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Thermomechanical durability of CVI-processed two-dimensionally woven and three-dimensionally braided SIC fibre-reinforced SiC composites

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The thermomechanical durability of a two-dimensionally woven and a three-dimensionally braided SiC/SiC composite fabricated by chemical vapour infiltration technique were studied. The effects of thermal shock, thermal ageing, and thermal cycling at high temperatures on mechanical properties were determined. The thermal degradation mechanisms were also investigated. The results indicated that the fibre geometry, matrix porosity, interlaminar shear strength and testing conditions affect the thermomechanical durability of the SiC/SiC composites.

1. Introduction

The demand for strong, tough, defect-free and near net shape structural ceramic composites for various high-temperature applications is growing rapidly. One of the most promising ceramic composites currently being considered for high-temperature applications is silicon carbide/silicon carbide (SiC/SiC) fabricated by chemical vapour infiltration (CVI) technique. SiC has high stiffness, low thermal conductivity and diffusivity, which result in good thermal shock resistance. The incorporation of continuous SiC fibres (Nicalon) improves the fracture toughness and damage tolerance of the ceramic matrix. A fracture toughness of 30 MPa $m^{1/2}$ has been reported for the composite, compared to about 3 MPa $m^{1/2}$ for monolithic SiC [1–6]. The composite exhibits a rising R-curve behaviour at ambient temperature; however, the R-curve effect is substantially reduced at 1200 °C [7]. SiC/SiC composites have also been reported to have strengths of up to 400 MPa, and show no significant strength reduction after thermal shock up to 1000 °C [3]. However, although SiC/SiC composites demonstrate good mechanical properties at temperatures up to 1000 °C, no significant research has been conducted to determine the thermomechanical durability of the composite at high temperatures.

The purpose of this work was to investigate the effect of thermal shock, thermal ageing, and thermal cycling on the mechanical properties of both two-dimensionally woven and three-dimensionally braided SiC/SiC composites. The thermal degradation mechanisms were also studied.

2. Experimental procedure

The materials used in this study were two-dimensional plain-weave laminates and three-dimensionally braided SiC/SiC composites fabricated using a chemical vapour infiltration (CVI) process. A detailed description of the CVI processing conditions and fibre architecture for both the two- and three-dimensional SiC/SiC composites can be found elsewhere [4]. The porosity of the two-dimensional material was found to be approximately 15%, while the three-dimensional composites had a porosity of about 17%. The panels of two- and three-dimensional SiC/SiC composite were cut with a diamond saw into specimens with dimensions of 5.1 cm × 0.64 cm × 0.38 cm for bend testing.

Thermal shock testing was conducted by heating the SiC/SiC samples to the test temperature (500, 750, 1000, or 1200 °C), holding the sample at that temperature for 15 min to obtain a constant temperature profile throughout the sample, and then dropping it into a water bath, rapidly quenching the sample to room temperature. The effect of exposure at high temperature on SiC/SiC composites was determined using a thermal ageing test. The samples were exposed to temperature for various times (5, 15, 50, and 100 min). The specimens were then taken out of the furnace and allowed to cool to room temperature naturally. Thermal cycling was conducted to determine the composite's tolerance to changing temperature environments. The sample was heated (at 1000 or 1200 °C) for the particular cycle time (5 or 15 min). The composites were then cooled using different

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cooling methods (water quench, air blast, or naturally cooled.) The length of the cooling cycle was 5 s for water, 1 min for air, and 4.5 min for natural cooling. The procedure was repeated for a given number of cycles (1, 5, 10, or 20 cycles).

In order to determine the effect of the different thermal tests on the SiC/SiC composites, mechanical testing and optical observations of the samples were performed. The samples were first examined for changes in surface colouring. The four-point bending test was performed on heated and unheated samples to determine the strength loss of the composite due to temperature effects. The fracture surfaces of the mechanically tested samples were examined using a scanning electron microscope.

Instrumented Charpy impact testing on a single-edge notched-beam specimen was also conducted to study the energy absorbing capability and dynamic fracture behaviour of the composites after extended thermal ageing. The impact velocity was $1\ m\ s^{-1}$. The load versus time and the energy absorbing curves were recorded. The dynamic fracture toughness was calculated using the procedure outlined elsewhere [8].

