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Effect of thermochemical treatments on the strength and microstructure of SiC fibres

B. A. BENDER
Naval Research Laboratory, Washington, D.C. 20375-5000, USA
J. S. WALLACE
National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA
D. J. SCHRODT
Catalyst Research Corporation, Baltimore, Maryland 21201, USA

The room-temperature strength of commercially available polymer-derived SiC fibres degrades during the typical high-temperature thermal cycle used in ceramic matrix composite fabrication. Substantial improvements in retained room-temperature strength for two different commercially available fibres were observed after annealing in carbon powder at temperatures up to 1600 °C. Further improvements in strength were observed for both fibres when heat treated in CO atmospheres. X-ray diffraction, TEM, SEM, auger electron spectroscopy, and optical microscopy were used to characterize the microstructure and chemistry of these heat-treated fibres in order to understand better the degradation mechanisms of the fibres as well as their improved strength retention.

1. Introduction

Since the development by Yajima *et al.* [1] of a polymer precursor that could be spun and pyrolysed into a small diameter (15 μm) continuous SiC fibre, interest in ceramic fibre-reinforced ceramic composites (CMC) has soared. Processing of composites with various matrices such as glass-ceramics and ceramic oxides using Nicalon (Nippon Carbon Co., Tokyo, Japan) SiC fibres has been extensively investigated. Results from microstructural characterization and mechanical properties [2, 3] led to the early conclusions that the properties of CMCs greatly depend on the in situ properties of the reinforcing fibre, and that these properties were degrading during the high-temperature fabrication cycle. Although there is no consensus on the actual mechanism for degradation of these polymer-derived SiC fibres, various mechanisms have been proposed: grain growth, crystallization of the fibre, change in Young's modulus, formation of microporosity, formation of surface flaws, and exacerbation of pre-existing flaws [4–18].

Several studies [5–8] have identified SiO and CO as the major reaction products which are evolved when these fibres are exposed to high temperatures. Recognizing that thermodynamic instability can lead to critical changes in the chemistry and microstructure of polymer-derived SiC fibres, one approach to producing CMCs with superior properties is to make a more stable polymer-derived SiC fibre that would interact less with the matrix and atmosphere during processing and high-temperature exposure.

This paper discusses efforts to treat thermochemically two commercially available SiC fibres in order to make them more thermodynamically stable. Fibres were packed in carbon powder and annealed in nitrogen at high temperatures in order to modify the chemistry at the fibre surface. In other experiments, the fibres were heat treated in flowing CO in order to inhibit gas evolution and allow crystallization of the fibre to occur without change in the overall chemical composition. The results of these experiments are discussed in relation to the mechanisms of fibre degradation and compared to similar heat treatments in nitrogen and argon atmospheres.

2. Experimental procedure

Tyranno (UBE Industries Ltd, Tokyo, Japan) and ceramic-grade Nicalon fibres were chosen for this study. The fibres were cut into 75 mm sections and then heat treated in air at 350 °C for 3 h to remove the sizing. The fibres were then ultrasonically dispersed in hexane or a hexane/carbon (99.9% graphite, 2 μm average particle size, Consolidated Astronautics Inc., Hauppagauge, New York) slurry. After air drying, the fibres were placed in covered alumina crucibles and heat treated in a graphite furnace with flowing gas (CO, nitrogen or argon). The standard heating rate was 10 °C min^{-1} with a typical hold time of 3 h followed by furnace cooling. The fibres were then characterized microstructurally and mechanically. The tensile strength was measured using a testing apparatus which was modelled after ASTM Standard D3379-75 [19] using a 12.5 mm gauge length and a typical loading time of 10 sec. A minimum of 15 fibres was tested to determine the strength with a typical

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standard deviation ranging from 20% to 30%. The chemistry and microstructure of the fibres were characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), transmission electron microscopy (TEM), analytical electron microscopy (AEM), scanning electron microscopy (SEM), and optical microscopy. Cross-sections of fibres were prepared for TEM analysis by ion thinning fibres that had been embedded in an epoxy.

3. Results and discussion

3.1. Effect of carbon packing

The results of carbon packing on the thermochemical stability of Tyranno fibres have been discussed in detail elsewhere [20] and will only be summarized here. The results of that study (Fig. 1) showed that Tyranno fibres packed in carbon powder and heat treated in a nitrogen atmosphere retained more of their strength than fibres similarly heat treated without a carbon packing. The largest enhancement in strength occurred at 1600 °C where the carbon-packed fibres retained 45% of their as-received strength, compared to a 10% strength retention for fibres heat treated in nitrogen without carbon-packing powder. This behaviour was attributed to a SiC coating which formed on the fibre from the reaction of the carbon-packing powder and SiO which was evolving from the fibre.

