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Influence of high-temperature exposure on mechanical properties of zircon–silicon carbide composites

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Thermal stability of zircon matrix composites uniaxially reinforced with either uncoated or BN-coated silicon carbide monofilaments was determined by measuring mechanical properties and fibre–matrix interfacial characteristics in the as-fabricated state and after annealing treatments between 25 and 1430 °C for times up to 100 h. Composites reinforced with uncoated silicon carbide filaments retained their mechanical properties and fibre–matrix interfacial characteristics up to 1350 °C for 100 h. In contrast, composites reinforced with BN-coated silicon carbide filaments displayed changes in mechanical properties and fibre–matrix interfacial characteristics when annealed beyond 1300 °C for 100 h. Both types of composite displayed a significant reduction in strength and toughness after annealing at 1430 °C for 20 h. These results are consistent with changes in fibre–matrix interfacial properties, and with changes in mechanical characteristics of zircon matrix and silicon carbide filament as a result of the high-temperature annealing treatments.

1. Introduction

Application of ceramic matrix composites as high-temperature structural components requires thermomechanical and thermochemical stability for composite constituents at elevated temperatures. In particular, the reinforcing fibre and the matrix materials should be thermochemically compatible so that there is an insignificant fibre–matrix reaction that might degrade fibre properties. Furthermore, the fibre and the matrix thermal expansion characteristics must be such that they do not lead to matrix cracking as a result of improper expansion mismatch. Generally, thermal expansion of the matrix should be either equal to or less than the fibre thermal expansion coefficient to prevent matrix cracking as a result of tensile matrix stresses that are generated upon cool-down of samples from higher processing temperatures [1, 2]. A zircon matrix composite uniaxially reinforced with silicon carbide filaments was developed to have such a thermomechanical and thermochemical stability. A silicon carbide filament (AVCO SCS-6) was chosen as reinforcement because of its good mechanical properties to 1400 °C, and an oxide ($ZrO_2 \cdot SiO_2$) was selected as a matrix because it is expected to provide oxidation protection for the fibres.

The zircon–SiC composite materials system has the necessary fibre–matrix thermomechanical compatibility because matrix cracking was not observed in as-fabricated composites upon cool-down from consolidation temperatures between 1550 and 1650 °C [2]. In addition, this composite system has short-term internal thermochemical compatibility because as-fabricated composite samples have shown toughened-composite behaviour with strengths and toughness significantly higher than the monolithic zircon [2]. In this study, long-term internal thermochemical stabilities of composite constituents were determined by annealing composite samples between 1200 and 1430 °C in an inert atmosphere, and then measuring mechanical properties and fibre–matrix interfacial characteristics at 25 °C. The changes in mechanical properties, as a result of the annealing treatments, were related to measured values of the interfacial shear stress.

2. Experimental procedure

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-supplied powder indicated tetragonal zircon as the major phase. This powder was milled for 36 h to increase the surface area to about $4\ m^2\ g^{-1}$. Silicon carbide monofilaments (AVCO SCS-6) were used as reinforcement in the zircon matrix. These filaments are made by a chemical vapour deposition technique in which about 50 μm thick silicon carbide is deposited on a 37 μm diameter carbon core, followed by depositions of about 3 μm thick carbon and carbon–silicon layers that result in an overall filament diameter of 142 μm [3]. An elastic modulus of 400 GPa, strength of 3.4 GPa, and a failure strain between 0.8% and 1.0% are typical mechanical characteristics of these filaments at room temperature.

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Fibre–matrix interfacial properties have strong influence on the mechanical behaviour of ceramic matrix composites (CMC). For this reason, two types of fibre–matrix interfaces were created in the fully consolidated composites. In one case as-supplied filaments containing the carbon–silicon 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 process [4] to alter the fibre–matrix interfacial properties from composites containing as-supplied filaments. The interface between as-supplied filament and surrounding zircon matrix is designated interface A, and that between a BN-coated filament and surrounding zircon matrix is designated interface B.

The fabrication of composites was done by uniaxially aligning as-supplied or BN-coated SiC filaments, and then incorporating the zircon matrix around each of the filaments. The final consolidation was done by hot-pressing between 1550 and 1600 °C in a nitrogen atmosphere. This procedure resulted in fully dense composites with little (< 1%) porosity. The composite samples with a filament loading of 25% by volume had densities between 4.12 and 4.29 $g\,cm^{-3}$. The zircon matrix was fine-grained with an average grain size of 2.5 μm. The X-ray diffraction analysis of the fully consolidated composites showed zircon as the matrix phase. Free zirconia phase was not detected by X-ray diffraction analysis of the as-fabricated composites.

Thermal stability of the composite constituents at elevated temperatures was determined by annealing samples at temperatures between 1200 and 1430 °C for times up to 100 h. The annealing was done either in a purified argon gas or in an Ar–7% H_2 gas. The argon gas was purified by passing over the hot copper turnings. In addition, the samples were placed in a carbon liner in the annealing furnace to avoid oxidative degradation of SiC filaments. The changes in composite characteristics caused by the annealing treatments were assessed by measuring phase composition using X-ray diffraction, mechanical properties, and fibre–matrix interfacial shear stress as described below.

Mechanical properties of composite samples were determined from load–deflection data obtained in a three-point flexure mode. The uniaxially reinforced composite samples, having typical dimensions of 3.2 cm length, 0.8 cm width, and 0.15 cm thickness, were individually hot pressed and ground to a finish of 60 μm. The three-point flexure tests were performed with lower support pins, 2.54 cm apart, which resulted in a span-to-thickness ratio of about 17. All the tests were performed in a universal testing machine at a cross-head rate of 0.0127 $cm\,min^{-1}$ (0.005 $in.\,min^{-1}$). Cross-sections of failed composites were examined by scanning electron microscopy (SEM) to determine the fracture morphology and the extent of fibre pull-out. The mode of failure (tensile or shear) in three-point flexure tests was determined by visual observation of samples during the test. Generally, four samples were tested in the as-fabricated condition to establish the baseline properties, which were then used to compare with similar properties in thermally annealed samples.

A modified indentation technique was used to measure the fibre–matrix interfacial shear strength as described by Brun and Singh [5]. In this technique, a thin slice (1 mm thick) was cut perpendicular to the filament axis and was polished in such a way as to produce a small amount of filament relief. This thin slice was then placed on a resilient substrate, and the filaments were individually loaded by the indentor until the first evidence of filament movement was observed. The first evidence of filament motion was detected by a sudden load drop in the load–deflection curve, which was generated by measuring the load by a load-cell when pushing on the filament at a constant displacement rate of 0.002 $in.\,min^{-1}$ [6]. The interfacial shear stress was calculated from the load required to initiate filament motion and the circumferential area of the filament in contact with the matrix [5]. Then, the sample was turned over and measurements repeated on already pushed filaments. The load to move the filaments for the second time was invariably lower than that for the first push, which made it possible to separate bonding and frictional components of the interfacial shear stress. Typically, 10 to 15 filaments were pushed in each sample to obtain an average value of the interfacial shear strength. The interface responsible for filament–matrix sliding and the morphological changes at the fibre–matrix interface were determined by examination of pushed filaments using an SEM. The interfacial shear strength was measured for composite samples in the as-fabricated state and after high-temperature annealing treatments. Generally, interfacial shear stress and mechanical properties were measured on the same sample to establish a direct correlation between interfacial properties and mechanical behaviour.