3. Results and discussion

3.1. Thermal shock

Fig. 1 shows the thermal shock resistance of the two- and three-dimensional SiC/SiC composites for approximate temperature drops of 500, 750, 1000, and 1200 °C. For the two-dimensional material, there was no significant reduction in strength due to thermal shock until 800 °C, where the strength dropped rapidly and continued to decrease as the temperature reached 1200 °C. The strength degraded by over 44% after thermal shock test at 1200 °C. A previous study by Lamicq *et al.* [3] indicated that no reduction in strength occurred for thermal shocking up to 1200 °C in an inert atmosphere. The significant drop in strength (44%) for the two-dimensional composite in an oxidizing atmosphere clearly shows that the two-dimensional composite is susceptible to environmental attack. Although there was no catastrophic failure due to the rapid temperature changes, the reduction in strength does indicate detrimental effects of thermal shock on two-dimensional SiC/SiC composites.

The colour changes and fracture analysis gave evidence of changes in the two-dimensional material after thermal shock. The purple colouring, an indication of oxide layer formation, was present both on the sample surface as well as the fracture surface. X-ray diffraction analysis confirmed the presence of an SiO_2 layer on the surface. The samples exhibited no fibre pull-out on the fracture surface, which indicated a reduction in the fibres' ability to improve the strength and toughness of the composites. It also suggested that the fibre/matrix interface strength was increased due to thermal testing, which resulted in a degradation of the mechanical properties of the SiC/SiC composites.

From the results in Fig. 1, it is evident that the three-dimensional composites demonstrated excellent resistance to thermal shock up to 1200 °C. The three-dimensional composites exhibited no loss in flexural strength due to thermal gradients of up to 1200 °C. The purple colouring of the thermally shocked samples indicated the formation of an oxide layer; however, the fibres along the surface did not show any colouring due to the presence of a dense SiC surface layer. Because there was no catastrophic failure or reduction in bend strength, the effects of thermal shock on the three-dimensional SiC/SiC composites seem insignificant.

3.2. Thermal Ageing

The results for thermal ageing of the two-dimensional SiC/SiC composites at 1000 and 1200 °C were plotted in Fig. 2 for comparison. The data suggested a significant reduction in bend strength for both temperatures after 100 min exposure. The reduction was promoted by increased temperature, from 21.5% for 1000 °C to 67% for 1200 °C. Most of the degradation seemed to occur in the first 15 min, followed by a slower reduction up to 100 min. The fracture surface exhibited minimal fibre pull-out for samples heated more than 15 min. Fig. 3 is a scanning electron micrograph of the fracture surface of a sample exposed for 100 min at 1200 °C. The surface exhibited a significant reduction in fibre pull-out compared to the room-temperature samples. The surface colouring change at 1200 °C indicated the formation of the oxide layer, while the samples aged at 1000 °C did not show any significant

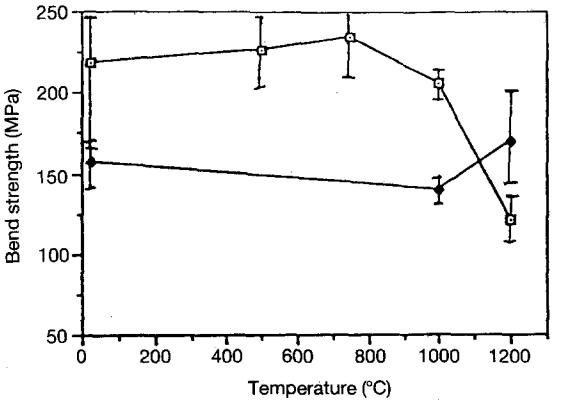

Figure 1 Strength retention versus thermal shock temperature for (□) two- and (◆) three-dimensional SiC/SiC composites.