Similar trends were also observed for Nicalon fibres packed in carbon powder during heat treatment. As can be observed in Fig. 2 Nicalon fibres heat treated in nitrogen dropped in strength at 900 °C to 2 GPa and remained more or less at that level up to heat-treatment temperatures of 1400 °C. On the other hand, Nicalon fibres packed in carbon powder and heat treated in nitrogen consistently retained a strength level of 2.5 GPa up to heat-treatment temperatures as high as 1300 °C.

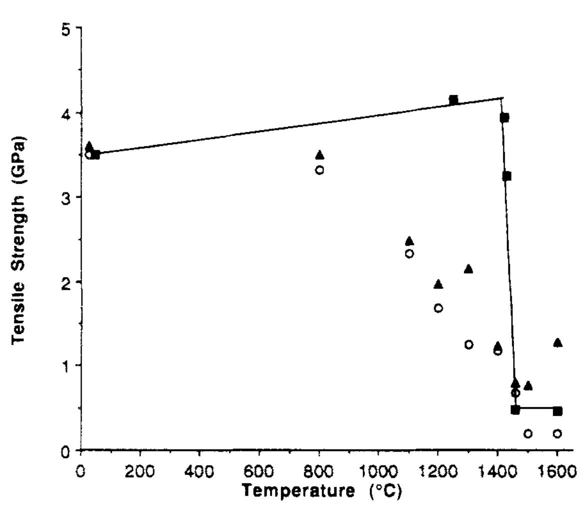


Figure 1 The effect of various thermochemical treatments on the retained room-temperature strength of Tyranno SiC fibres. The data for the CO heat treatments have been delineated to make more mainfest the improved retained room-temperature strength of these heat-treated fibres. (○) Nitrogen, (▲) nitrogen plus carbon, (■) CO only.

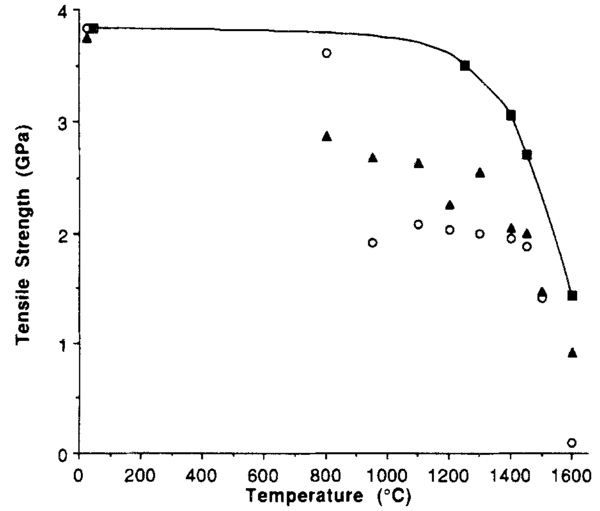


Figure 2 The effect of various thermochemical treatments on the retained room-temperature strength of Nicalon SiC fibres. The data for the CO heat treatments have been delineated to make more manifest the improved retained room-temperature strength of these heat-treated fibres. (○) Nitrogen, (▲) nitrogen plus carbon, (■) CO only.

Above 1300 °C the heat-treated Nicalon fibres packed in carbon remained substantially stronger than those fibres heat-treated just in nitrogen. However, SEM, TEM, and XRD results indicate that there are no major differences between the two. TEM examination indicates that the crystallite size has not significantly changed compared to the as-received fibre average crystallite size of 2 nm. The major reason for loss of strength appears to be the formation of relatively large 0.5 to 1.0 μm diameter pores on the surface of the fibres (Fig. 3) which can act as failure sites.

After heat treating at 1600 °C, Nicalon fibres treated in nitrogen or argon retained less than 5% of their original strength, as compared to fibres packed in carbon powder and heat treated in nitrogen which retained close to 30% of their original strength. The microstructures of the 1600 °C heat-treated fibres are quite different. The argon heat-treated fibres not packed in carbon (Fig. 4a) developed a fine porous, pin-holed microstructure. Individual grains about 50 nm in size and relatively large surface pores in the range of 0.5 to 1.0 μm diameter were also found. For those fibres heat-treated in nitrogen (Fig. 4b and c), silicon nitride whiskers formed on the surface of the fibres. These whiskers were irregular in shape and varied in diameter from 0.1 to 5 μm with varying lengths up to 30 μm. TEM results indicated that grain growth had occurred resulting in a bimodal distribution of grain size of around 3 and 10 nm.

