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Grain growth and strength degradation of SiC monofilaments at high temperatures

A. ELKIND, M. W. BARSOUM
Department of Materials Engineering, Drexel University, Philadelphia, PA 19104, USA

The microstructural stability of SCS-6 SiC monofilaments was determined by measuring the average grain size, tensile strength and critical length of the fibres as a function of various annealings in vacuum ($\approx$0.1 Pa) at different temperatures (1400–1600 °C). The average grain size, calculated from X-ray diffraction line broadening, increased from 23 nm for the as-received fibres to 46 nm for fibres annealed for 2 h at 1600 °C. The corresponding tensile strength measured at room temperature dropped from 3.6 GPa for the as-received fibres to $\approx$2 GPa for the treated fibres. Simultaneously, the average critical lengths, measured using the glass-slide technique decreased from 0.37 mm for the as-received fibres to an average of 0.23 mm for the heat-treated fibres. The degradation of the mechanical properties was attributed to a combination of coarsening of the β-SiC grains as well as interactions with the annealing environment, namely the vacuum hot-press chamber.

1. Introduction

Silicon carbide SCS-6 monofilaments (Textron Speciality Materials, Lowell, MA) are one of the more promising fibres for reinforcing ceramic matrices that are commercially available to date. These fibres, manufactured by chemical vapour deposition of SiC on a carbon core, have strength in the range of 4 GPa, stiffnesses of the order of 400 GPa and are fairly oxidation resistant.

The microstructure of the filament bulk consists of heavily faulted, columnar nano-subgrains of β-SiC extending radially from a carbon core [1–5]. The lengths of β-SiC grains in as-received SCS-6 fibres were measured to be in the range 20–100 nm with an aspect ratio of about 10 [1, 2]. More recent work has shown that the C–Si ratio decreases in a stepwise fashion from $\approx$3:2 to $\approx$1:1 in going from the innermost to the outermost layers [3–5].

The microstructural and strength stability of the SiC fibres was studied by Bhatt and Hull [6], who found that recrystallization and growth of near-stoichiometric SiC grains is the dominant mechanism for the strength degradation of SCS-6 fibres beyond 1400 °C. They observed a distinct coarsening layer in the periphery of the outer zone of the fibres after heat treatment. Exaggerated grains from this layer grew towards the core. A strong correlation between the loss of fibre tensile strength and the thickness of the coarsening zone was also established [6]. McHenery and Tressler [7] reported a strength degradation in the 900–1000 °C range and suggested that recrystallization and/or grain growth of SiC may be responsible. However, their X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis failed to identify a specific mechanism. Ning *et al.* [5] also showed that annealing the fibres for 1 h at 2000 °C resulted in a coarsening of the SiC grains in the outermost layer to an average value of 3000 nm. The annealing resulted in a decrease in the room-temperature tensile strength of the fibres from around 4 GPa to $\approx$ 700 MPa [5]. Further evidence in the literature that microstructural changes take place in the SiC fibre in the temperature range 900–1400 °C comes from creep measurements data; DiCarlo [8] concluded that thermally induced microstructural changes that occurred between 1200° and 1400 °C, reduce the creep rate.

The coefficient of thermal expansion (CTE) of SCS-6 SiC monofilaments is also altered with extended heat treatments – the CTE drops from 6.5×10^{-6} °C^{-1} for the as-received fibres to 5.7×10^{-6} °C after heat treatment for 2 h in vacuum at 1500 °C [9]. The XRD data obtained by Elkind *et al.* [9] also showed a clear increase in the intensity of SiC peaks concomitant with a decrease in the width at half maximum of the peaks upon heat treatment, strongly indicating that grain growth had occurred.

The anticipated use of these fibres is as reinforcements for ceramic matrix composites at elevated temperatures. Curtin has shown that the characteristic length of fibre fragments, δ_c, was a key indicator of the uniaxial tensile composite performance [10]. Thus, in addition to thermal stability, another important parameter is δ_c, given by [10]

$$\delta_c = \left[\frac{\sigma_0 \rho (2\lambda)^{1/m}}{\tau}\right]^{\frac{m}{m+1}} \tag{1}$$

where 2λ, ρ, σ_0 and m, are respectively, the fibre gauge length, diameter, average tensile strength and the

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TABLE I Effects of various heat treatments on strength, average grain size, Weibull moduli and average critical lengths of SCS-6 fibres.

