudden drops in load as indicated by blips in the load–deflection curve are probably due to filament failure. These blips were always accompanied by audible acoustic emission signals. In spite of filament failures, the composite samples display increasing load-bearing capacity as the samples continue to deform under the imposed motion of the cross-head. This behaviour is only possible if the filaments do not break in the plane of the major crack and at the same time they pull out to accommodate the imposed deflection. Both of the composite samples show a maximum in load-carrying capacity followed by two types of behaviour depending on the nature of the filament–matrix interface. In the case of composites fabricated with filaments in the as-supplied state (interface A) the load–deflection data show a significant drop in load after the point of maximum load (solid curve in Fig. 2). In contrast, composites fabricated with the BN-coated filaments (interface B) show a gradual decrease in load after the point of maximum load as shown by the dotted curve in Fig. 2. Both of

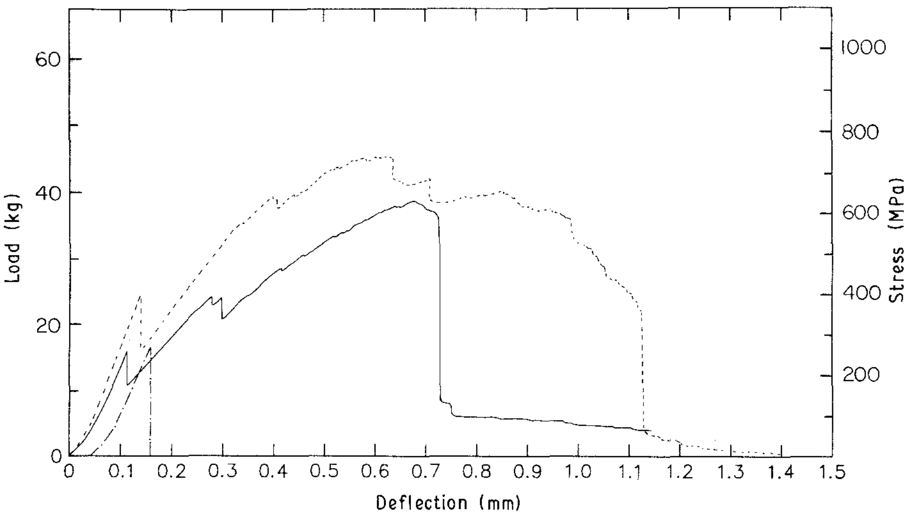

Figure 2 Load–deflection behaviours for (—·—) monolithic zircon and zircon composites reinforced with (——) as-supplied (interface A) and (– – –) BN-coated silicon carbide filaments.

the composites display a significant increase in strength and toughness over the value obtained for monolithic zircon. In addition, the load–deflection behaviour displayed by zircon–SiC composites of this study is similar to that expected of an ideal ceramic–matrix composite because all the essential elements of composite behaviour (i.e. critical load for matrix cracking, ultimate composite strength, and toughness) are present in the data shown in Fig. 2.

The different types of load–deflection curves for zircon–silicon carbide composites with different types of fibre–matrix interfaces can be rationalized on the basis of fibre–matrix interfacial shear stress and its role on fibre pullout. A lower value of the interfacial shear stress is expected to produce more fibre pull-out and consequently a gradual load drop and tougher composite [1, 3–5]. In contrast, a tightly bonded fibre–matrix system will produce little or no fibre–matrix slippage and consequently a more brittle ceramic-like behaviour. The measured interfacial shear stress values were 96 MPa for interface A and 12 MPa for interface B [6]. These values are consistent with the observed load–deflection behaviours and toughening due to a fibre pull-out mechanism.