In the case of Nicalon fibres packed in carbon the microstructure of the fibre was quite different. The fibre surface was dense in appearance. SEM observations indicated that a possible surface reaction layer, which was approximately 30 nm thick, had formed. Scanning transmission electron microscopy on relatively thicker thin sections indicated that there was a layer which AEM indicated to be α-SiC. The formation of this layer from the reaction of evolving SiO with the carbon-packing powder prevented further

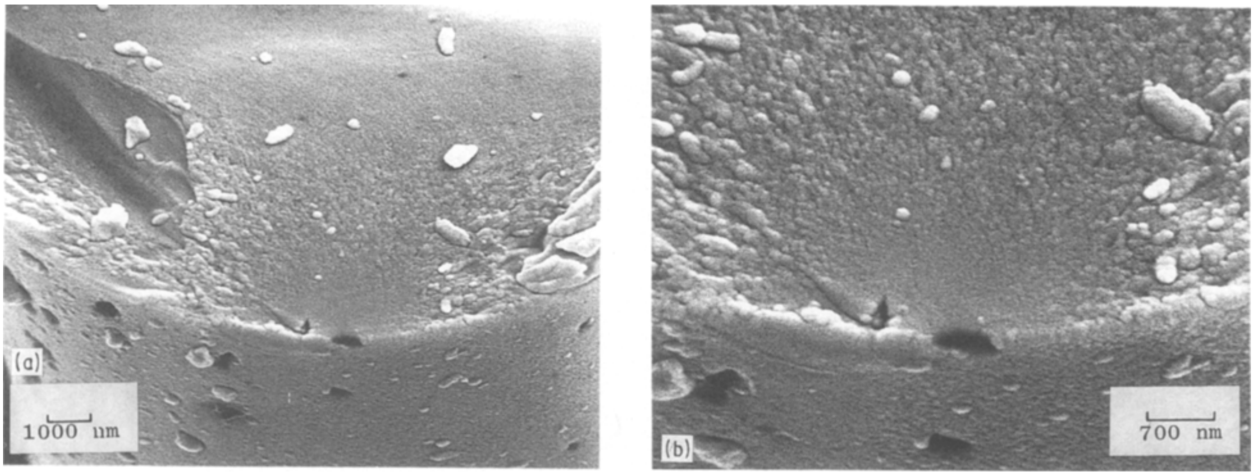


Figure 3 SEM fractographs of Nicalon heat treated at 1300 °C in nitrogen.

massive gas evolution, as evinced from the porous surfaces of the fibres that were not packed in carbon. The fibres therefore underwent fewer microstructural and chemical changes and remained stronger. It is interesting to note that large cavities (Fig. 5c) were occasionally seen in the carbon-packed fibres. These could result from the SiO and CO gases (which are evolving internally from the fibre [5, 6] being trapped at the near surface of the fibre by the dense reaction layer creating a build up in pressure that finally blows a large cavity in the fibre during the heat-treament cycle.

3.2. Effect of CO heat treatments

CO heat treatments had a dramatic effect on the strength and microstructural retention of Nicalon fibres. Fig. 2 indicates that the CO heat-treated fibres were at least 30% stronger than those annealed in nitrogen at temperatures greater than 1000 °C, and that at 1600 °C the fibres retained an average strength of close to 1.4 GPa. SEM observations indicated that the overall microstructure of the heat-treated fibres changed very little from the as-received microstructure. The only changes noted with increasing heat-treatment temperature were that the fracture surfaces become less rough and the fracture mirrors were larger, as is expected for weaker fibres. The fact that the mirror size–strength–fracture toughness relation [21] held for all the strength–mirror size data, including the 1600 °C results, implies that the overall nature of the microstructure had not changed. The calculated value for the fracture toughness of the fibres was approximately 2 MPa $m^{1/2}$ which is in close agreement to the room-temperature value as determined by Sawyer *et al.* [22]. TEM examination of Nicalon fibres (Fig. 6) heat treated at 1600 °C in CO showed that the

