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Heat Treatment Effects on the Tensile Properties and Microstructure of a SiC/RBSN Composite in Nitrogen

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Abstract: The room-temperature tensile properties and constituent microstructures of a unidirectionally reinforced SiC/RBSN composite have been investigated after heat treatments at 1400, 1600, or 1800°C in nitrogen for up to 100 h. The composite consisted of ~24 vol% of aligned 140 μm diameter, continuous length, chemically vapour deposited SiC fibres in a ~40% porous silicon nitride matrix. The composites heat treated at 1400°C for up to 100 h showed elastic modulus, first matrix cracking strength and ultimate tensile strength values similar to those of the as-fabricated composites, but those heat treated for 1 h beyond this temperature displayed losses in all three properties. Recrystallization of the SiC fibres, loss of carbon from the carbon-rich interface coating on the fibres, and dissociation of the RBSN matrix are the reasons for the loss of mechanical properties. Published by Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

In recent years a variety of fibre-reinforced ceramic matrix composites (FRCMC) have been developed for high temperature applications. This new class of materials has the potential for retaining the key advantages of monolithic ceramics, namely, low density, high temperature strength, and good oxidation and creep resistance, while providing the microstructural mechanisms for improved reliability over monolithic ceramics. Among various potential FRCMC, silicon- and glass-based FRCMC have been investigated extensively.[1–3] One of the silicon-based FRCMC that shows promise for high temperature applications is the SiC fibre-reinforced reaction-bonded silicon nitride matrix composite system (SiC/RBSN).[3] In this system, the SiC fibre is chemically compatible with the RBSN matrix. From a processing point of view, RBSN is a low cost, near net shape process which can be adapted to the fabrication of complex shaped components. In addition, the processing conditions for RBSN can be tailored to avoid degradation in the SiC fibres and the fibre–matrix interface while attaining desirable matrix properties.

For the past ten years, RBSN composites have been fabricated using large diameter (~140 μm), chemically vapour deposited (CVD) SiC fibres, and small diameter (~14 μm) polymer derived SiC fibres.[3,4] However, because of the instability of small diameter SiC fibres during processing to date, composites fabricated using these fibres did not yield acceptable properties. The large diameter SiC fibre-reinforced RBSN matrix composites have the best strength, toughness, thermal shock resistance and flaw tolerance at room temperature.[3] Although complex shape capability is limited for the SiC/RBSN composites containing large diameter SiC fibres, these composites can be used as a model system to develop strong, tough and thermally stable composites, and for applications where simpler shapes will suffice. A variety of studies have been performed in this system to correlate constituent microstructure with mechanical and thermal properties and to model mechanical performance.[3,5,6] However, factors influencing the upper temperature limit of this composite have not been established.

The objectives of this study are to determine the intrinsic strength and microstructural stability limit for the RBSN composites reinforced by large diameter (~140 μm) SiC fibres and to determine the strength degrading mechanisms.

2 EXPERIMENTAL PROCEDURE

2.1 Composite fabrication

For SiC/RBSN composite fabrication, commercially available silicon powder of 3 μm average particle size and SiC monofilaments of nominal diameter 140 μm were used as starting materials. The fibres, obtained from Textron Specialty Materials, Lowell, Massachusetts, were produced by a CVD method. The fibre is itself a composite and consists of a SiC outer sheath of 140 μm diameter surrounding a 37 μm diameter pyrolytic carbon-coated graphite core.[7] At the outer surface of the SiC sheath is a carbon-rich surface coating of 3 μm thickness.[7] The coating is provided to improve abrasion resistance and enhance fibre strength. Commercial purity (~99%) silicon powder was obtained from Union Carbide. This powder was attrition milled in a non-aqueous medium for 24 h to reduce its average particle size from 3 μm to 0.7 μm.

The SiC/RBSN composites were fabricated by the fibre lay-up method. The details of the fabrication procedure are described elsewhere.[8] This method can be used to fabricate either 1-D or 2-D laminated composites. However, for this investigation, only 1-D composites were fabricated. Typical dimensions of the 1-D composite panels were 125 mm×50 mm×3 mm, and each panel contained ~24 vol% fibres.