3. Results and discussion

3.1. Mechanical properties of as-fabricated composites

Load–deflection behaviour for zircon composites uniaxially reinforced with as-supplied or BN-coated silicon carbide filaments is shown in Fig. 1. Both types of composite show an initial elastic region in which filaments and matrix are essentially intact. This is followed by a small, but sudden load drop, which is indicative of the first evidence of matrix cracking. Beyond this point, composites show an inelastic behaviour and increasing load-carrying capability because most of the filaments are still intact and can carry additional load because of their high failure strength and strain. Both of the composite samples show a maximum in load-carrying capacity followed by two types of behaviour as composites are further deformed as a result of the imposed motion of the cross-head. A sudden load drop is displayed by the composite sample reinforced with as-supplied SiC filaments (interface A). In contrast, a more gradual load drop is shown by the composite containing BN-coated filaments (interface B). The result for only one sample of each type is shown in Fig. 1, but this is a typical

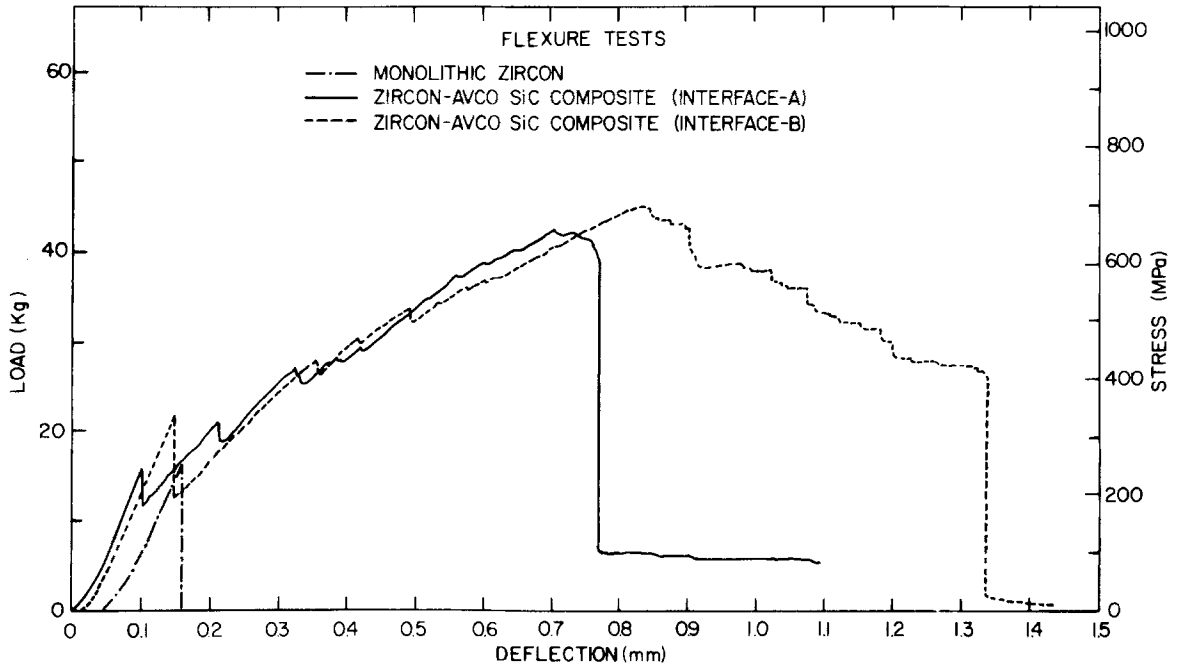

Figure 1 Load–deflection behaviour for monolithic zircon and zircon composites reinforced with (——) uncoated (interface A) and (– – –) BN-coated (interface B) silicon carbide filaments.

behaviour for most of the composite samples containing either the as-supplied or the BN-coated filaments. At least four composites of each type were tested to determine the general nature of the load–deflection behaviour from which a number of composite characteristics were obtained. Table I gives average values and standard deviations for critical stress for first matrix cracking (σ_{cr}), ultimate composite strength (σ_u), and work of fracture (WOF). The work of fracture can be considered to be a measure of composite toughness, which was calculated from the area under the load–deflection curve and dividing this by the cross-sectional area of the sample. An average value of 287 MPa for first matrix cracking stress, an average ultimate strength of 700 MPa, and an average value of 18 kJ m^{-2} for WOF were measured in composites reinforced with as-supplied SiC filaments. Similar measurements in composites reinforced with BN-coated filaments gave an average strength of 357 MPa for first matrix cracking, an average ultimate strength of 681 MPa, and an average WOF value of 25 kJ m^{-2}. These results indicate that there is an insignificant influence of the type of the fibre–matrix interface on critical stress for first matrix cracking and ultimate composite strength, but the WOF was higher for composites reinforced with BN-coated filaments compared to composites containing as-supplied SiC filaments.

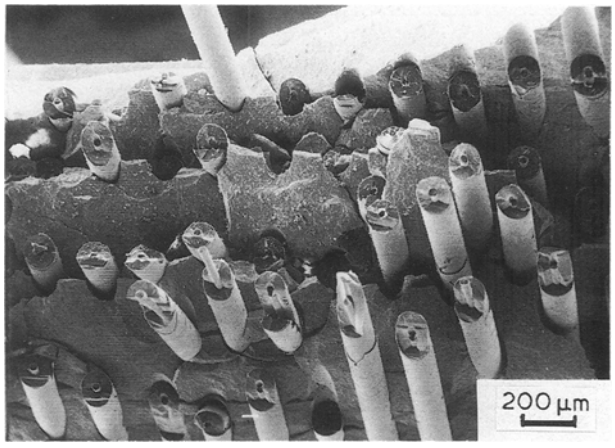

Figure 2 Fractured cross-section of an as-fabricated zircon–silicon carbide composite showing fibre pull-out.