Different types of load–deflection behaviour were also shown by composite samples with interface B depending on the mode of failure as shown in Fig. 3. Typically, samples that failed via tensile mode under the centre loading pin showed a gradual load drop after reaching the maximum load, whereas the samples showing buckling and shear delamination exhibited a sudden load drop (Fig. 3). Examination of samples during the three-point flexure test and after failure indicated that most of the composites fractured in a tensile mode under the middle loading pin, but there was a small fraction of samples which failed on the compression side via buckling and shear delamination. Buckling and delamination mode failures of composites tested in three-point flexure have been observed by us and other investigators [1, 7], and it is generally agreed that testing in pure tension is a preferred technique for the determination of composite properties. Testing in pure tension is more difficult, and for this reason a three-point flexure test is a good compromise because it mimics composite behaviour under tensile, compressive, and bending stresses, all of which may be present in practical applications of ceramic–matrix composites.

Polished and as-fractured cross-sections of failed composite samples were examined using SEM and optical microscopy to determine the nature of the fracture process. A scanning electron micrograph of the as-fractured surface of zircon–SiC composite is shown in Fig. 4a. Filament pull-out, debonded filament–matrix interface, and a rough fractured surface, are evident. Also evident is nonplanar propagation of the crack front because of crack deflection by the reinforcing filaments. A polished cross-section from the failed composite is shown in Fig. 4b which exhibits the nature of crack propagation and crack deflection processes. The cracks are propagated from one filament to the next and are diverted by the filaments as shown in Fig. 4b. In most cases the propagating cracks are deflected around the filaments, but there are locations where cracks have fractured the reinforcement. These observations suggest that toughening in zircon–silicon carbide composites is via a combination of fibre pull-out, crack deflection, and possibly microcracking mechanisms. The fibre pull-out mechanism contributes the most to the overall level of toughness in this class of composites because other mechanisms are unable to produce the observed toughness [4, 5].

3.3. Comparison with model predictions

Mechanical properties of monolithic zircon and zircon–silicon carbide composites are summarized in Table II. Table II contains data on first matrix cracking stress, ultimate strength and strain at maximum load, and effective modulus of elasticity for monolithic and composite samples. An average strength of 281 MPa and an average strain of 0.19%were obtained for monolithic zircon samples failed in a brittle

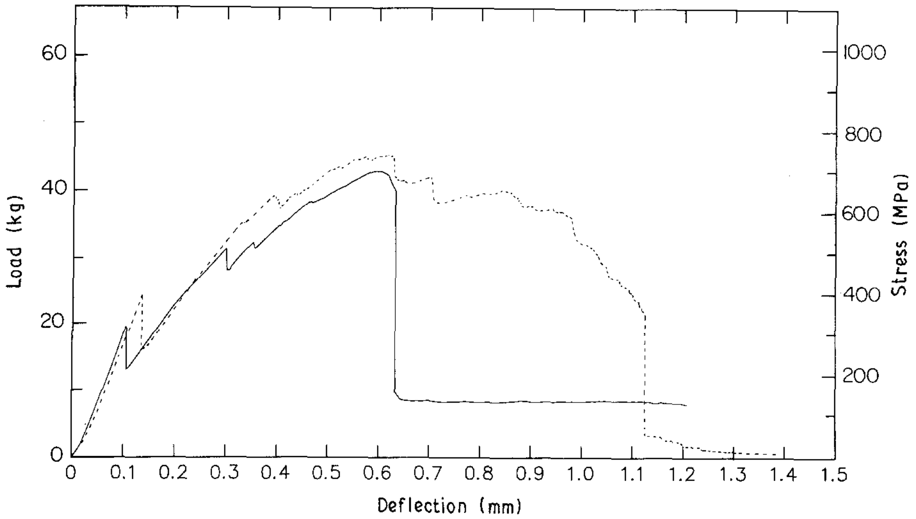

Figure 3 Influence of (- - -) tensile and (——) buckling–delamination type failures on the load–deflection behaviour of zircon composites reinforced with BN-coated silicon carbide filaments (interface B).