2.2 Specimen preparation and testing

The composite panels were ground first and then the tensile specimens of dimensions 125 mm× 6 mm×2 mm were machined from the panels using diamond impregnated metal bonded wheels. The specimens were heat treated in 0.1 MPa nitrogen in a graphite lined box furnace for 1–100 h between 1200 and 1800°C. Both as-fabricated and heat-treated specimens were sectioned normal to the fibres, mounted in a metallographic mould, ground successively on 40 μm down to 3 μm diamond particle impregnated metal disks, and polished in a vibratory polisher on a micro cloth using 0.03 μm diamond powder paste. Some specimens were also plasma etched to delineate the microstructure in the fibre. The etched specimens were observed under a scanning electron microscope (SEM).

For tensile testing of the heat-treated specimens, two fibre reinforced epoxy tabs of dimensions 37 mm×6 mm×1 mm were bonded at each specimen end, leaving ~60 mm for the gauge section. A wire wound strain gauge was bonded at the centre of the gauge section to monitor the strain during the tensile test. The specimens were tested at room temperature in a servo-controlled tensile testing machine at a cross-head speed of 1.3 mm/min. Some of the specimens were tested to ultimate failure and some to 80% of the ultimate strength. This latter batch was used to calculate the interfacial shear strength of the composite. Details of this technique are reported elsewhere.[9]

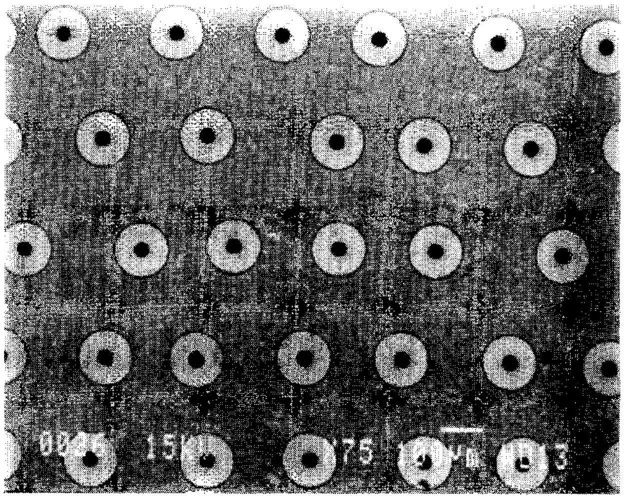

Fig. 1. Cross-section showing microstructure of unidirectional SiC/RBSN composite ($V_f = 24\%$).

3 RESULTS AND DISCUSSION

A polished cross-section of a typical 24 vol% SiC/RBSN composite specimen is shown in Fig. 1. The fibres are uniformly distributed in the non-uniform pore size matrix.

The room-temperature tensile stress–strain curves for the 1-D SiC/RBSN composites after 1 h heat treatment in nitrogen at 1400, 1600 and 1800°C are shown in Fig. 2. Since the stress–strain curves of the as-fabricated composite and the composite heat treated in nitrogen for 1 h at 1400°C are similar, the stress–strain curve of the as-fabricated composites is not shown in Fig. 2. The 1400 and 1600°C curves show three regions: an initial linear elastic region, a non-linear region, and a second linear region. The existence of a non-linear region in the stress–strain curve indicates bridging of matrix cracks by the fibres, and tough composite behaviour. The stress–strain curve of the 1800°C heat-treated composite displays an initial linear region and no strain capability beyond matrix fracture. The slope of this line is slightly lower than that of the other two.