T(°C)	Time (h)	σ_0 (GPa)	d^a (nm)	Weibull modulus	Av. critical length (mm)	Comments
As-received	–	3.6 ± 0.4	23	2.8	0.37	
1400	2	2.4 ± 0.3	36	2.0	0.27	Vacuum hot press
1400	2	2.8 ± 0.3	35			(Annealed in carbon-bed in nitrogen)
1400	10	1.0 ± 0.1	44			Vacuum hot press
1500	2	2.0 ± 0.2	44	3.3	0.24	Vacuum hot press
1600	2	2.1 ± 0.2	46	2.0	0.23	Not plotted in Fig. 4 for clarity
1600	4	1.5 ± 0.2	^{b}	–	–	Not plotted in Fig. 4 for clarity
2000	1	0.7	3000	–	–	[5]

[a] Calculated from X-ray line broadening.

[b] Not measurable because width at half maximum was comparable to instrument broadening.

Weibull modulus of the fibres. τ is the average frictional sliding resistance between fibre and matrix.

In polymer matrix composites, δ_c is usually measured by embedding the fibres in a large strain-to-failure matrix and loading the latter to the point that the fibres fragment [11, 12]. While this technique is fairly straightforward, it has not been applied to ceramic fibres because, for the most part, their strains-to-failure are higher than those of most ceramic matrices.

The common procedure for measuring the fibres critical length in ceramics has been to measure the distribution of pull-out lengths of fractured fibres in a failed composite [13]. This technique, however, only measures the pull-out or critical lengths of the fibres *after* processing of the composites and has only been used, to date, to measure the critical lengths of Nicalon SiC fibres (average diameter 15–20 μm, Nippon Carbon Co., Japan) containing composites. As far as we are aware, the only data for the critical length of SCS-6 monofilaments measured to date are the ones reported previously [14]. In that paper, we demonstrated the general validity of Equation 1 using a limited set of data.

The objective of this work was to investigate further the mechanisms of strength degradation in SCS-6 SiC fibres by simultaneously measuring the average grain size, fibre critical length and fibre strength as functions of various heat treatments.

2. Experimental procedure

The SiC fibres were annealed under vacuum ($\approx$ 0.1 Pa) in a hot press (Series 3600, Vacuum Industries, Inc., Somerville, MA) for the various times and temperatures summarized in Table I. The hot press was used for the heat treatments for two reasons. The first is that it simulated the environment under which most fibre-reinforced ceramic matrix composites are fabricated. The second is that the hot-press environment with the graphitic heating elements should be, in principle, but as reported here are not quite, a sufficiently reducing atmosphere to prevent oxidation of the fibres.

The as-received and heat-treated SiC fibres were powdered and mixed with silicon powder as an internal standard [15]. XRD measurements were conducted using Cu K_α radiation with a nickel filter and a graphite monochromator at a scanning rate of $0.005° \mathrm{s}^{-1}$, time constant 2 s and a receiving slit of 0.6°. The average grain size was calculated from the width at half maximum of the (1 1 1) reflection peak of the β-SiC using the Scherrer formula [16]. Scanning electron microscopy (SEM), examination of the fibre cross-section was unsuccessful in discerning any microstructural differences between the as-received and heat-treated fibres.

The room-temperature tensile strength of the fibres, both as-received and heat treated, were measured by placing the fibre in a paper mounting frame and epoxied in place leaving 50 mm as gauge length. Fibre specimens were pulled to failure using an Instron (Instron, Canton MA) at a constant crosshead speed 0.05 mm min^{-1}. An average of at least three samples was tested for each heat-treatment condition.

The critical lengths of the fibres were measured using the technique described elsewhere [14]. Briefly, short strands of the monofilaments were cut and their lengths were carefully measured using a machinist's microscope (Gaertner Scientific Corp., Chicago, IL) with a resolution estimated to be ± 2 μm. Single fibre strands (1.5–2.5 cm long) were placed between two borosilicate glass slides (2–3 cm long, 0.5–1.5 cm wide and 0.15 cm thick), heated in air at 10 °C min^{-1} to 700 °C under a dead load corresponding to a stress level of 0.5 MPa. The samples were heated to the processing temperature, held at temperature for 30 min and then furnace cooled under the dead load (cooling rate was approximately 5 °C min^{-1}). Because the glass plates were not constrained from flowing, it was concluded elsewhere [14] that glass flow normal to the applied load entrained the embedded fibres and resulted in a significant enhancement in the residual stresses. At higher loads (i.e greater than 0.2 MPa), the residual stresses generated during cooling were high