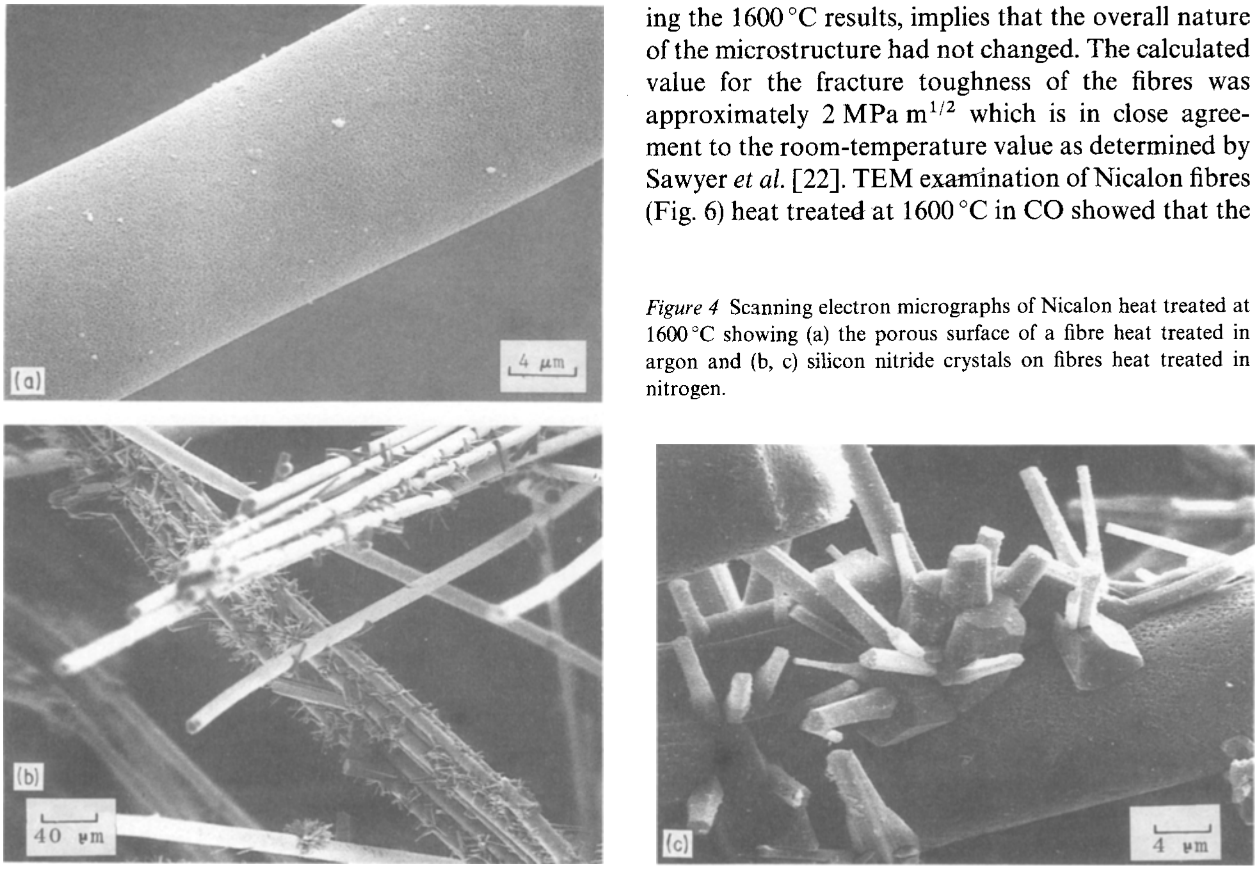
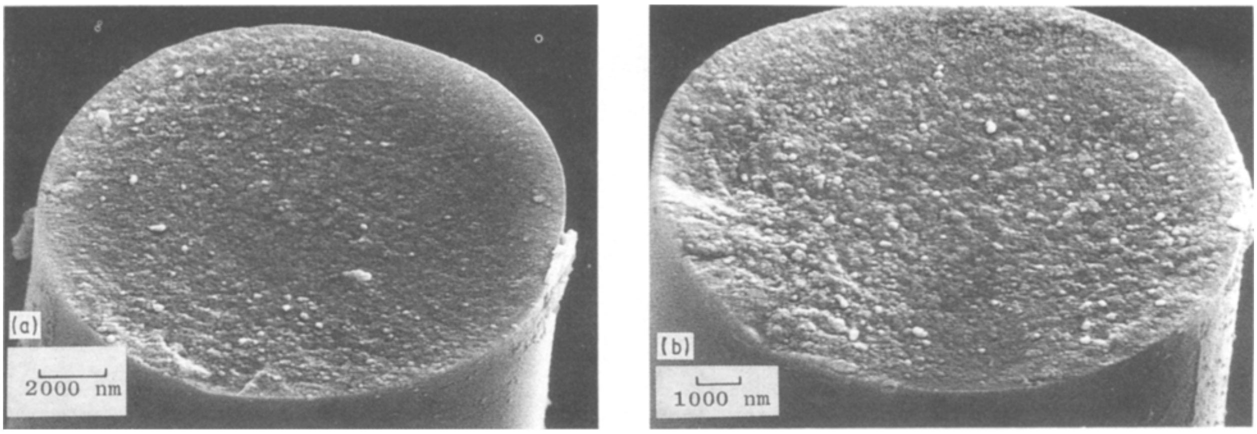


Figure 4 Scanning electron micrographs of Nicalon heat treated at 1600 °C showing (a) the porous surface of a fibre heat treated in argon and (b, c) silicon nitride crystals on fibres heat treated in nitrogen.