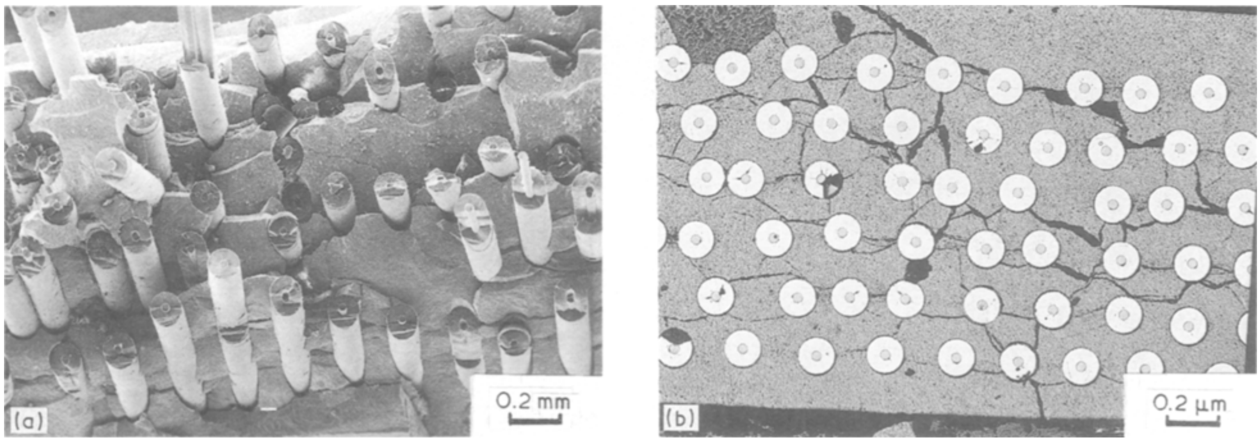

Figure 4 Failed cross-sections of zircon–silicon carbide composite showing (a) filament pull-out and (b) crack deflection and propagation.

TABLE II Summary of mechanical property data for monolithic zircon and zircon–silicon carbide composites

Sample no.	Monolithic (M) or composite (C)	Interface type	First matrix cracking		Properties at maximum load		Elastic modulus (GPa)
			Stress (MPa)	Strain (%)	Stress (MPa)	Strain (%)	
1	M	None	384	0.18	384	0.18	214
2	M	None	256	0.15	256	0.15	202
3	M	None	215	0.15	215	0.15	162
4	M	None	267	0.13	267	0.13	201
1-A	C	A	273	0.11	635	1.10	247
2-A	C	A	257	0.12	690	1.20	237
3-A	C	A	296	0.11	702	1.11	248
4-A	C	A	321	–	771	0.90	–
1-B	C	B	349	0.11	712	1.43	209
2-B	C	B	300	0.15	656	1.06	254
3-B	C	B	385	0.13	712	1.04	259
4-B	C	B	395	0.18	645	0.70	216

mode. In comparison, the composites with uncoated and BN-coated SiC filaments had significantly higher average strengths of 700 and 681 MPa and corresponding average failure strains of 1.08 and 0.9%, respectively. An average first matrix cracking stress of 287 MPa for the composites reinforced with uncoated SiC filaments, and an average value of 357 MPa for the composites with BN-coated SiC filaments, were measured. These values are similar to the average strength of 281 MPa for monolithic zircon. An average elastic modulus of 195 GPa was obtained for the monolithic zircon samples. In comparison, the composites containing uncoated filaments produced an average modulus of 244 GPa and those with BN-coated filaments resulted in an average modulus of 235 GPa. These moduli for composites are higher than the value for monolithic zircon and in excellent agreement with the value of 246 GPa calculated on the basis of the rule of mixtures. In this calculation, a filament modulus of 400 GPa, a matrix modulus of 195 GPa, and a filament content of 25 vol% were used.