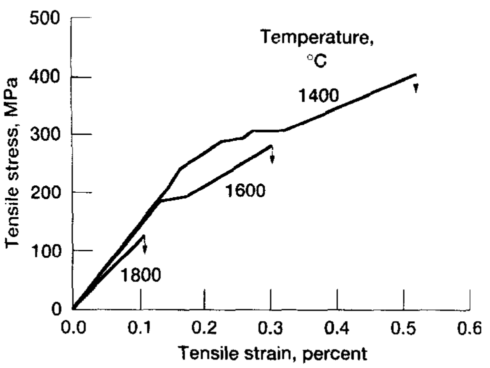

Fig. 2. Room-temperature tensile stress–strain curves of SiC/RBSN composites ($V_f = 24\%$) after 1 h heat treatment in nitrogen: (a) 1400°C, (b) 1600°C, and (c) 1800°C.

The effect of 1 and 100 h heat treatment in nitrogen on primary elastic modulus (*E*), first matrix cracking stress (FMCS) and ultimate tensile strength (UTS) of the composites are illustrated in Fig. 3. Each data point represents an average of three tests. Since the specimens heat treated at 1800°C for 100 h were very weak, their tensile data could not be plotted in Fig. 3. As seen in the figure, for up to 100 h of exposure at 1400°C, the composites retained as-fabricated mechanical properties. With increasing temperature of exposure the elastic modulus, the first matrix cracking strength and the ultimate tensile strength decreased, but the ultimate tensile strength showed greater loss with exposure temperature than did the matrix fracture strength or the elastic modulus.

The loss of mechanical properties can be caused by the degradation of the SiC fibres, the carbon-rich interface, and/or the RBSN matrix. To determine the reasons for the loss of mechanical properties, microstructures of the constituents and the interfacial shear strength between the matrix and the fibres were analysed.

The matrix crack spacing method[9] was used to calculate τ, the interfacial shear strength (ISS). This method yields information about the frictional characteristics of the interface. The interfacial frictional shear strength, τ, between the SiC fibre and the RBSN matrix can be estimated from the equation,

$$\tau = \sigma_m D E_m V_m / 2.98 X V_f (1 + E_c)$$

where σ_m is the first matrix cracking stress, X is the average separation between the matrix cracks, D is the fibre diameter, E_c is the composite elastic modulus and V_f is the volume fraction. The subscripts m and f indicate matrix and fibre, respectively. Substituting $E_f = 390^{10}$ GPa, $E_m = 110^3$ GPa, $D = 140$ μm, and the values of σ_m and X (the average matrix crack spacing) from Table 1 in the above equation, τ values were calculated for the

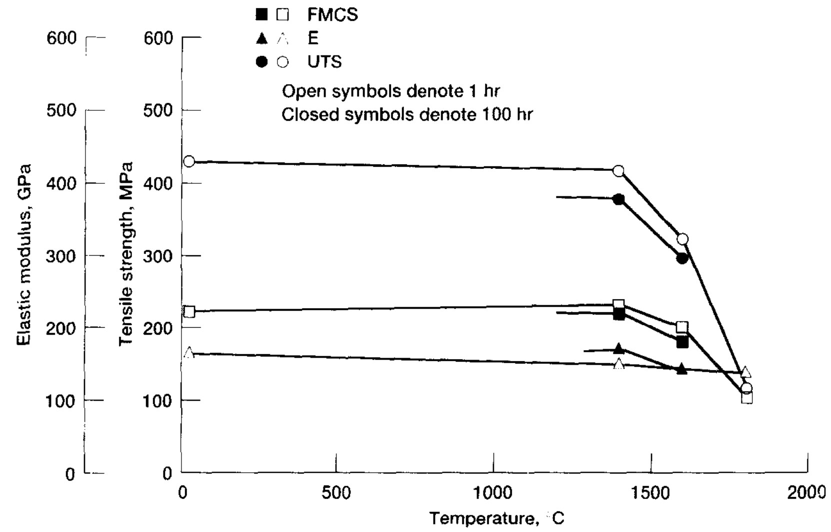

Fig. 3. Effects of heat-treatment temperature and time on the tensile properties of SiC/RBSN composites.