Monolithic zircon specimens were also fabricated and tested in a similar fashion. These samples were brittle and weak. An average strength of 281 MPa and a WOF value of 1.2 kJ m^{-2} were obtained, as shown in Table I. In contrast, the composite samples were significantly stronger and tougher than the monolithic zircon. A significant amount of fibre pull-out was displayed by composite samples (see Fig. 2) which is consistent with the enhanced WOF or toughness. The

TABLE I Average mechanical properties of as-fabricated monolithic zircon and zircon–SiC composites

Material	Monolithic (M) or composite (C)	Filament coating	Mechanical properties		
			σ_{cr} (MPa)	σ_u (MPa)	WOF (kJ m^{-2})
Zircon	M	–	281 ± 88	281 ± 88	1.2 ± 0.1
Zircon–SiC	C	Uncoated	287 ± 28	700 ± 56	18 ± 4.2
Zircon–SiC	C	BN-Coated	357 ± 43	681 ± 36	25 ± 5.6

critical stress for first matrix cracking, in composite samples reinforced with either uncoated or BN-coated SiC filaments, is similar to the monolithic zircon strength, i.e. the filament reinforcement did not affect the first matrix cracking stress in this class of composites.

3.2. Mechanical properties of annealed composites

Composites were annealed at 1200, 1300, 1350, and 1430 °C for 20, 40, and 100 h in a flowing Ar–7% H_2 atmosphere. Each sample was then tested in three-point flexure to determine the load–deflection behaviour, and failed composites were examined in an SEM to determine the fibre pull-out. Monolithic zircon samples were also annealed and tested in a similar fashion. The results are summarized in Table II.

Monolithic zircon samples showed brittle behaviour and no degradation in strength after annealing to a temperature as high as 1430 °C for 20 h duration. The strength values between 240 and 304 MPa after annealing treatments, as listed in Table II, are within the scatter band of data for monolithic zircon in the as-fabricated condition. The WOF values also remained stable between 0.9 and 1.1 kJ m^{-2} after annealing. These results show that the zircon matrix is thermally stable up to 1430 °C in an Ar–7% H_2 atmosphere.

Zircon matrix composites uniaxially reinforced with uncoated silicon carbide filaments showed an insignificant change in mechanical properties when annealed up to a temperature of 1350 °C for times up to 100 h. However, a composite sample annealed at 1430 °C for 20 h in Ar–7% H_2 atmosphere showed a significant degradation in mechanical properties. These results are given in Table II. The samples annealed at 1200, 1300, and 1350 °C for 100 h show critical stress for first matrix cracking between 218 and 285 MPa, ultimate composite strengths between 635 and 901 MPa, and WOF values between 24 and 50 kJ m^{-2}. These values for first matrix cracking stress and ultimate composite strength are comparable to the average values for composites in the as-fabricated condition, as given in Table I. The WOF values for annealed samples are higher than the average value of 18 kJ m^{-2} for com-

TABLE II Influence of thermal treatments on mechanical properties of monolithic zircon and zircon–SiC composites

Sample	Reinforcement/ coating/matrix	Annealing treatment		Mechanical properties		
		Temp. (°C)	Time (h)	σ_{cr} (MPa)	σ_u (MPa)	WOF (kJ m^{-2})
1-A	None/none/zircon	As-fabricated		267	267	1.2
2-A		1300	100	240	240	1.1
3-A		1430	20	304	304	0.9
1-B	AVCO SiC/none/zircon	As-fabricated		273	635	24
2-B		1200	100	218	675	31
3-B		1300	100	285	740	49
4-B		1350	100	240	901	50
5-B		1430	20	207	328	12
1-C	AVCO SiC/BN/zircon	As-fabricated		395	645	26
2-C		1200	100	240	647	40
3-C		1300	100	210	478	22
4-C		1350	100	203	436	29
5-C		1430	20	218	305	10

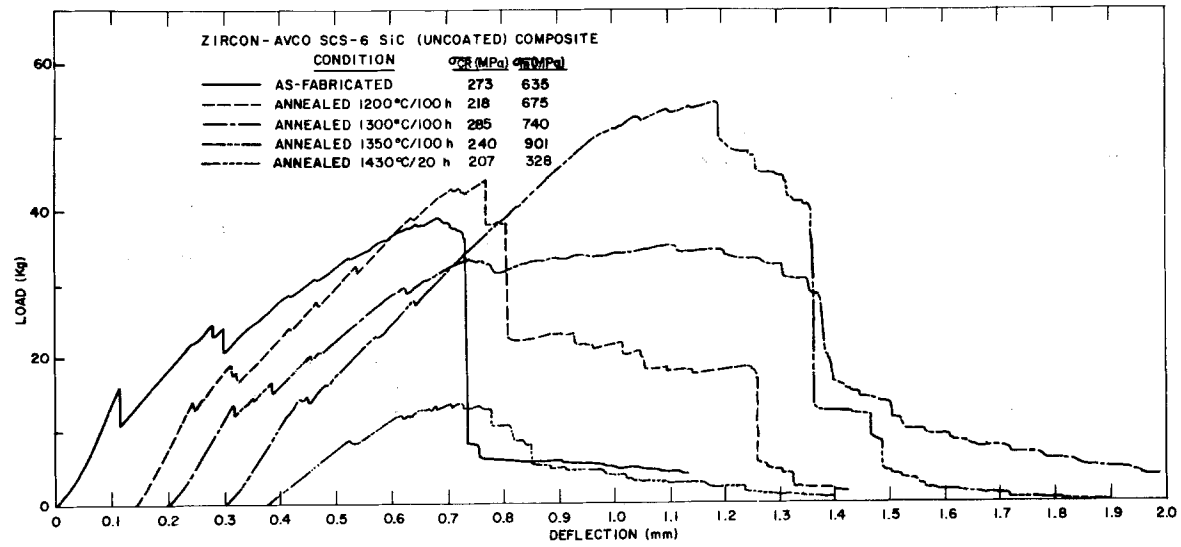

Figure 3 Load–deflection behaviour for an as-fabricated and annealed composites reinforced with uncoated silicon carbide filaments.

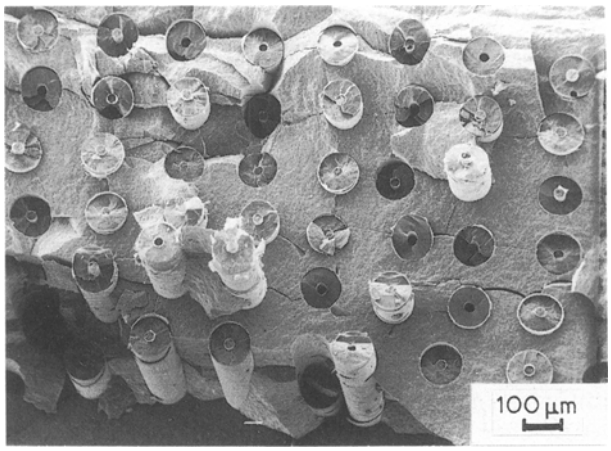

Figure 4 Fractured cross-section of an annealed (1350 °C for 100 h) zircon composite reinforced with uncoated silicon carbide filaments.

posites in the as-fabricated state. A significant reduction in mechanical properties for a sample annealed at 1430 °C for 20 h is in sharp contrast to the behaviour of monolithic zircon matrix that showed no degradation in mechanical strength after a similar annealing treatment at 1430 °C. Therefore, degradation in mechanical properties of the composite annealed at 1430 °C can be attributed to degradation in fibre properties and/or changes in fibre–matrix interfacial characteristics.