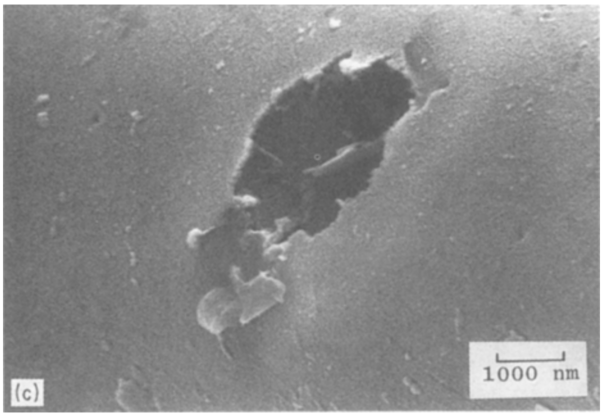


Figure 5 Scanning electron micrographs of Nicalon fibres packed in carbon and heat treated at 1600 °C in nitrogen.

grain size had increased from 2 nm to 5 to 10 nm in size. The development of fine channels of porosity (Fig. 6a) has just started and the overall microstructure appears very similar to Nicalon fibres packed in carbon powder and heat treated in nitrogen at 1300 °C. This indicates that the presence of excess CO allowed the fibre to maintain its starting chemistry and original microstructure. This occurred because the CO partial pressure in the furnace was greater than the equilibrium CO partial pressure for the reaction of carbon and oxygen in the fibres, thus CO formation is suppressed. As a result, microporosity channels were not formed and the fibre maintained its integrity. This is further supported by other experiments in which CO treatments were performed with an equal flow of nitrogen and CO gas; the beneficial effects of using CO were cut drastically.

Heat treating Tyranno fibres in CO also had a dramatic effect on the retained strength and microstructure of these Si–Ti–C–O fibres. As seen in Fig. 1, the actual retained strength of Tyranno fibres heat treated for 3 h in flowing CO at 1250 °C increased by 20%. Bright-field TEM (Fig. 7) showed that the microstructure of the 1250 °C heat-treated fibre

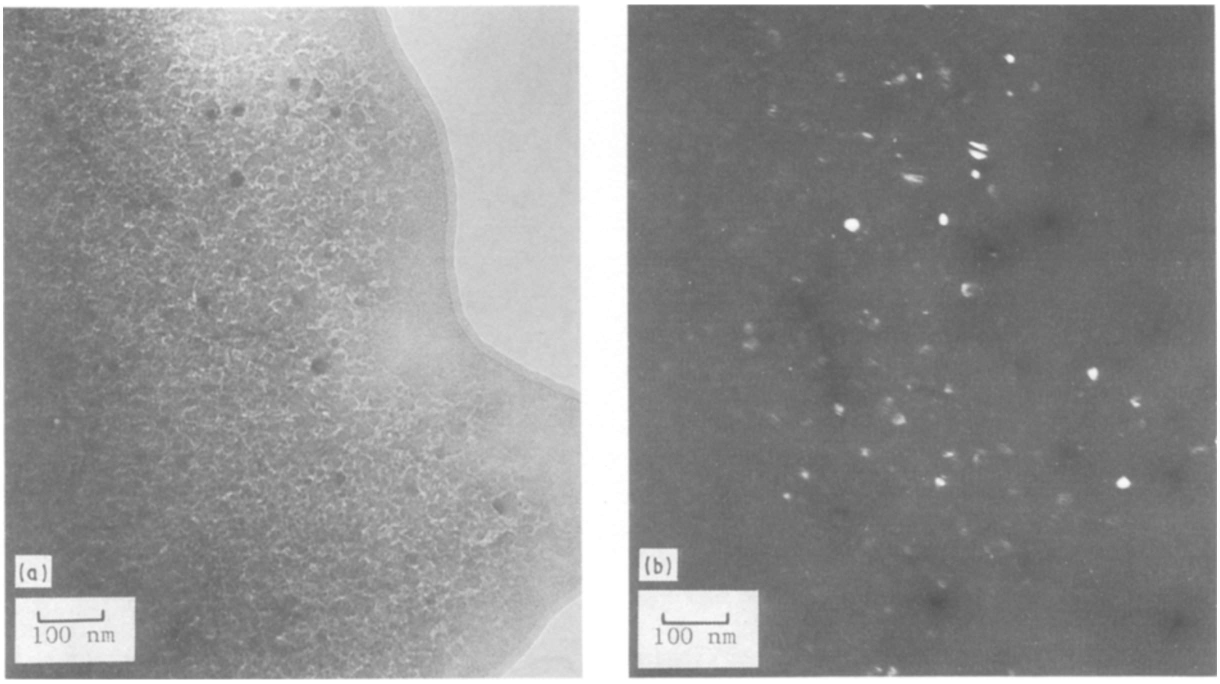


Figure 6 (a) Bright-field and (b) dark-field transmission electron micrographs of Nicalon heat treated at 1600 °C in CO. Note the irregular-shaped whitish markings which are channels of microporosity.