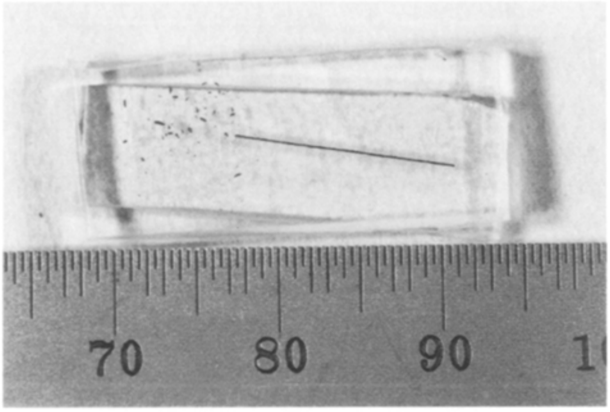

Figure 1 Picture of fragmented fibre ends embedded between two glass slides after cooling from 700 °C under an applied stress of 0.5 MPa.

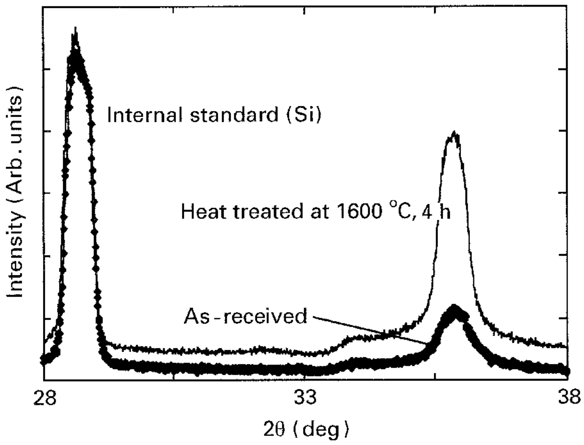

Figure 2 Effect of heat treatment (1600 °C for 4 h) on intensity and shape of (1 1 1) β-SiC peak compared to as-received fibres. Heat treatment resulted in a clear increase in the intensity of the peaks and their sharpening. The peaks on the left are those of the silicon internal standard. The curves are shifted vertically for clarity.

enough to cause the fibre edges to fragment as shown in Fig. 1. The lengths of these fragments were measured using a machinist's microscope and analysed using Weibull statistics.

3. Results and discussion

Fig. 2 compares the X-ray diffraction pattern of the as-received fibres to those annealed at 1600 °C for 4 h (the peaks on the left are the internal standard silicon peaks; the two curves are shifted vertically for clarity). From the figure it is obvious that the heat treatment resulted in a dramatic increase in intensity of the SiC peaks as well as a sharpening of the diffraction peaks. The other intermediate heat treatments all fall in between these two extremes and were omitted for the sake of clarity.

X-ray peak sharpening can be attributed to a number of factors: (i) an increase in the grain size of the structure, (ii) the annealing of lattice strains, (iii) annihilation of stacking faults. Given that the fibres were fabricated at ≈ 1200 °C and were treated here at temperatures of at least 1400 °C, we believe that peak sharpening is mostly related to grain coarsening, rather than the annealing of lattice strains. It is worth noting that no shift in the peaks was observed as a result of heat treatments, which is further evidence that the relaxation of the lattice strains was not responsible for the changes observed.

It is well established that stacking fault annihilation in SiC results in peak sharpening [17]. For example, it has been shown that the presence of peaks at 2θ of 33.6° and 41.4° in SiC usually implies the presence of stacking faults and that their annihilation resulted in a decrease in the intensity of the 33.6° peak and a concomitant increase in the intensity, and the sharpening of the 41.4° peak [17]. Careful examination of our X-ray data shows that upon annealing, the 33.6° peak becomes *more* intense, while the 41.4° peak does not appear at all, which leads to the conclusion that the increase in intensity of the (1 1 1) SiC and its sharpening observed here were not due to changes in the stacking fault density.