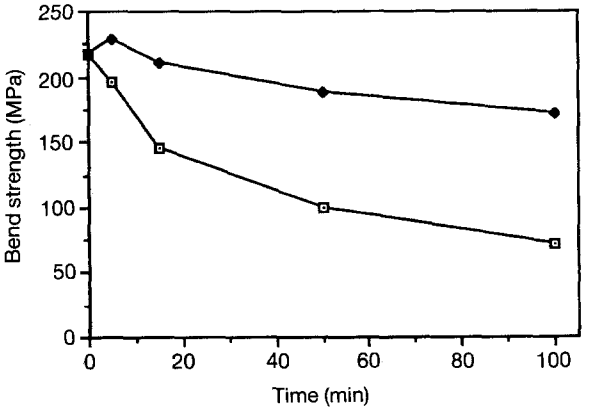

Figure 2 Strength retention after thermal ageing at (◆) 1000 and (□) 1200 °C for two-dimensional SiC/SiC composites.

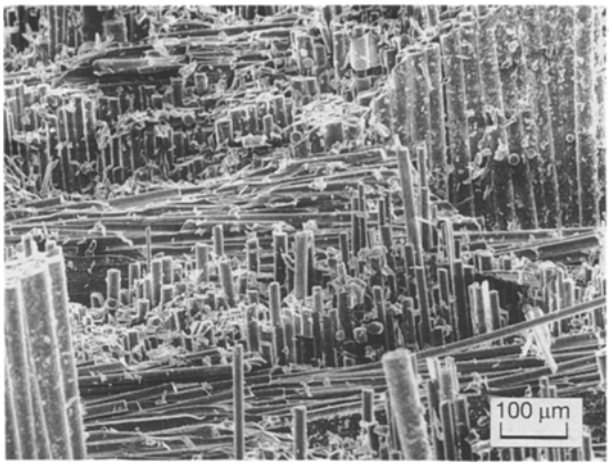

Figure 3 Scanning electron micrograph of a two-dimensional SiC/SiC composite after 100 min at 1200 °C, showing little fibre pull-out.

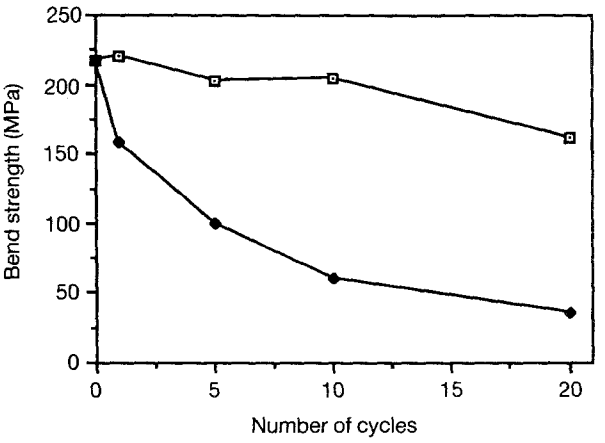

Figure 5 Comparison of thermal cycling results at (□) 1000 and (◆) 1200 °C for two-dimensional SiC/SiC composites.

colour changes. From these results, it seems that the oxidation of the sample at high temperature degraded the strength significantly.

The effect of thermal ageing at 1200 °C on the three-dimensional samples is shown in Fig. 4. Unlike the two-dimensional material, the three-dimensional samples showed no detrimental effects of thermal exposure at 1200 °C for up to 100 min. The change in colouring of the sample surfaces to purple after 100 min exposure indicated once again the formation of the SiO_2 layer. However, in this case, the layer did not seem to affect the mechanical properties of the composite. The fact that the fracture surface of the three-dimensional material did not exhibit this oxidation indicated that the fibres were protected from oxidation by the matrix material. The large amount of fibre pull-out also indicated that the fibre/matrix interface integrity is maintained throughout the thermal ageing process at 1200 °C for the three-dimensional composites.

3.3. Thermal cycling

The thermal cycling behaviour of two-dimensional SiC/SiC at 1000 and 1200 °C are plotted for comparison in Fig. 5. The bend strength reduction was 26% for 1000 °C and 84% for 1200 °C after 20 cycles. The reduction in bend strength indicated a dramatic change in the material after cycling. The colour change for the 1000 °C did not indicate the formation of an oxide layer. However, the purple colour found after 20 cycles at 1200 °C did reveal the presence of oxidation. Fibre pull-out along the fracture surface was observed for both of these specimens. Fig. 6 shows a scanning electron micrograph of the fracture surface of a sample cycled 20 times at 1000 °C. A large amount of fibre pull-out and evidence of delamination between the layers can be seen. The fracture surface for the sample cycled 20 times at 1200 °C is shown in Fig. 7, exhibiting large amounts of fibre pull-out. No significant degradation of the fibres was apparent in the photographs.