Table 1. Matrix fracture properties and interfacial shear strength for SiC/RBSN composites

Condition	First matrix cracking stress σ_m (MPa)	Composite elastic modulus E_c (GPa)	Average matrix cracking spacing X (mm)	Average interfacial shear strength τ (MPa)
As-fabricated	224 ± 8	166 ± 26	2.0 ± 0.5	10 ± 5
After 1 h heat treatment in N_2 at: 1400°C	267 ± 7	149	2.7 ± 1.0	12 ± 6
1600°C	201 ± 34	141	9.2 ± 1.6	8 ± 4
1800°C	103 ± 41	138	—	—

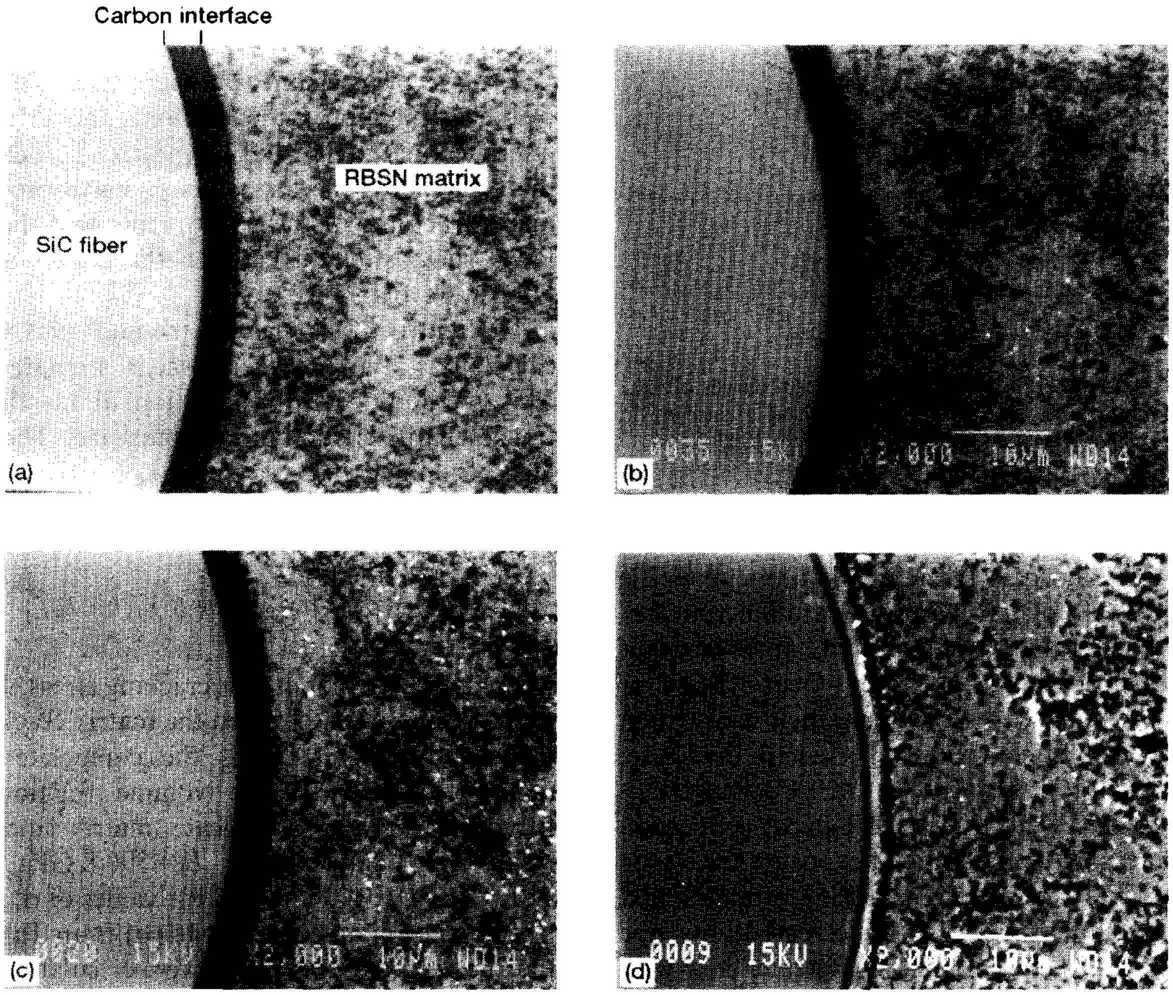

Fig. 4. Influence of 1 h heat treatments in nitrogen on the microstructure of SiC/RBSN composite: (a) as-fabricated, (b) 1400°C, (c) 1600°C, and (d) 1800°C.