Thus we conclude that the increase in intensity of the peaks is clear and unambiguous evidence for an increase in the *crystallinity* of the fibres. This increase in crystallinity is believed to result from the coarsening of the structure and the elimination of the amorphous grain-boundary "phase". These results are similar to the ones obtained elsewhere [9], and the explanation proposed earlier is still valid: in a material where the grain size is of the same order of magnitude as the grain-boundary width, the grain boundary constitutes a significant volume fraction of that material.

The effects of the various annealings on the average grain size, d_{av}, and the tensile strength, σ_0, of the fibres are summarized in Table I. Also included in Table I is the datum point of Ning *et al.* [5]. The results clearly indicate that, as the average grain size increases, the tensile strength, σ_0, decreases in agreement with the results obtained by Bhatt and Hull [6], who showed that the strength degradation was related to the coarsening of the SiC grains in the outer zone of the fibre. Further evidence that the strength is dominated by the grain size is obtained when the tensile strength is plotted versus $d_{av}^{-1/2}$ as shown in Fig. 3. Least squares fit of the data yields a correlation coefficient of 0.9, and whereas this result does not unequivocally prove that the degradation in strength is related to the coarsening, it is consistent with it. An increase in grain size would also explain the enhancement in creep properties [8] as noted by others.

Although the fibres were annealed in a vacuum of 10^{-4} torr (1 torr = 133.322 Pa), some oxygen in the chamber could not be avoided and it is possible that active oxidation of the fibres, which could lead to degradation in strength, did occur. To deconvolute the effects of oxidation from those of grain growth, we performed the following experiments: about 15 fibres were carefully inserted in a 1.3 mm diameter alumina tube which, in turn, was packed with graphite powder. The whole assembly was then placed in a tube furnace and heated in nitrogen for 2 h at 1400 °C. At 2.8 GPa, the strength of these fibres was found to fall between the as-received and those treated at 1400 °C for 2 h in the vacuum hot press, but their average grain size was

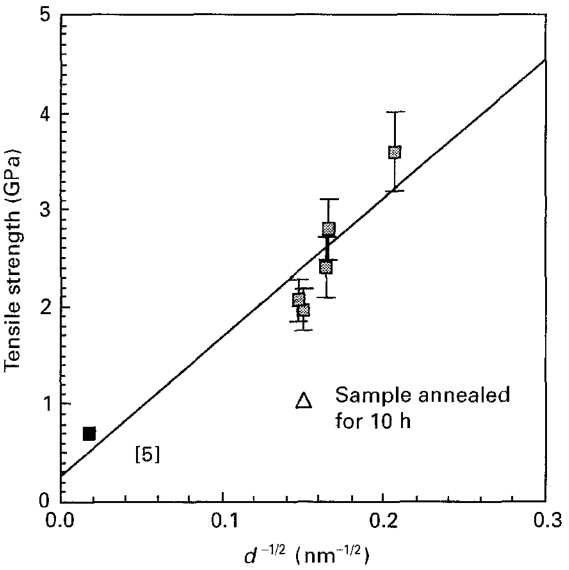

Figure 3 Strength–grain size behaviour for SCS-6 SiC fibres subjected to various heat treatments.

almost identical to the ones treated in the vacuum hot press (see Table I). Because it is a fairly good assumption that the fibres packed in graphite did not oxidize, then one must attribute the drop in strength from 3.7 GPa to 2.8 GPa to grain growth. The further drop from 2.8 GPA to 2.4 GPa, which is not very significant, can thus be attributed to environmental effects, the exact nature of which are not clear at this point. Further evidence that the hot-press environment did affect the strength comes when the effect of time at temperature is considered. The fibres that were held at 1400 °C for 10 h had comparable grain sizes to the ones held at higher temperatures for shorter times, yet their strength was significantly lower, once again presumably due to surface oxidation. It is worth noting that this is especially true if we were in a regime where active oxidation of the SiC was occurring.

The Weibull distributions of the fibre fragments are shown in Fig. 4, where S is the probability of having a fibre of length x. Each line represents the cumulative results from at least two different runs after each heat treatment indicated. Because of the anomalous nature of the data for the fibres annealed at 1500 °C for 2 h, the data shown represent three separate runs. The average critical lengths and Weibull moduli are also listed in Table I. The heat treatments invariably resulted in a *decrease* in the average fibre fragment lengths, in accordance with the decrease in strength. However, despite that fact that the average fibre fragment lengths were comparable for all heat-treated fibres, the results shown in Fig. 4 and Table I, indicate that the heat treatment at 1500 °C resulted in a narrower distribution of fibre fragment length. The reason for this state of affairs is not clear, but again could be related to whether active or passive oxidation was occurring. Regardless of the reason behind these observations, these results indicate that, in addition to measuring the strength, it is also important to measure the distribution in fibre lengths because the latter are important in determining the performance of fibre-reinforced composites.