Load–deflection behaviour for as-fabricated and annealed zircon composites containing uncoated SiC filaments is shown in Fig. 3. All of the samples show an initial elastic region, a sudden drop in load caused by matrix cracking, and then an extended inelastic regime of increasing load-carrying capacity. All the samples, whether as-fabricated or annealed, also show a maximum in load-bearing capacity followed by different load–deflection behaviours depending on the specific processing history. The as-fabricated sample shows a more sudden load drop beyond the point of maximum load, whereas composites annealed at progressively higher temperatures between 1200 and 1350 °C show an increased tendency for a more gradual load drop. A tougher behaviour is shown by progressively higher values of WOF from 24 to 50 kJ m^{-2} (Table II) as the composites are annealed for 100 h between 1200 and 1350 °C. Fig. 4 shows a scanning electron micrograph of a composite sample annealed at 1350 °C for 100 h. The filament pull-out and a rough fractured surface are evident and qualitatively support the mechanical property data.

Mechanical properties of zircon composites uniaxially reinforced with BN-coated SiC filaments were different after annealing from those in the as-fabricated condition as given in Table II. The critical stress for first matrix cracking gradually decreased from an average value of 357 MPa for as-fabricated composites to a value of 203 MPa for a sample annealed at 1350 °C for 100 h. However, the ultimate strength of composites remained stable up to the annealing temperature of 1200 °C, but decreased to lower values of 478 and 436 MPa, respectively, as the samples were annealed at 1300 and 1350 °C. The WOF values remained between 22 and 40 kJ m^{-2} which are similar to data in the as-fabricated state. A sample annealed at 1430 °C for 20 h showed a significant reduction in all of the mechanical characteristics which was also observed for a composite reinforced with uncoated SiC filaments. This behaviour indicates that there is a significant degradation in fibre properties because of thermal annealing at 1430 °C, which results in degraded composite properties. Such degradation of composite properties cannot be associated with changes in fibre–matrix interfaces because composites with two different interfaces showed a similar degradation in mechanical properties.

Load–deflection behaviour of as-fabricated and annealed composites reinforced with BN-coated filaments is shown in Fig. 5. All of the samples show an elastic regime, evidence of first matrix cracking, an inelastic region, an ultimate in load-carrying capacity, and toughened composite-like behaviour. In addition, all of the as-fabricated and annealed samples show a

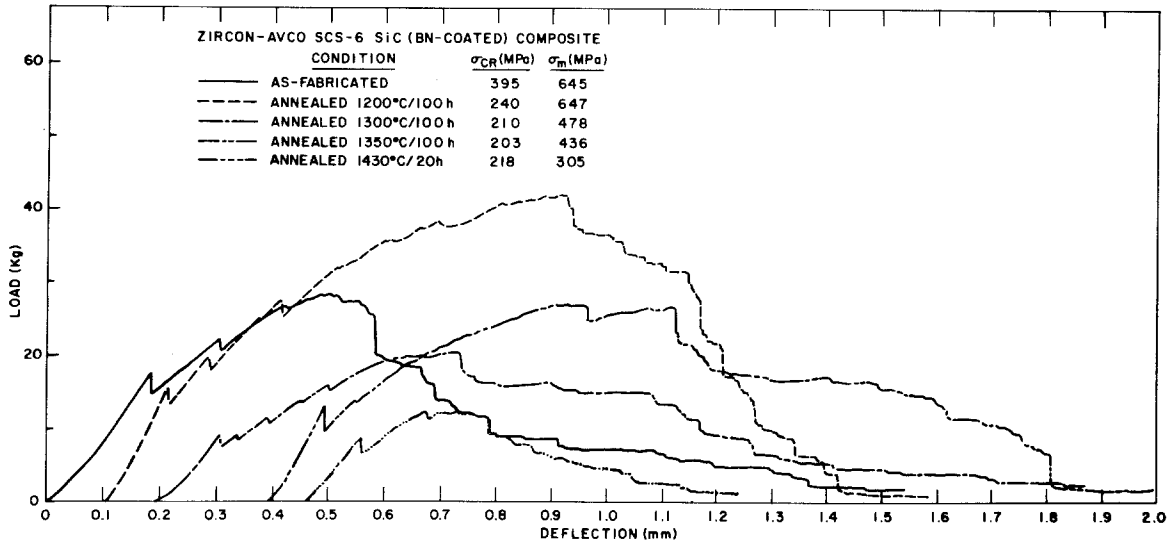

Figure 5 Load–deflection behaviour for an as-fabricated and annealed composites reinforced with BN-coated silicon carbide filaments.

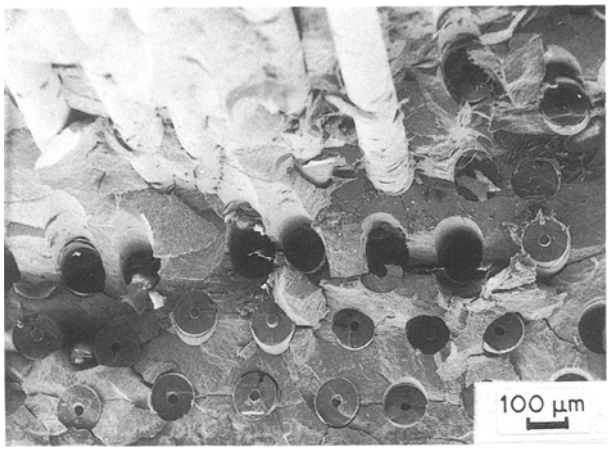

Figure 6 Fractured cross-section of an annealed (1350 °C for 100 h) zircon composite reinforced with BN-coated silicon carbide filaments.

much more gradual drop in load beyond the point of maximum load. This behaviour is different from that observed for composites containing uncoated filaments, which showed a more sudden drop in load after the point of maximum load (see Fig. 3). Fig. 6 shows a fractured cross-section of a composite sample annealed at 1350 °C for 100 h. The filament pull-out and a rough fracture morphology are evident.