These results were similar to those found for thermal ageing testing. Figs 8 and 9 plot the thermal cycling versus thermal ageing resistance for the two-dimensional samples at 1000 and 1200 °C, respectively. It can be seen that a substantial part of the reduction in bend strength can be attributed to the effect of thermal ageing. In fact, for the 1000 °C case, there was no significant difference between thermal ageing and thermal cycling. However, there was a difference between the two curves for 1200 °C, which demonstrated the additional effect of cycling on the mechanical

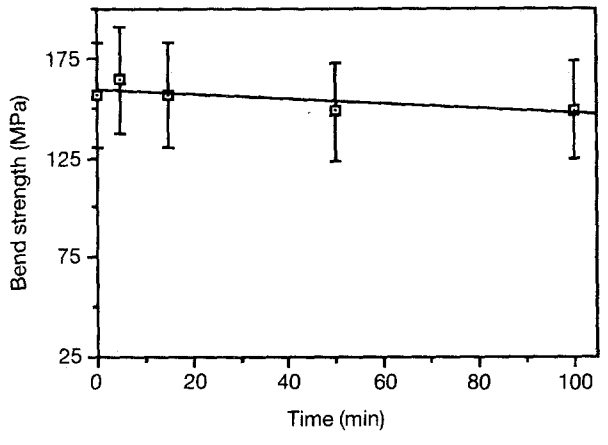

Figure 4 Bend strength versus exposure time at 1200 °C for three-dimensional composites. (□) After ageing.

Figure 6 Fracture surface of two-dimensional SiC/SiC composite after 20 cycles at 1000 °C with a 5 min heating time, showing significant fibre pull-out.

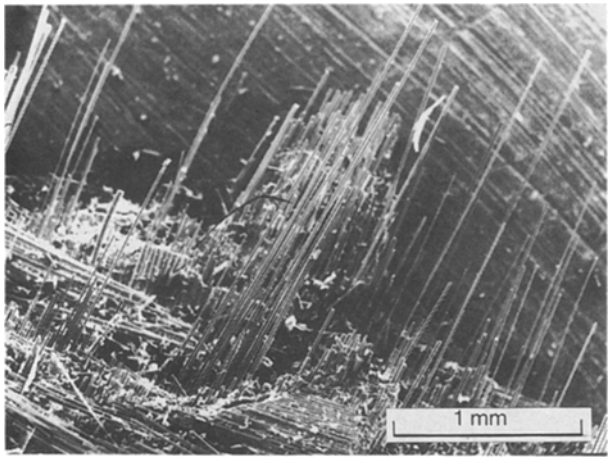

Figure 7 Fracture surface of two-dimensional SiC/SiC composite after 20 cycles at 1200 °C with a 5 min heating time, showing significant fibre pull-out.

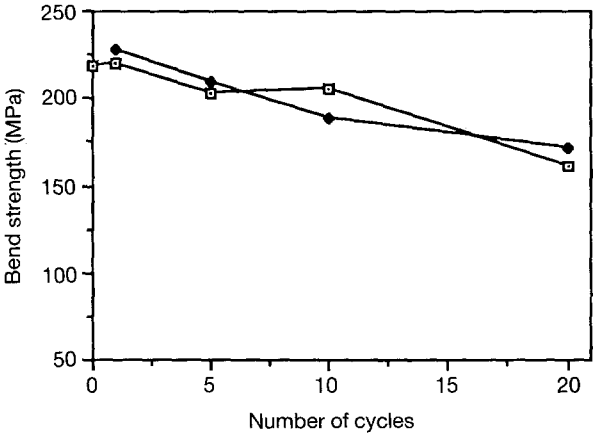

Figure 8 Comparison of (□) thermal cycling in air for 5 min and (◆) thermal ageing results at 1000 °C for two-dimensional SiC/SiC composites.