The ultimate strength of the composite, i.e. the stress at the point of maximum load, appears to be similar for samples with uncoated and BN-coated silicon carbide filaments. This behaviour is not unreasonable because at this point the matrix is cracked and as a consequence all the load is carried by the bridging filaments. The composite strength then should be equal to the strength of the filament (σ_f) times the volume fraction (V_f) of the filament in the composite. An ultimate strength of 840 MPa was calculated for the composite using an average as-supplied filament strength of 3.36 GPa and a filament volume fraction of 0.25. This value is somewhat higher than the average ultimate strengths of 700 and 681 MPa, respectively, for composites reinforced with uncoated and BN-coated silicon carbide filaments. It is quite possible that the filament strength in the consolidated composite is lower than the as supplied strength because of the processing-induced damage. This, along with probabilistic nature of filament strength, are expected to result in somewhat lower observed ultimate composite strength than the predictions.

Applications of zircon composites reinforced with silicon carbide filaments as high-temperature structural components will require design stress below the first matrix cracking strength to maintain dimensional stability and to avoid oxidative degradation of filaments. For this reason, it will be desirable to fabricate composites with the highest possible critical stress for first matrix cracking. One way to do this is to increase the filament–matrix interfacial shear stress according to the ACK model after Aveston *et al.* [8]. In this model the first matrix cracking stress, σ_{cr}, is related to the interfacial shear stress, τ, as

$$\sigma_{cr} = E(6V_f^2 E_f / V_m E_m E)^{1/3} (\tau \gamma_m / a E_m)^{1/3} \quad (1)$$

where E_f, E_m, and E are the moduli of filament, matrix, and composite, V_f and V_m are the filament and matrix volume fractions, τ is the fibre–matrix interfacial shear stress, γ_m is the matrix surface energy, and a is the filament diameter. The model [5] suggests that the toughness of the composite will be lower if the interfacial shear stress is increased to raise σ_{cr}. However, our measured values of the first matrix cracking strengths of 287 and 357 MPa in zircon composites reinforced with the as-supplied and the BN-coated silicon carbide filaments, respectively, are independent of the measured filament–matrix interfacial shear stress. The measured interfacial shear stress values are 96 and 12 MPa in zircon composites with as-supplied and BN-coated SiC filaments, respectively [6]. The calculated values of 293 and 147 MPa were obtained [9] as critical stress for first matrix cracking using the ACK model and measured interfacial shear stress values of 96 and 12 MPa. The first value is close to the measured stress of 287 MPa for samples with as-supplied filaments. But, the second calculated stress of 147 MPa for composites with BN-coated filaments is much lower than the experimentally measured first matrix cracking stress value of 357 MPa.

These observations can be rationalized on the basis of matrix failure strains as suggested by Davidge [10]. If the failure strain of the monolithic matrix is lower than the strain calculated from the ACK model, the matrix failure strain of the composite will be enhanced. In this situation the values of matrix cracking stress calculated from the ACK model will be more realistic for comparison with the experimental results. Conversely, if the failure strain of the monolithic matrix is higher than the composite failure strain calculated from the ACK model, the composite strain for first matrix cracking will not be enhanced over the monolithic failure strain. This is apparently the case for zircon–SiC composites of this study. Average matrix failure strains of 0.15% for monolithic zircon, 0.11% for zircon–SiC composites with the uncoated filaments, and 0.14% for zircon–SiC composites with the BN-coated filaments were measured. The values of matrix failure strain, as calculated using the ACK model, are 0.12% for composites with the uncoated SiC filaments, and 0.06% for composites with the BN-coated filaments. Both of these strain values are lower than the failure strain of the monolithic zircon. Therefore, the first matrix cracking strain or stress of the zircon–SiC composites will be similar to the monolithic zircon. This appears to be a reasonable explanation for our observation that the first matrix cracking stress is independent of the measured interfacial shear stress in zircon–SiC composites of this investigation.