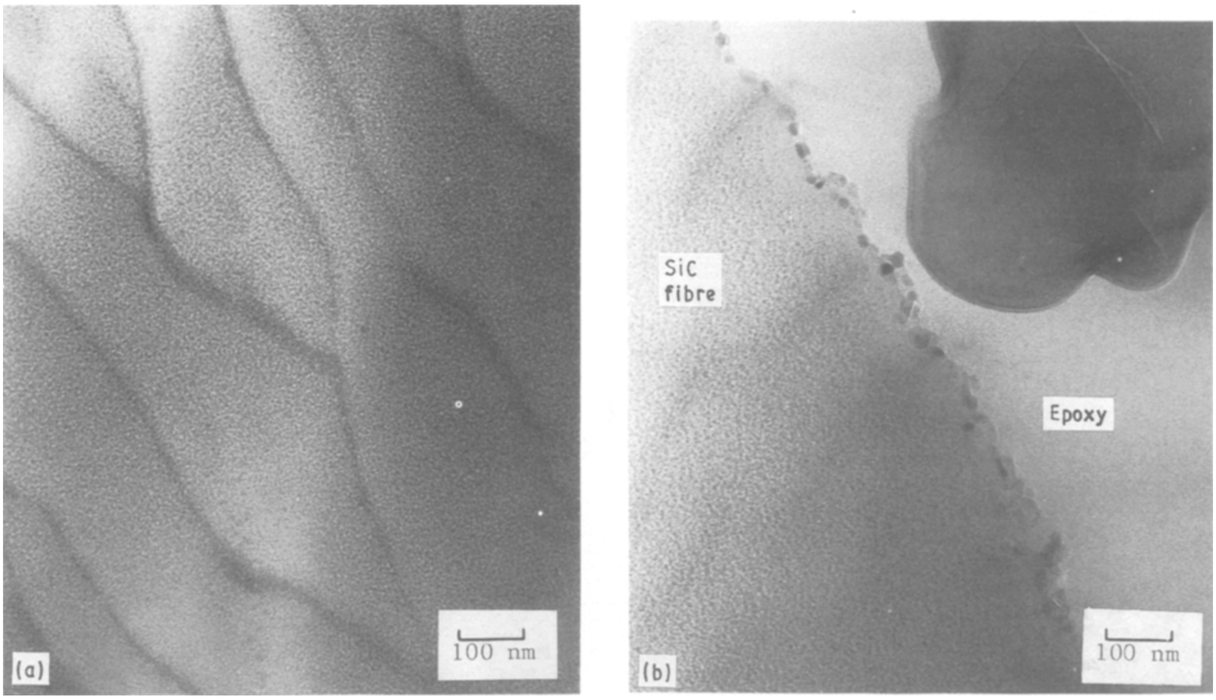


Figure 7 Bright-field transmission electron micrographs of Tyranno heat treated at 1250 °C in CO. (b) The surface of the fibre where a thin layer of small TiC crystallites has formed.

looked very similar to as-received Tyranno. However, dark-field TEM and electron diffraction revealed that the fibre was just starting to transform from its amorphous state to a microcrystalline state with the growth of 1 nm microcrystallites of β-SiC and TiC. Also, at the very surface of the fibre (Fig. 7b) a 10 nm thick non-contiguous one-grain thick layer of TiC had formed which appeared to cause a slight undulation of the periphery of the fibre. AES confirmed the presence of the TiC layer at the surface of these fibres and also indicated that the surface of the fibre was oxygen rich. This has also been found by other researchers who have observed a similar effect when desizing Nicalon in an oxidizing atmosphere [23]. This lends further support to the TEM observations that by heat treating in CO, the chemistry and the microstructure of the fibre does not drastically change and the fibre retains its good strength. The fact that crystallite growth also occurs without loss of strength indicates that the amorphous to crystalline transformation is innocuous, contrary to previous reports [4, 10, 14]. The only finding that explains the strength increase is the SEM observation that the surfaces of the CO heat-treated fibres are smoother than the surfaces of the as-received Tyranno fibres. This would result in fewer and smaller surface flaws and thus a higher strength. It appears that heat treating Tyranno fibres in CO at 1250 °C inhibits any reactions which lead to gas evolution and the formation of microporosity and/or the exacerbation of any pre-existing flaws. As a result, the fibre retains its starting chemistry with very little change in microstructure.

Little change is also seen in the strength of Tyranno fibres heat treated in CO at 1400 or 1430 °C (Fig. 1). The strength data are very interesting at these temperatures because at 1400 °C the CO-treated fibre is as strong as as-received Tyranno and that even at 1430 °C the CO heat-treated fibre has lost only 10% of its strength. The fact that the fibres follow the mirror size–strength–fracture toughness relation quite well (the strength–mirror size data yield a fracture toughness value of around 2 MPa $m^{1/2}$ which is in good agreement with Sawyers et al. [22] data for various polymer-derived SiC based fibres) up to this temperature indicates that the overall nature of the fibres has not changed. SEM examination of the fracture and