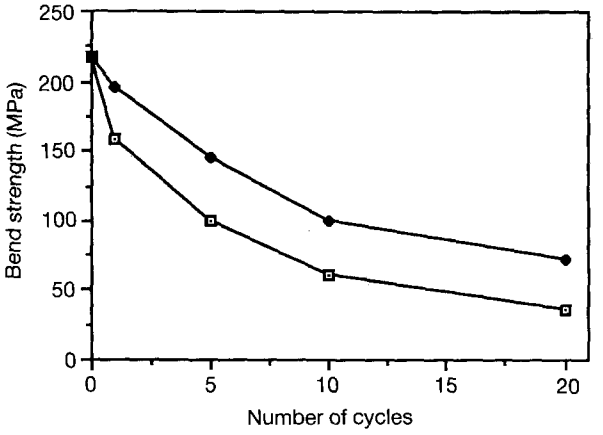

Figure 9 Comparison of (□) thermal cycling in air for 5 min and (◆) thermal ageing results at 1200 °C for two-dimensional SiC/SiC composites.

properties of the composite. The difference was 19% for one cycle, and as large as 50% for the 20 cycle test specimens. Thus, the stress created by the thermal gradients imposed on the samples causes additional reductions in the strength of the SiC/SiC composites.

Fig. 10 shows the thermal cycling resistance of the three-dimensional SiC/SiC composites at 1200 °C. A 5 min heating and the air-blast cooling method were used. The bend strength remained roughly constant for up to 20 cycles. A significant amount of fibre pull-out was present for all samples. The high-magnification scanning electron micrograph of the fibres in the three-dimensional composite after 20 cycles can be seen in Fig. 11. There is no evidence of fibre degradation in the photograph. Changes in surface colouring were similar to the ageing samples; from silver/grey to purple after 20 cycles. Thus, the three-dimensional material demonstrated good thermal cycling resistance at 1200 °C.

An important factor in determining the effect of thermal cycling on the composites was the cooling method used during testing. Figs 12 and 13 show the effect of cooling method on the bend strength reduction for the two-dimensional SiC/SiC composites. Fig. 12 shows natural versus air-blast cooling, while Fig. 13 shows water quenching versus air-blast cooling. From these figures, it can be concluded that the faster the sample is cooled, the faster the bend strength is reduced. The most severe temperature change was that of the water quench, which resulted in the largest drop

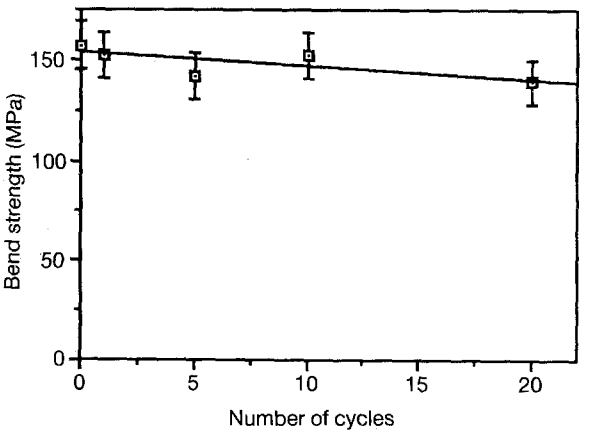

Figure 10 Strength retention versus number of cycles using (□) a 5 min heating time and air-blast cooling method at 1200 °C for three-dimensional SiC/SiC composites.

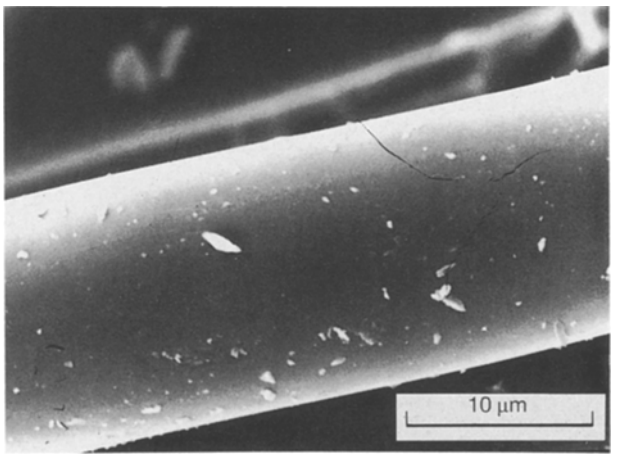

Figure 11 High-magnification scanning electron micrograph of a three-dimensional SiC/SiC composite after 20 cycles at 1200 °C with a 5 min heating time, exhibiting no evidence of fibre degradation.