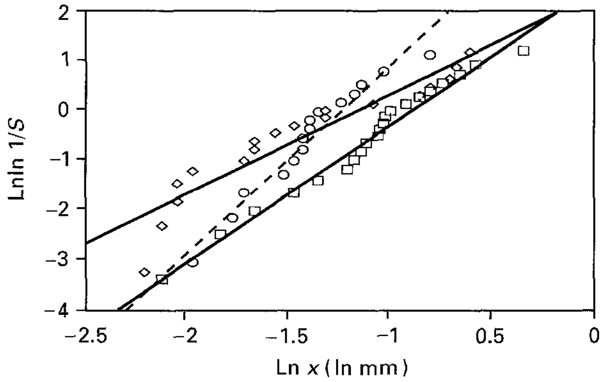

Figure 4 Weibull distributions of fibre fragments as a function of heat treatments: (□) as-received, and heat treated for 2h at (◇) 1400 °C, (○) 1500° C.

Typically the more refractory ceramic matrix composites are processed by hot pressing at temperatures in excess of 1400 °C. Consequently, the practical implications of the results presented here are that until the problem of grain coarsening and interaction with the atmosphere and or matrix can be solved, it is important to appreciate that the post-fabricated and in-use strength of these fibres will be significantly lower than their as-received strength.

4. Conclusion

Annealing of SCS-6 SiC monofilaments at temperatures greater than 1400 °C results in a significant increase in the intensity and a sharpening of the (1 1 1) SiC peaks. Concomitant with these changes was a significant degradation of the fibre strengths at room temperature and a decrease in their average critical lengths. All these observations can be attributed to a combination of coarsening of the β-SiC grains as a result of the heat treatments, as well as interactions with the annealing environment.

References

1. S. R. NUTT and F. E. WAWNER, *J. Mater. Sci.* **20** (1985) 1953.
2. X. J. NING and P. PIROUZ, *J. Mater. Res.* **6** (1991) 2234.
3. X. J. NING, P. PIROUZ and R. BHATT, *Mater. Res. Soc. Symp. Proc.* **250** (1992) 187.
4. X. J. NING, P. PIROUZ and K. P. D. LAGERLOF and J. DICARLO, *J. Mater. Res.* **5** (1990) 2865.
5. X. J. NING, P. PIROUZ and S. FARMER, *J. Amer. Ceram. Soc.* **76** (1993) 2033.
6. R. T. BHATT and D. R. HULL, *Ceram. Engng. Sci. Proc.* **12** (1991) 1832.
7. K. D. McHENERY and R. E. TRESSLER, *J. Compos. Mater.* **9** (1975) 73.
8. J. DICARLO, *J. Mater. Sci.* **21** (1986) 217.
9. A. ELKIND, M. BARSOUM and P. KANGUTKAR, *J. Amer. Ceram. Soc.* **75** (1992) 2871.
10. W. A. CURTIN, *ibid.* **74** (1991) 2837.
11. H. F. WU, G. BIRESAW and J. T. LAEMMLE, *Polym. Compos.* **12** (1991) 281.

12. A. N. NETRAVALI, R. B. HENSTENBURG, S. L. PHOENIX and P. SCHWARTZ, *ibid.* **10** (1989) 226.
13. M. D. THOULESS, O. SBAIZERO, L. S. SIGL and A. G. EVANS, *J. Amer. Ceram. Soc.* **72** (1989) 525.
14. M. BARSOUM and A. ELKIND, *J. Mater. Sci.* **30** (1995) 69.
15. B. D. CULLITY, "Elements of X-Ray Diffraction" (Addison-Wesley, Reading, MA, 1978).
16. H. P. KLUG and L. E. ALEXANDER, "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials" (Wiley, New York, 1974).
17. W. S. SEO, C. H. PAI, K. KOUMOTO and H. YANAGIDA, *J. Ceram. Soc.* **99** (1991) 429.

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