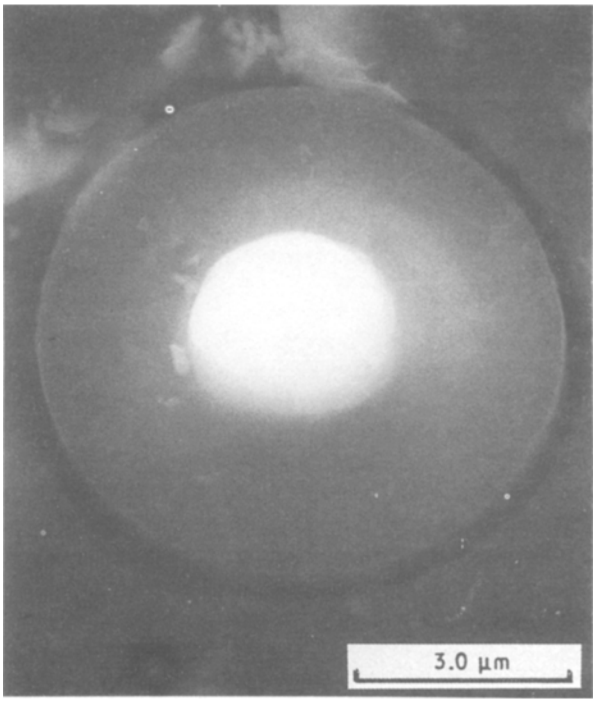


Figure 8 Scanning electron micrograph of a polished cross-section of a Tyranno SiC fibre heat treated at 1460 °C for 3 h in CO.

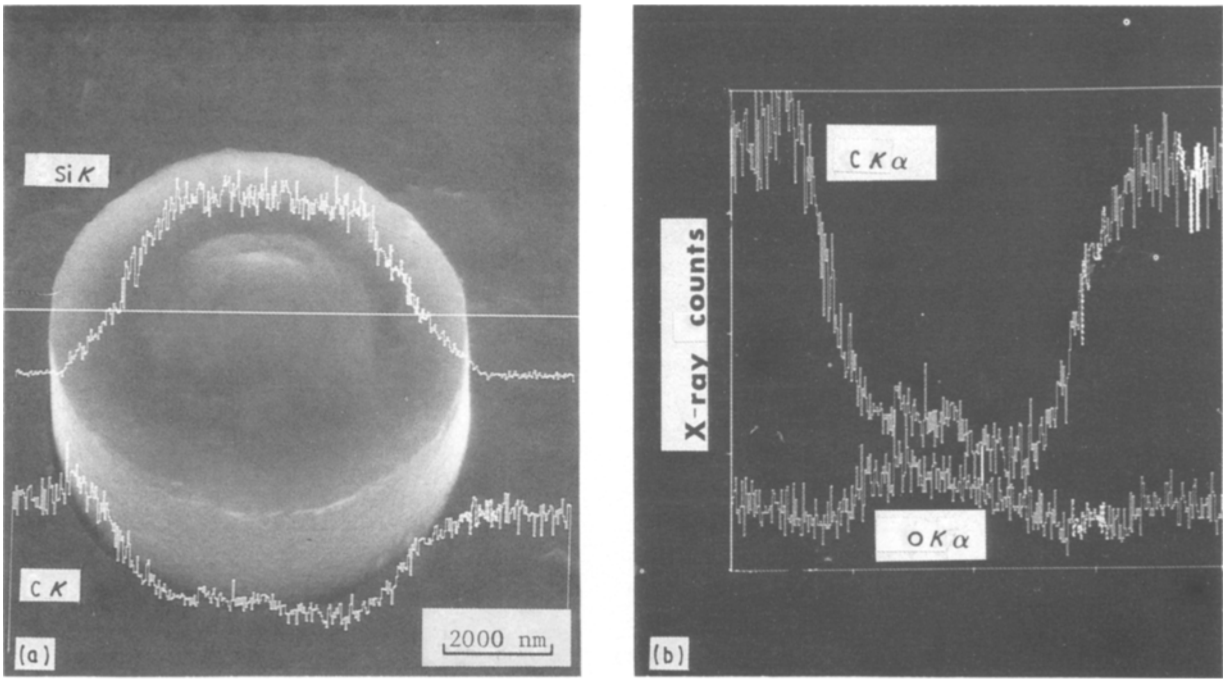


Figure 9 X-ray line profiles of a cross-section of a Tyranno SiC fibre heat treated at 1460 °C in CO showing (a) the enrichment of carbon and the depletion of silicon in the outer layer as well as the depletion of oxygen (b) in the outer layer.

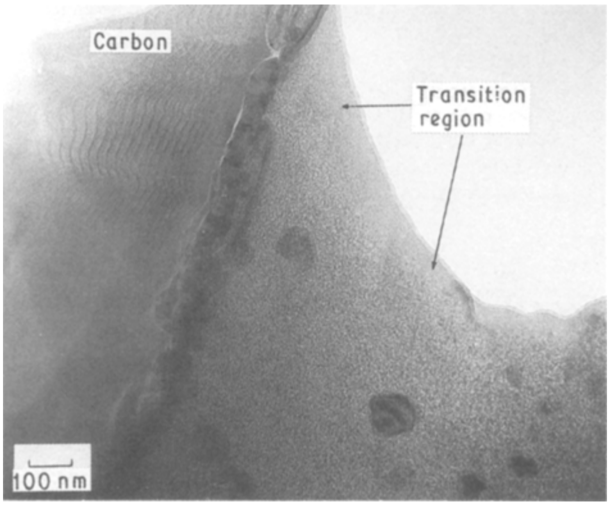


Figure 10 Bright-field transmission electron micrograph of Tyranno heat treated at 1460 °C in CO showing a portion of the carbon-rich outer layer and the transition region to the unchanged inner core of the fibre.

fibre surfaces shows no difference in the microstructure of the CO heat-treated fibres at 1430 °C with the exception of the development of small voids on the surfaces of the fibres which could act as flaws and lead to a weaker fibre.