as-fabricated and heat-treated composites, and these values are also shown in Table 1. The ISS valves of the as-fabricated and the 1400°C for 1 h heat-treated composites are nearly the same. At 1600°C, a small loss in the average ISS value is seen compared to that of the as-fabricated composites.

Examination of the cross-sections of the heat-treated composites indicates that up to 1600°C, the RBSN matrix and carbon-rich interface coating remained stable (Fig. 4(c)). Beyond this temperature, the carbon-rich interface coating thickness decreased significantly compared to that of the as-fabricated composite (Fig. 4(d)). In addition, the size of the matrix pores has increased. Limited X-ray measurements performed on composites heat treated at 1800°C showed increasing amounts of silicon in the RBSN matrix with increasing exposure time. Increasing amounts of silicon in the RBSN matrix indicates dissociation of silicon nitride to silicon and nitrogen. In fact, it is known that silicon nitride dissociates at ~1800°C in 0.1 MPa nitrogen.[11] Composites heat treated for 1 h at and beyond 1600°C also showed fibre degradation. A diffusion zone started emanating from the outer surface of the SiC fibre adjacent to the carbon-rich surface coating. The thickness of this zone increased with increasing temperature of exposure or with increasing time of exposure at a given temperature. A photomicrograph of the cross-section of the composite heat treated at 1800°C for 1 h showing the growth of the zone is shown in Fig. 5. The growth of the diffusion zone at the interface of the carbon coating and the SiC sheath is similar to that observed in the individual SiC fibres heat treated beyond 1500°C for 1 h in an argon environment,[12] but the thickness of the zone in the composite is smaller than that in the individual fibres. It has been shown by TEM analysis of heat-treated SiC fibres that the diffusion zone consists of equiaxed recrystallized SiC grains.[12] This study showed that strength degradation in this fibre is caused by recrystallization and growth of SiC grains and that a relationship exists between the strength of the heat-treated fibres and the thickness of the recrystallization zone.

Although ISS loss, Si_3N_4 dissociation and reduction of carbon-rich coating thickness are observed in the SiC/RBSN composites heat treated

Fig. 5. Photomicrograph of the cross-section of a SiC/RBSN composite heat treated in nitrogen at 1800°C for 1 h. Note the growth of a diffusion zone at the interface of the carbon coating and the SiC sheath of the SiC fibre.

for 1 h at and beyond 1600°C, none of these seem to significantly affect the elastic modulus and first matrix cracking stress. In addition, the loss of carbon at the interface does not affect the fracture behaviour of the composite as matrix crack deflection in both the as-received and heat-treated composites occurred within the carbon coating. Based on these facts we conclude that the carbon coating and RBSN matrix reaction even if it is feasible may not have significant influence on UTS of the composite. Certainly, loss of ultimate tensile strength of the composite starts with the growth of the recrystallization zone. Therefore, fibre degradation has major impact on the mechanical performance and UTS of the composite.

In summary, the upper temperature capability of the SiC/RBSN composites in an inert environment is primarily limited by the microstructural stability of SiC fibres. Based on fibre data,[12] it appears that the maximum use temperature is ~1300°C for SiC/RBSN composites under no load conditions.

4 CONCLUSIONS

The SiC/RBSN composites, containing 140 μm diameter SiC monofilaments, remain strong and tough after 100 h exposure in nitrogen to 1400°C. Beyond this temperature, ultimate tensile strength of the composite decreases due to intrinsic microstructural stability of the SiC fibres. By choosing stronger and more stable SiC fibres than the CVD SiC fibres used in this study as reinforcement, the upper use temperature of SiC/RBSN composites should be improved.

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