Composite and monolithic zircon samples were annealed at 1300 and 1350 °C as a function of time to determine the rate of change in mechanical properties. The influence of annealing temperature on the ultimate strength of monolithic zircon and composites is shown in Fig. 7a. There is an insignificant change in the ultimate strength of monolithic zircon because of annealing for 100 h up to 1350 °C. In contrast, composites containing BN-coated filaments show a decreased strength when annealed beyond 1200 °C. On the other hand, composites containing uncoated SiC filaments do not show any evidence of lowered strength when annealed under similar conditions. Fig. 7b shows the influence of annealing time, at 1300 and 1350 °C, on ultimate strength. Again, there is an insignificant change in strength of monolithic sample. But the composites containing BN-coated filaments display strength degradation within 20 h of annealing at 1300 °C. Beyond this point, there appears to be no further decrease in strength caused by annealing time of up to 100 h. Composites reinforced with uncoated SiC filaments do not show any degradation in strength even after annealing for 100 h at either 1300 or 1350 °C. A similar behaviour is displayed in Fig. 8 where critical stress for first matrix cracking is plotted as a function of annealing temperature for samples annealed at 1200, 1300, and 1350 °C for 100 h. Composite samples reinforced with uncoated filaments do not show degradation in critical matrix cracking strength, whereas samples reinforced with BN-coated filaments show lowered strength with increasing annealing temperature.

The degradation in mechanical properties of composites reinforced with BN-coated filaments can be attributed to degradation in mechanical properties of zircon matrix, SiC filaments, and/or fibre–matrix interface. Monolithic zircon matrix and composites reinforced with uncoated SiC filaments did not show strength degradations, which suggest that the zircon matrix and SiC filaments were not degraded by the annealing treatments. Therefore, it must be the presence of BN coating and associated fibre–matrix interface that is responsible for strength degradation in composites containing BN-coated filaments. Fibre–matrix interfacial shear stress was measured in as-

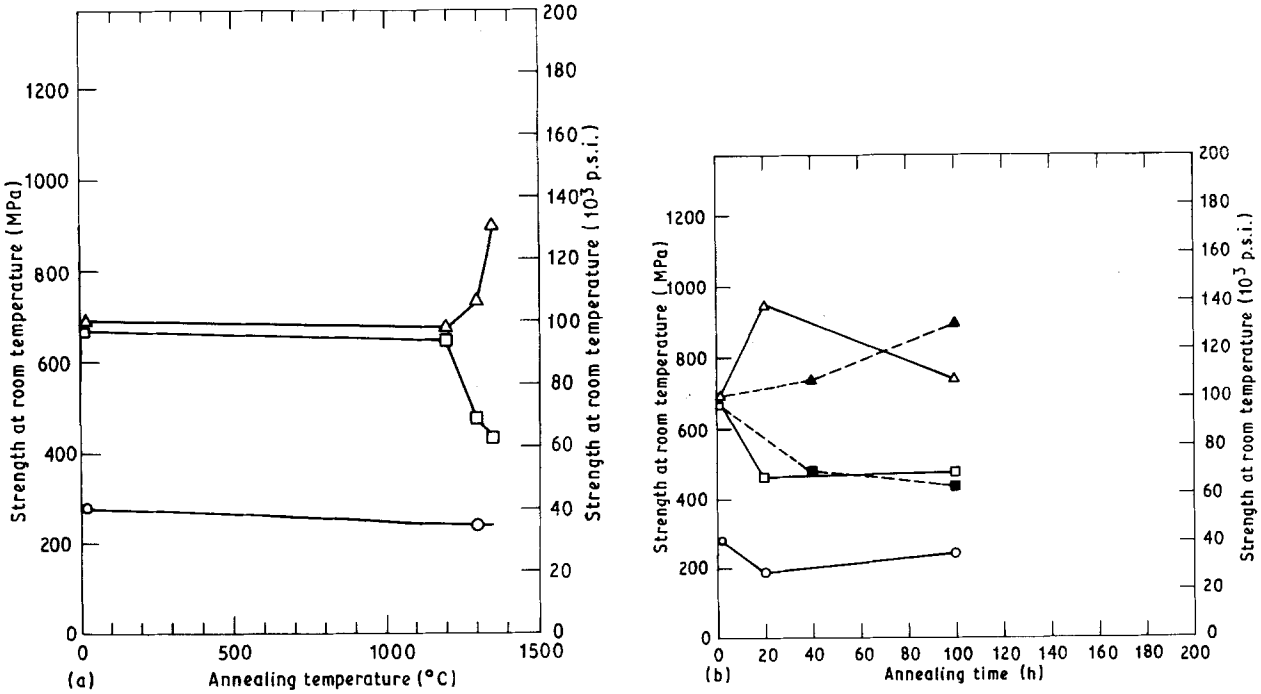

Figure 7 Influence of (a) annealing temperature for 100 h in Ar–7% H_2 and (b) annealing time on ultimate strength of (○) monolithic zircon and zircon composites reinforced with (△, ▲) uncoated and (□, ■) BN-coated silicon carbide filaments. (b) Annealing temperature (▲, ■) 1350 °C, (○, △, □) 1300 °C. 10^3 p.s.i. = 6.89 N mm^{-2}.

TABLE III Fibre–matrix interfacial shear stress in as-fabricated and annealed zircon–SiC composites

Sample	Reinforcement/ coating/matrix	Annealing treatment		Interfacial shear stress	
		Temp. (°C)	Time (h)	Debond (MPa)	Frictional (MPa)
1-B	AVCO SiC/none/zircon	As-fabricated		39.0 ± 4.0	16.0 ± 4.0
4-B		1350	100	15.0 ± 3.0	10.0 ± 2.0
1-C	AVCO SiC/BN/zircon	As-fabricated		18.0 ± 2.0	15.0 ± 2.0
4-C		1350	100	8.0 ± 3.0	3.5 ± 2.0

fabricated and annealed composites to identify the cause of strength degradation.

3.3. Fibre–matrix interfacial properties

Fibre–matrix interfacial shear stress was measured in four types of composite. Two of the samples were selected from composites reinforced with uncoated filaments, and the other two samples were selected from composites reinforced with BN-coated filaments. In each category, a sample was chosen in the as-fabricated condition, and a sample was annealed at 1350 °C for 100 h to observe a relative change in interfacial shear strength caused by the annealing treatment. The results are summarized in Table III.

An average debond stress of 39 MPa and a frictional stress of 16 MPa were measured in an as-fabricated composite reinforced with uncoated filaments. A similar composite after annealing at 1350 °C for 100 h resulted in an average debond stress of 15 MPa and a frictional stress of 10 MPa. The debond stress was always higher than the frictional stress in all the tested composites whether in the as-fabricated state or in the annealed condition. However, the difference between the debond and the frictional components of the interfacial shear stress was smaller in annealed composite in comparison to the as-fabricated sample. This difference suggests that there is a stronger adhesion between the outer carbon layer on the filament and the zircon matrix in the as-fabricated composite because of the high temperature of 1580 °C used for hot pressing. The annealed composite produced lower values of interfacial shear strength as compared to the as-fabricated sample indicating a reduced fibre–matrix adhesion. However, this amount of lowered interfacial shear stress was not sufficient to affect mechanical properties of annealed composites as presented earlier, but led to a more gradual drop in load on composite failure (as shown in Fig. 3).