However, Tyranno fibres heat-treated at 1460 °C in CO undergo drastic changes in their microstructure and lose 90% of their strength. Fig. 8 shows that the microstructure consists of an inner core surrounded by a softer outer layer which polishes away much faster. X-ray line profiles (Fig. 9) show that the outer layer is basically carbon with very little silicon or oxygen present and that the inner core consists of a mixture of silicon, carbon and oxygen. EDS analysis of the centre core indicates that the Si:C:O ratio is very similar to that as measured in as-received Tyranno fibres. TEM examination confirms these results. As seen in Fig. 10 the outer layer of carbon is amorphous with a thin layer of TiC at the interface of the carbon layer and transition region. AES of the outer core of the Tyranno fibre confirmed that the outer layer was about 90% carbon with increasing concentrations of silicon and titanium detected as the beam sputtered towards the centre of the fibre. The transition region consists of relatively large TiC crystallites in a Si–C–O matrix where AEM indicates that the silicon concentration is increasing as the inner core is approached. TEM analysis of the inner core indicated that its microstructure was similar in nature to Tyranno fibres heat treated in nitrogen at 1300 °C. The observation that the microstructure of the inner core is similar to that of fibres heat treated at lower temperatures is confirmed by strength measurements. Assuming that the load in a degraded fibre is carried only by the remaining inner core (typically 3 μm diameter), the calculated strength of this core is very similar to fibres heat-treated below 1430 °C.

The very precipitous drop in strength over a small range of temperatures points to a shift in a reaction equilibrium. Calculations by Luthra [7] have shown that the CO partial pressure of Si–C–O compositions at these temperatures approaches 100 kPa (1 atm). As a result, the presence of the CO atmosphere no longer inhibits CO from being evolved from the fibre. Channels of microporosity form and SiO and CO evolve rapidly from the fibre leaving behind a soft amorphous outer layer of carbon and a degraded fibre whose chemistry and microstructure have drastically changed. Given sufficient time the process would carry itself to completion and a carbon skeleton which has virtually zero strength would remain.

4. Conclusions

Nicalon fibres packed in carbon during heat treatment in flowing nitrogen had higher room-temperature strengths for all annealing temperatures up to 1600 °C compared to fibres not packed in carbon. At intermediate temperatures (1200 to 1500 °C) it is unclear why the carbon-packed heat-treated fibres are stronger, as there are no major detectable microstructural differences between the two heat-treated fibres. At 1600 °C the carbon-packed fibres form a thin dense reaction layer which somewhat inhibits the evolution of SiO and CO from the fibre, limiting the amount of microporosity that is formed, leading to a fibre that retains 30% of its starting strength.

Heat treating Nicalon and Tyranno fibres in flowing CO led to dramatic improvements in the thermochemical stability of these fibres. In the case of Nicalon fibres heat-treated in CO, they are at least 20% stronger than fibres heat-treated in nitrogen, with a retained strength of 1.4 GPa for these fibres when annealed at 1600 °C. From the microstructural analysis it appears that the presence of CO inhibits evolution of CO and SiO from the fibres resulting in a fibre which has improved structural integrity.

A similar effect was found in heat-treated Tyranno fibres. Fibres annealed up to 1400 °C for 3 h in flowing CO lost none of their strength. In fact, fibres heat-treated at 1250 °C were 20% stronger as a result of reducing the number of surface flaws during the CO heat treatment. At 1460 °C or higher, the presence of CO cannot stop the evolution of CO from the fibre. As a result, the fibre degrades and a weak outer layer of carbon forms around an inner core of SiC and the fibre looses 90% of its strength.

These results show that evolution of CO must be inhibited from polymer-derived SiC-based fibres if they are going to maintain their thermochemical stability. As shown by the heat treatments in CO and the carbon packing of the fibres in nitrogen, these fibres can maintain strengths of up to 1.25 GPa or more after annealing 3 h at 1600 °C. This high-temperature strength retention indicates that the fibres could be processed in ceramic oxides composites at much higher temperatures than the 1250 or 1300 °C hot-pressing temperatures that are currently being used. This can lead to the use of more refractory ceramic matrices with the end result leading to more heat-resistant CMCs.

Acknowledgements

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