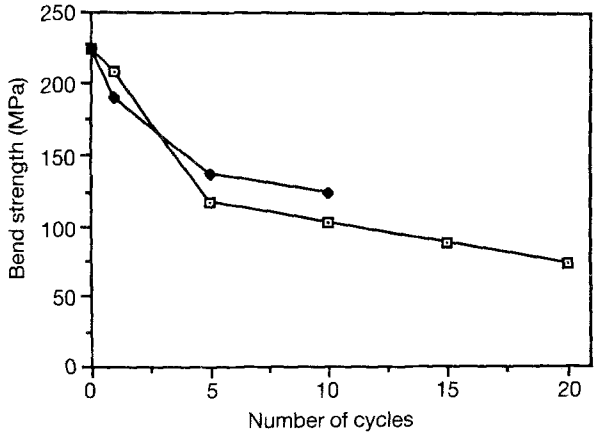

Figure 12 Comparison of the effect of (◆) natural and (⊡) air-blast cooling methods on bend strength after thermal cycling using a 5 min heating time at 1200 °C for SiC/SiC composites.

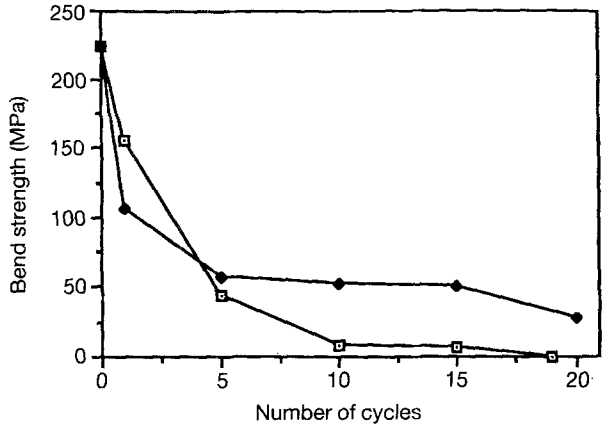

Figure 13 Comparison of the effect of (⊡) water and (◆) air-blast cooling methods on bend strength after thermal cycling using a 15 min heating time at 1200 °C for SiC/SiC composites.

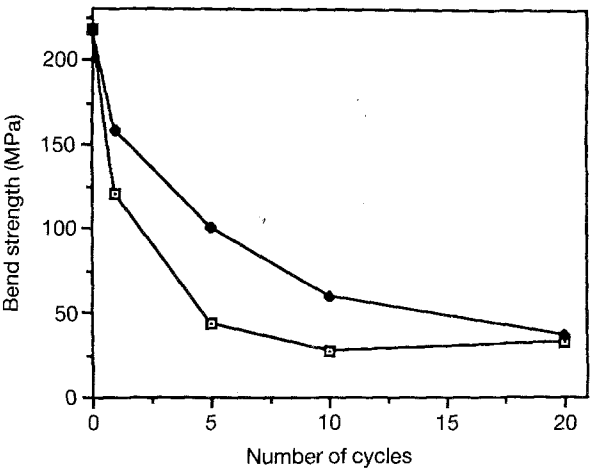

Figure 14 Comparison of the effect of (◆) 5 min and (⊡) 15 min heating times on bend strength after thermal cycling using the air-blast cooling method at 1200 °C for two-dimensional SiC/SiC composites.