The composite sample reinforced with BN-coated filaments produced lower values of the interfacial shear stress as given in Table III. A debond stress of 18 MPa and a frictional stress of 15 MPa were obtained for the as-fabricated composite. A similar composite after annealing at 1350 °C for 100 h produced an average debond stress of 8 MPa and a value of 3.5 MPa for frictional shear stress. The debond stresses are higher than the frictional stresses, but the difference between the two values is much smaller in these samples than in samples reinforced with uncoated filaments. The interfacial shear stress values for annealed composite reinforced with BN-coated filaments are significantly lower than the values for as-fabricated composite and are responsible for lower strength values in composites annealed at 1350 °C for 100 h (Figs 7, 8). The composites containing BN-coated filaments show a more gradual load drop in mechanical tests than do the composites containing uncoated filaments because of the lower values of the interfacial shear stress (compare Figs 3 and 5).

Composite samples were examined by SEM, after the filament push-out experiments, to determine the location of fibre–matrix interfacial sliding. The results for an as-fabricated and annealed (1350 °C, 100 h) composite reinforced with uncoated SiC filaments are shown in Fig. 9. The filament–matrix sliding, for a sample in the as-fabricated state, is between the two carbon layers on as-supplied filaments as shown in Fig. 9a and b. Each of these carbon coatings is about 1.5 μm thick. The outer of these coatings (lightly coloured ring) is tenaciously attached to the zircon matrix, whereas the inner carbon coating (dark coloured ring) has moved below the matrix plane along with the rest of the filament as shown in Fig. 9b. A similar behaviour was displayed by the annealed composite as shown in Fig. 9c and d. These results indicate that although somewhat lower values of the interfacial shear stress were obtained for the annealed sample in

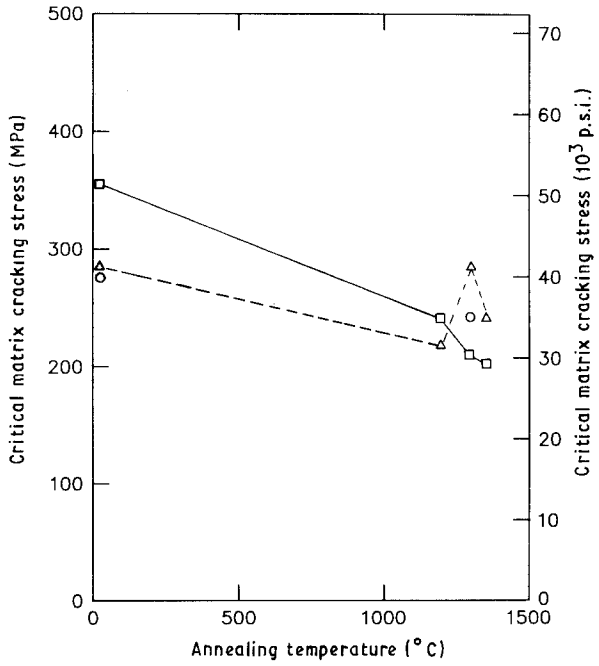

Figure 8 Influence of annealing temperature for 100 h in Ar–7% H_2 on critical stress for first matrix cracking in (○) zircon and zircon composites reinforced with (△) uncoated and (□) BN-coated silicon carbide filaments. 10^3 p.s.i. = 6.89 N mm^{-2}.

comparison to the as-fabricated sample, the interface responsible for sliding remained the same.

Still lower values of interfacial shear stress were measured in composites reinforced with BN-coated filaments because of a different interface responsible for sliding. The results for as-fabricated and annealed composites containing BN-coated filaments are shown in Fig. 10. The interfacial sliding, for an as-fabricated composite, is between the BN coating and the zircon matrix as shown in Fig. 10a and b because both of the carbon-rich layers have moved below the matrix plane (Fig. 10b). A similar behaviour is displayed by the composite sample annealed at 1350 °C for 100 h as shown in Fig. 10c and d. The BN coating on top of the two carbon-rich layers of a silicon carbide filament is clearly visible in Fig. 10d, which is a further evidence of interfacial sliding between the BN coating and the zircon matrix. A significant reduction in interfacial shear stress for the annealed composite sample cannot be explained on the basis of the location of interfacial sliding because the as-fabricated composite containing BN-coated filaments showed a similar behaviour. Densification and crystallization of BN coating as a result of the annealing at 1350 °C for 100 h may be responsible for the lowered values of interfacial shear stress. The as-deposited BN coating is amorphous and is expected to crystallize to hexagonal structure because of high-temperature annealing [4], which may result in a lower value of the interfacial shear stress.

3.4. Thermal stability of zircon–silicon carbide composites

Composites fabricated with zircon matrix and silicon carbide monofilament reinforcement were internally stable to 1350 °C for an extended time. But these composites showed a significant amount of strength degradation when annealed at 1430 °C for 20 h because of degradation in filament properties although a toughened composite-like behaviour was still maintained. The degradation in filament properties caused by annealing at 1430 °C is not unexpected because of the possible presence of free silicon in the as-fabricated AVCO-SCS6 SiC monofilaments [7]. To verify this hypothesis, uncoated silicon carbide filaments were annealed at 1000, 1200, 1300, and 1430 °C for 20 h in a flowing Ar–7% H_2 environment, and their strength was measured by a fibre-bending technique as described by Hillig [8]. The dependence of filament strength on annealing temperature is shown in Fig. 11. The as-fabricated filament strength of about 3.9 GPa (570×10^3 p.s.i.) was maintained up to the annealing temperature of 1300 °C. However, filaments annealed at 1430 °C for 20 h produced a significant reduction in strength to a value of 2.5 GPa (360×10^3 p.s.i.). These results, along with data on composites annealed up to 1350 °C for 100 h, suggest that composites reinforced with AVCO-SCS6 silicon carbide filaments may have an ultimate useful temperature limit of about 1350 °C for long-term applications.