The toughness of monolithic zircon and zircon composites were determined by measuring the area under the load–deflection curves (Fig. 2), and dividing by the cross-section area of the sample. A value of 24 kJ m^{-2} was obtained for the sample with as-supplied SiC filaments, and a value of 41 kJ m^{-2} was determined for the composite reinforced with BN-coated filaments [6]. These values are significantly higher than the observed value of about 0.95 kJ m^{-2} for monolithic zircon. These results also suggest that the critical stress for first matrix cracking and toughness can be simultaneously enhanced in this class of ceramic matrix composites.

4. Conclusions

Some of the physical and mechanical characteristics of zircon–ceramic composites uniaxially reinforced with silicon carbide filaments are given below.

1. The as-fabricated composites were fully dense, and the filaments were uniformly distributed and surrounded by the zircon matrix.

2. Composite failure strengths between 635 and 771 MPa and failure strains between 0.9 and 1.4% were measured. These values are significantly higher

than the values of strength between 215 and 384 MPa and strain between 0.15 and 0.25% for the monolithic zircon.

3. All the composite samples showed toughened-composite behaviour in three-point flexure, and all the monolithic zircon samples failed in a brittle manner. The load–deflection behaviour for composite samples was dependent on the type of fibre–matrix interface and the mode of failure. A sudden load drop from the point of maximum load was associated with the higher fibre–matrix interfacial stress and shear delamination failure, and a gradual load drop with the lower interface stress and tensile failure.

4. The critical stress for first matrix cracking ranged from 257 to 321 MPa for zircon composites with as-supplied filaments, and from 300 to 395 MPa for composites with BN coated SiC filaments. These values do not scale with the measured interfacial shear stress.

5. Average composite moduli of 244 and 235 GPa were measured for specimens with uncoated and BN-coated filaments, respectively. These values are in excellent agreement with the calculated value of 246 GPa on the rule of mixtures.

6. Composite samples with BN-coated filaments were tougher than those with as-supplied filaments (41 compared to 24 $kJ\,m^{-2}$), and significantly tougher than the monolithic zircon (0.95 $kJ\,m^{-2}$).

7. Examinations of failed composites showed that toughening in these composites is predominantly via fibre pull-out mechanism although crack deflection and microcracking processes also contribute to the overall toughness.

8. It appears that composites with high first matrix cracking stress and toughness can be designed via proper attention to the selection of the matrix and reinforcement materials and creation of an optimum fibre–matrix interfacial shear stress.

Acknowledgements
The authors thank W. A. Morrison for help in sample preparation and P. M. Breslin for manuscript preparation.

References
1. R. N. SINGH and A. R. GADDIPATI, *J. Amer. Ceram. Soc.* **71** (1988) C-100.
2. R. N. SINGH, in "Proceedings of the Tenth International Conference on Chemical Vapor Deposition (CVD-X)", V. 87-7, Honolulu, Hawaii, edited by G. W. Cullen, The Electrochemical Society (1987) p. 543.
3. B. BUDIANSKI, J. W. HUTCHINSON, and A. G. EVANS, *J. Mech. Phys. Solids* **34** (1986) 167.
4. D. B. MARSHALL and A. G. EVANS, *J. Amer. Ceram. Soc.* **68** (1985) 225.
5. M. SUTCU, *Acta Metall.* **37** (1989) 651.
6. R. N. SINGH, *Mater. Res. Soc. Symp. Proc.* **120** (1988) 259.
7. T. MAH, M. G. MENDIRATTA, A. P. KATZ, R. RUH and K. S. MAZDIYASNI, *J. Amer. Ceram. Soc.* **68** (1985) C-27.
8. J. AVESTON, G. A. COOPER and A. KELLY, in "Properties of Fiber Composites", Conference Proceedings of the National Physical Laboratory (IPC Science and Technology Press, Surrey, UK, 1971) pp. 15–26.
9. M. SUTCU, "Computer Program CERCOM.FOR", GE Research and Development Center, Schenectady, New York (1988).
10. R. W. DAVIDGE, *Composites* **18** (1987) 92.

*Received 17 May
and accepted 26 September 1989*