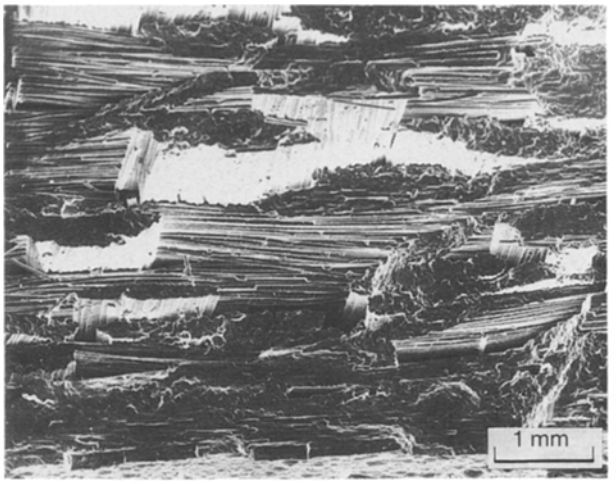

Figure 15 Scanning electron micrograph of a two-dimensional SiC/SiC composite cycled 20 times at 1200 °C with a 15 min heating time, showing no significant fibre pull-out and some delamination.

in strength after 20 cycles. The air blast was the second fastest gradient, followed by the naturally cooled method. Thus, the naturally cooled samples were the strongest after a given number cycles, followed by the air-blasted samples, and followed finally by the samples that were water quenched.

The heating time used during cycling also determined the extent of thermomechanical damage to the composite. Fig. 14 shows the effect of heating time on the two-dimensional composites at 1200 °C. The samples cycled using a 15 min heating time showed a faster reduction in bend strength than those cycled with a 5 min heating time. This can be explained by the ageing effects described previously. The 15 min samples were in the furnace for a longer period of time after a given number of cycles. Thus, their bend strength should be less than the 5 min cycles. After 20 cycles, the ageing effect was no longer apparent. The 1200 °C samples tested with a 15 min heating time demonstrated an increase in the fibre/matrix interfacial bond strength. Fig. 15 shows scanning electron micrographs of the fracture surface for the sample cycled 20 times. There is no fibre pull-out exhibited in the photographs. Also, a substantial debonding between laminae is indicated.

3.4. Impact behaviour

A typical load versus time and absorbed energy curves obtained during the instrumented impact test for the as-fabricated two-dimensionally woven and three-dimensionally braided composites are shown in Fig. 16. The total energy absorbed is 6.2 and 8.7 kJ m^{-2} for the two-dimensionally woven and three-dimensionally braided composites, respectively. It is obvious that the three-dimensionally braided composite exhibits a better impact damage tolerance than that of two-dimensionally woven laminated composite. The impact data, including crack initiation energy, cracking propagation energy and dynamic fracture toughness, of the three-dimensionally braided composite after extended thermal ageing in air are listed in Table 1. The crack initiation energy is the amount of energy absorbed from the start of the impact to the maximum load, and the crack propagation energy is that from the maximum load to the end of the impact event. The results indicate that the energy-absorbing characteristics and dynamic fracture toughness remain almost unchanged after ageing at temperatures