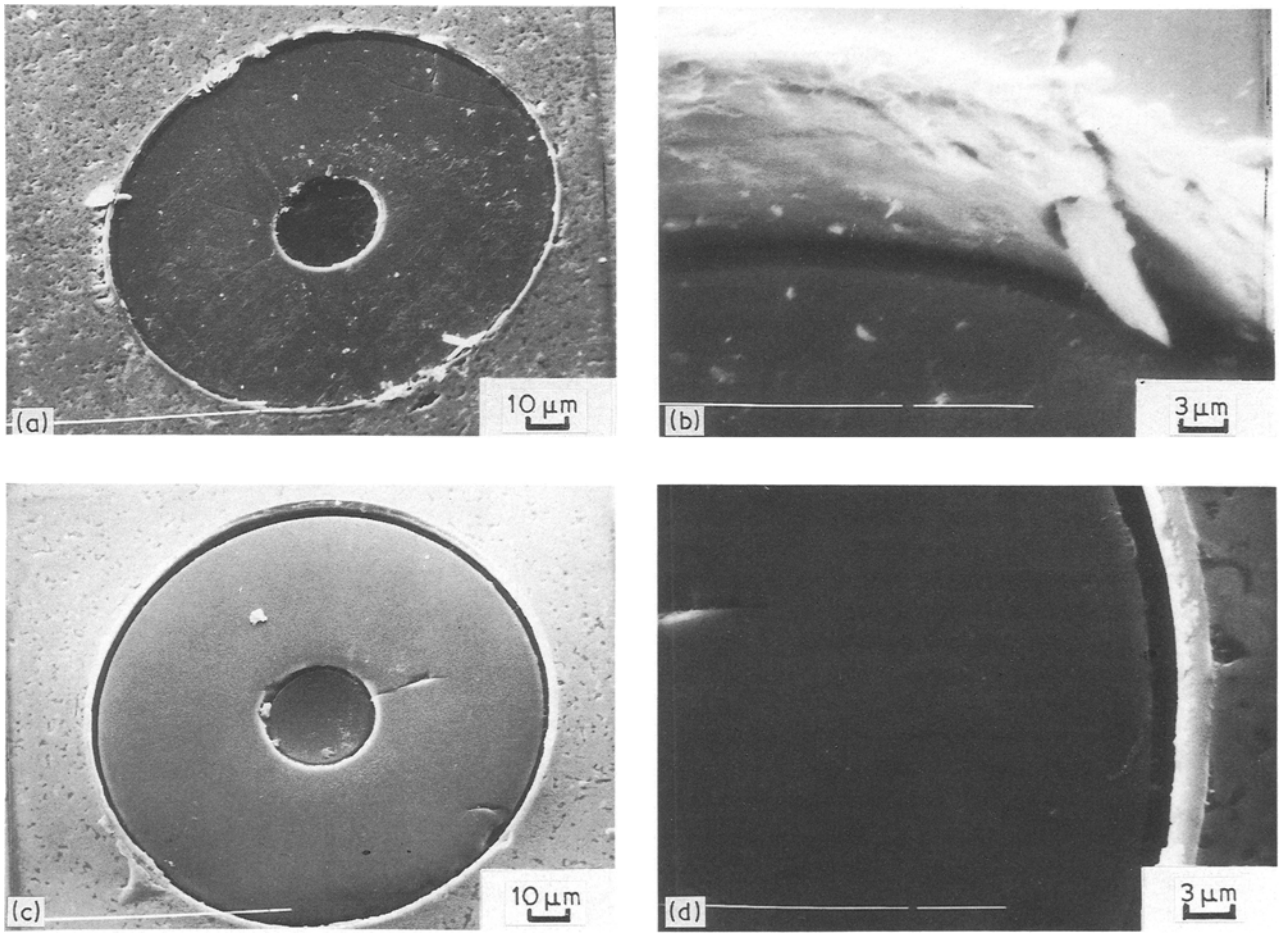

Figure 9 Scanning electron micrographs showing the location of fibre–matrix interfacial sliding in composites reinforced with uncoated SiC filaments in (a, b) as-fabricated state and (c, d) after annealing at 1350 °C for 100 h.

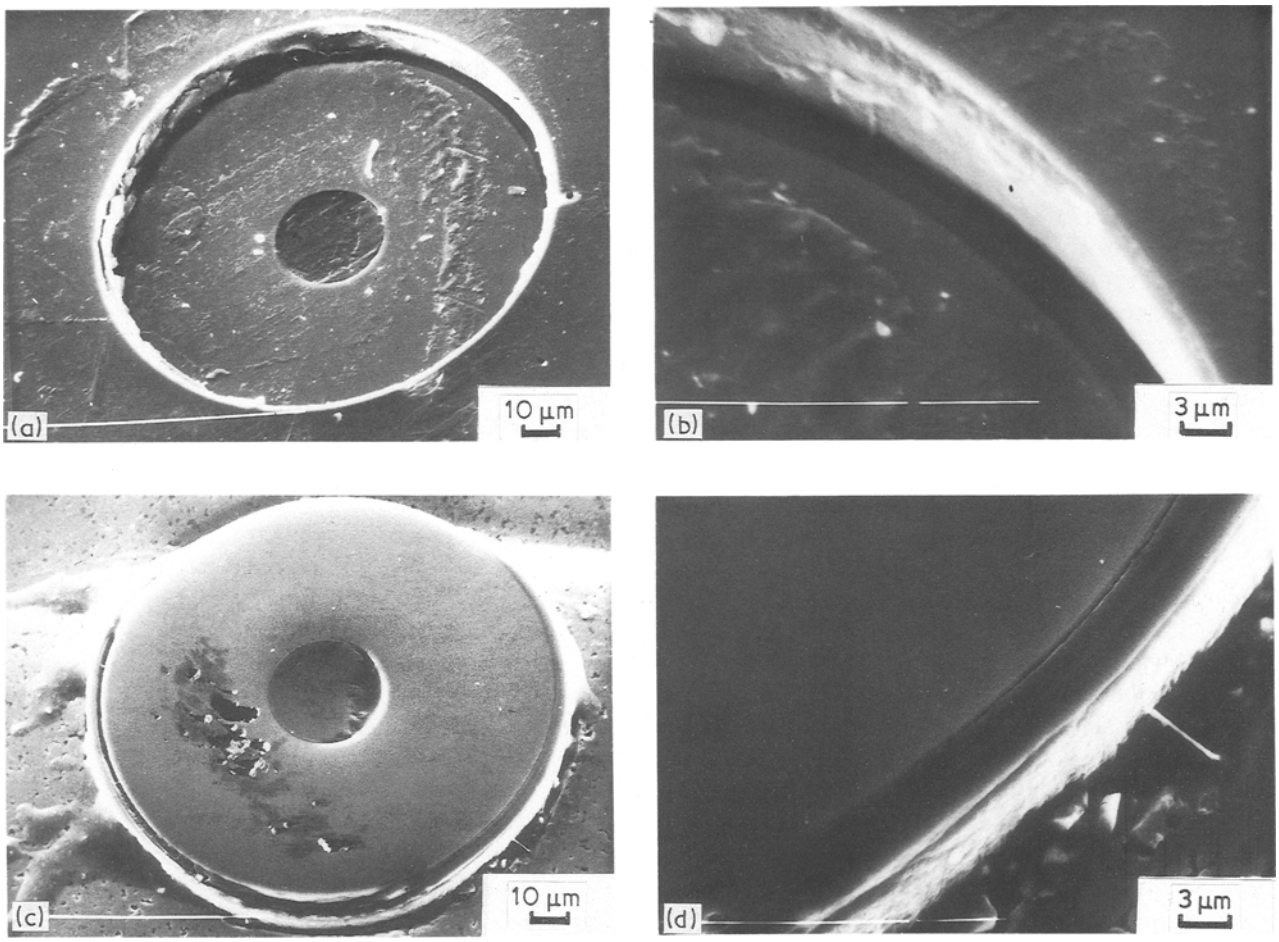

Figure 10 Scanning electron micrographs showing the location of fibre–matrix interfacial sliding in composites reinforced with BN-coated SiC filaments in (a, b) as-fabricated state and (c, d) after annealing at 1350 °C for 100 h.