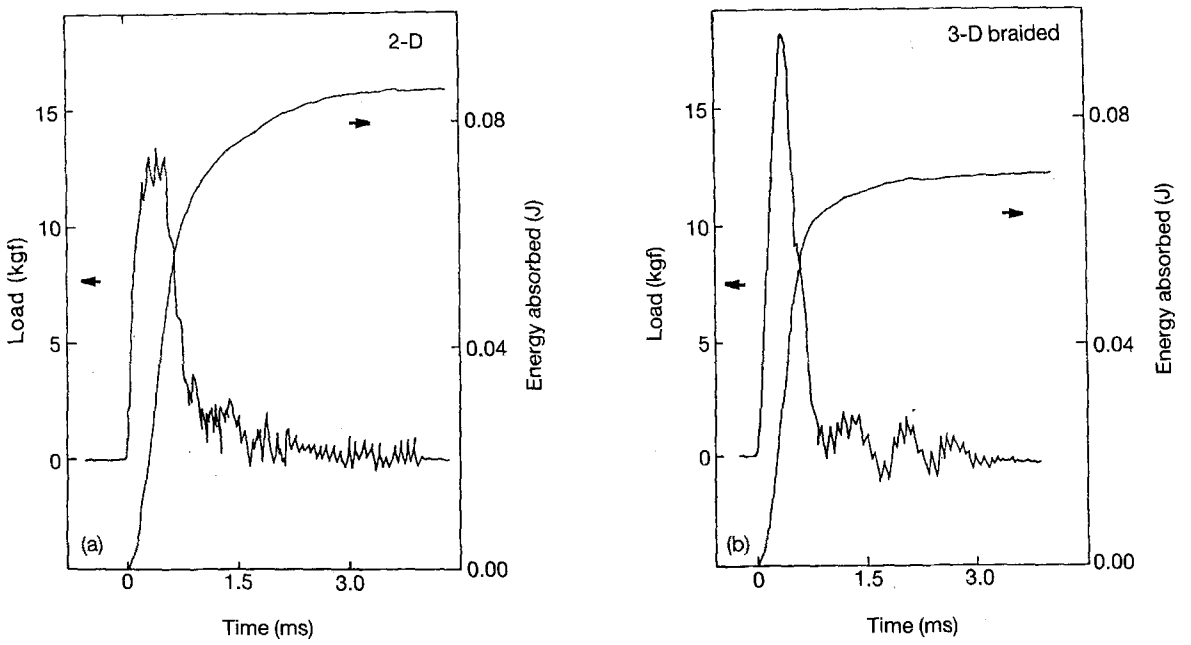

Figure 16 Load versus time and energy versus time curves for (a) two-dimensionally woven composite, and (b) three-dimensionally braided composite.

TABLE I Impact properties of three-dimensionally braided SiC/SiC composite after thermal ageing

Thermal ageing	E_i(kJ m^{-2})	E_p(kJ m^{-2})	E_t(kJ m^{-2})	K_{ID}(MPa m$^{1/2}$)
As-fabricated	4.2 ± 0.1	4.5 ± 0.3	8.7 ± 0.4	7.6 ± 0.4
600 °C/24 h	4.6 ± 0.5	5.5 ± 0.5	10.1 ± 1.0	8.1 ± 0.4
600 °C/100 h	5.0 ± 1.0	4.5 ± 0.5	9.5 ± 0.5	8.0 ± 1.0
1000 °C/24 h	4.0 ± 0.4	5.5 ± 0.5	9.5 ± 0.9	7.0 ± 0.2
1000 °C/100 h	4.8 ± 1.0	5.6 ± 0.6	10.4 ± 1.6	8.1 ± 1.0
1200 °C/100 h	3.2 ± 0.3	4.6 ± 0.4	7.8 ± 0.7	5.3 ± 0.6

below 1000 °C. However, the energy-absorbing capability decreases significantly after ageing at 1200 °C for 100 h. Examination of the fracture surface of the three-dimensionally braided composite after ageing at 1200 °C/100 h indicated that the amount of fibre pull-out decreases significantly, as shown in Fig. 17. Fibre strength degradation appears to be the dominant factor responsible for the degradation of impact damage tolerance.

4. Conclusion

The three-dimensionally braided SiC/SiC composites exhibited substantially better thermo-mechanical durability than the two-dimensionally woven composites after thermal exposure at high temperatures. This may be due to the difference in fibre distribution, matrix porosity and interlaminar shear strength. Firstly, the fibre orientation in the three-dimensionally braided structure was predominantly unidirectional, which may have allowed for better heat flow through the composite. Secondly, the weak bond between laminae in the two-dimensional composite resulting from poor matrix infiltration may also have contributed to its poor bend strength properties after thermal testing. The strength between laminaes was reduced significantly in the two-dimensional composite after thermal shock, which drastically affected the bend strength of the material. Because the three-dimensionally braided composites do not have layers, delamination is not a factor affecting their mechanical properties. Thirdly,

Figure 17 The impact fracture surface of the three-dimensionally braided composite after ageing at (a) 1000 °C for 100 h, × 25, and (b) 1200 °C for 100 h, × 40.

the oxygen penetration through matrix porosity may severely degrade the fibre strength and fibre/matrix interfacial bonding. Therefore, it can be concluded that both the two- and three-dimensional SiC/SiC composites need substantial improvements in their fabrication methods and the development of an oxidation-resistant coating before they could conceivably be used in high-temperature engine environments.

Acknowledgments

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