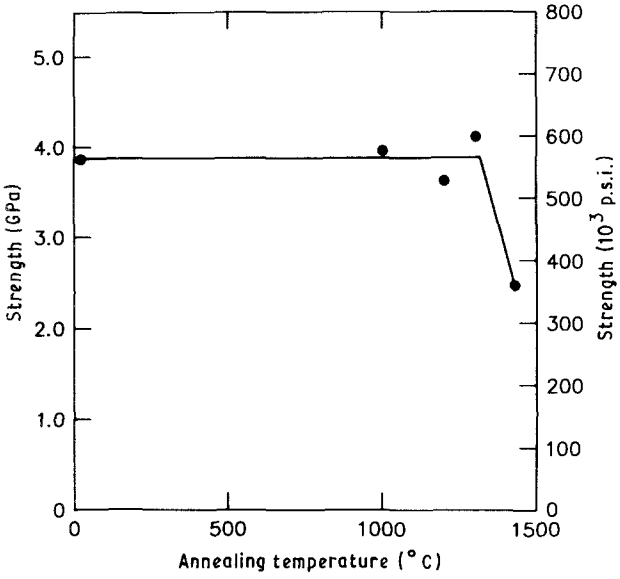

Figure 11 Influence of annealing temperature on strength of AVCO SCS-6 silicon carbide filaments annealed in Ar–7% H_2 for 20 h. 10^3 p.s.i. = 6.89 N mm^{-2}.

Fibre–matrix interfacial properties, as characterized by interfacial shear stress measurements and determination of sliding interfaces, are also indicative of internal thermal stability in zircon–SiC composites. Composites containing uncoated filaments in the zircon matrix showed a decreased interfacial shear stress after annealing at 1350 °C for 100 h. But, this decrease was still not significant enough to influence mechanical properties. There was no change in the location of interfacial sliding because of the annealing treatment. Composites reinforced with BN-coated filaments produced lower values of interfacial shear stress and displayed interface stability to 1200 °C, but samples annealed at 1350 °C for 100 h produced much lower interfacial shear strength. This change was responsible for lower strengths (critical matrix cracking and ultimate strength) although composite toughness was retained. These results indicated that although BN-coated filaments led to a more gradual drop in load beyond the point of maximum load in the load–deflection data as a result of the lower interfacial shear stress, there was no other advantage of using BN coating to enhance thermal stability of zircon–SiC composites. Interfacial stability in this class of composites is expected to be good even beyond 1350 °C because composites annealed at 1430 °C for 20 h displayed toughened composite-like behaviour, although their strengths were reduced because of degradation in filament strength.

4. Conclusions

Samples of monolithic zircon, AVCO-SCS6 silicon carbide filaments, and zircon–SiC composites were annealed between 25 and 1430 °C for times up to 100 h

to study the influence of thermal treatments on mechanical properties and fibre–matrix interfacial characteristics. Important conclusions from this study are described below.

1. Monolithic zircon ceramics were brittle and weak (strength 281 MPa, WOF 1.2 kJ m^{-2}). In contrast, as-fabricated zircon composites reinforced with uncoated and BN-coated SiC filaments were significantly stronger (strength 681 to 700 MPa) and tougher (WOF 18 to 25 kJ m^{-2}) than the monolithic zircon.

2. The critical stress for first matrix cracking in as-fabricated composites reinforced with either uncoated or BN-coated SiC filaments was similar to the monolithic zircon strength.

3. Monolithic zircon samples displayed no degradation in strength after annealing up to 1430 °C in an Ar–7% H_2 atmosphere.

4. Zircon matrix composites reinforced with uncoated SiC filaments retained their critical matrix cracking stress, ultimate strength, and toughness when annealed up to 1350 °C for 100 h. In contrast, composites reinforced with BN-coated SiC filaments displayed a decreased critical matrix cracking and ultimate strengths after annealing beyond 1200 °C for 100 h; however, their toughness was retained.

5. Composites reinforced with either uncoated or BN-coated SiC filaments showed a significant reduction in strength and toughness when annealed at 1430 °C for 20 h.

6. Fibre–matrix interfacial debond stress of 39 MPa and a frictional stress of 16 MPa were measured in zircon composites reinforced with uncoated SiC filaments using a fibre pull-out technique. A lower debond stress of 15 MPa and a frictional stress of 10 MPa were measured for a similar composite after annealing at 1350 °C for 100 h. In contrast, composites reinforced with BN-coated SiC filaments resulted in a debond stress of 18 MPa and in a frictional stress of 15 MPa in the as-fabricated state, and a significantly lower debond stress of 8 MPa and a frictional stress of 3.5 MPa after annealing at 1350 °C for 100 h.

7. The location of fibre–matrix interfacial sliding was between the two carbon-rich layers on AVCO-SCS6 SiC filaments in zircon composites reinforced with uncoated SiC filaments. In contrast, composites reinforced with BN-coated filaments displayed interfacial sliding between the BN coating and the zircon matrix. The different location for the interfacial sliding was responsible for lower interfacial shear stress values in composites containing BN-coated filaments.

8. There was no degradation in strength of AVCO-SCS6 SiC filaments after annealing for 20 h between 1000 and 1300 °C. However, filaments annealed at 1430 °C for 20 h showed a significant reduction in strength.

9. Changes in mechanical properties of zircon–SiC composites as a result of the annealing treatments are consistent with changes in matrix, fibre, and fibre–matrix interfacial properties. The thermal stability of zircon composites containing uncoated SiC filaments to 1350 °C for 100 h is due to insignificant degradation in matrix, filament, and interfacial properties. Degradation in critical matrix cracking and ultimate strengths of composites reinforced with BN-coated filaments after annealing at 1350 °C for 100 h can be attributed to lowered fibre–matrix interfacial shear stress. Similarly, a significant degradation in mechanical properties of zircon composites reinforced with either uncoated or BN-coated SiC filaments after annealing at 1430 °C for 20 h can be ascribed to degradation in filament properties.

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