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Effect of Composition and Heat Treatment Conditions on the Tensile Strength and Creep Resistance of SiC-based Fibers

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Abstract

Polymer-derived SiC-based fibers with fine-diameter (~10–15 μm) and high strength (~3 GPa) were prepared with carbon-rich and near-stoichiometric compositions. Fiber tensile strengths were determined after heat treatments at temperatures up to 1950 °C in non-oxidizing atmospheres and up to 1250 °C in air. The creep resistance of fibers was assessed using bend stress relaxation measurements. Fibers showed excellent strength retention after heat treatments in non-oxidizing atmospheres at temperatures up to 1700 °C for the carbon-rich fibers and up to 1950 °C for the near-stoichiometric fibers. The near-stoichiometric fibers also showed considerably better strength retention after heat treatments in air. Creep resistance of the as-fabricated fibers was greatly improved by high-temperature heat treatments. Heat-treated near-stoichiometric fibers could be prepared with ~3 GPa tensile strengths and bend stress relaxation creep behavior which was significantly better than that reported for the Hi-Nicalon™ Type S near-stoichiometric SiC fibers. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: SiC, fibres, strength, creep, SiC-fibres.

1 Introduction

Yajima *et al.* were the first to demonstrate that organosilicon polymers could be used to fabricate fine-diameter SiC-based fibers with high tensile strength.[1,2] Nicalon™ and Tyranno™ fibers were the first generation of commercially-available polymer-derived fibers which were based on the methods of Yajima *et al.* However, these fibers are not pure stoichiometric SiC and they contain relatively high concentrations of excess carbon and oxygen. (In addition, Tyranno™ fibers are actually Si–Ti–C–O fibers.) As a consequence, these fibers degrade extensively at high temperatures due to carbothermal reduction reactions between the carbon and siliceous materials.[3–6] To minimize this problem, there has been considerable effort in recent years to prepare organosilicon polymer-derived SiC fibers with low oxygen content.[7–20] SiC fibers with both carbon-rich and near-stoichiometric compositions have been reported by various researchers, including those at Nippon Carbon Co. (carbon-rich Hi-Nicalon™ and near-stoichiometric Hi-Nicalon™ Type S fibers),[7–12] Dow Corning Co. (near-stoichiometric Sylramic™ fibers),[13–16] and the University of Florida (carbon-rich UF and near-stoichiometric UF-HM fibers).[17–20] These SiC-based fibers show significantly improved thermomechanical properties compared to fibers containing large amounts of oxygen, such as Nicalon™ and Tyranno™ fibers. In this study, the tensile strength of both carbon-rich SiC fibers and near-stoichiometric SiC fibers were determined before and after heat treatments in oxidizing and non-oxidizing atmospheres. The creep resistance of these fibers was assessed under inert-atmosphere heat-treatment conditions using the bend stress relaxation (BSR) method of Morscher and DiCarlo.[21]

2 Experimental

2.1 Processing

Carbon-rich fibers and near-stoichiometric SiC-based fibers were fabricated using a high-molecular-weight polycarbosilane (PCS) polymer as the primary ceramic precursor.[17–20] The infusible PCS polymers were prepared by pressure pyrolysis of polydimethylsilane.[18,19] Fine-diameter (~10–15 μm) fibers were formed by dry spinning of concentrated PCS-based polymer solutions. (Spinning solutions

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also included soluble additives in order to improve spinnability, incorporate sintering additives, etc.[18,19]) The as-spun polymeric fibers were dried and subsequently given different heat treatments depending on the desired composition. Carbon-rich fibers (designated 'UF fibers') were prepared by directly pyrolyzing the dried fibers at temperatures in the range of ~1000–1200 °C in a non-oxidizing atmosphere (e.g. nitrogen). Fibers with near-stoichiometric composition (designated 'UF-HM fibers') were produced by carrying out controlled carbothermal reduction reactions at elevated temperatures. After drying, the spun polymeric fibers were initially heat treated in air or oxygen at low temperatures (~100–200 °C) to incorporate oxygen into the organosilicon polymer. The fibers were then heat treated in inert atmosphere (e.g. argon) to decompose the oxidized organosilicon polymer to an $SiC/C/SiC_xO_y$ ceramic (at < 1200 °C) and to subsequently effect the carbothermal reduction reductions (at ~1400–1600 °C) in which excess carbon was eliminated from the fiber by reaction with siliceous phase. This resulted in near-stoichiometric microporous SiC fibers which were subsequently sintered (at ≥1750°C) in inert atmosphere. Boron additions (typically ~1 wt%) were used as a sintering aid.

2.2 Characterization

Several techniques were used to characterize fiber composition, microstructure, and properties. Quantitative bulk elemental analyses were carried out on individual fibers using an electron microprobe analyzer, EMA (Superprobe 733 Scanning Electron Microprobe, JEOL, Tokyo, Japan) equipped with X-ray wavelength dispersive spectrometers. High purity single-crystal silicon, CVD silicon carbide, silicon dioxide, and silicon nitride (all from Geller Microanalytical Laboratory, Peabody, MA) were used as measurement standards for Si, C, O, and N analyses, respectively. Bulk oxygen concentrations were also determined by neutron activation analysis, NAA, (Nicolet Electron Services, San Diego, CA). NAA was also used to determine bulk boron concentrations (University of Missouri Research Reactor, Columbia, MO). Compositional analyses of the near-surface region of individual fibers were carried out using a scanning Auger microprobe, SAM (model PHI 660, Perkin–Elmer Corp., Eden Prairie, MN).

SEM (Model JSM-6400, JEOL) and TEM (Models 200CX and 4000FX, JEOL) were used to characterize the fiber microstructural features, including the external surface morphology, phases present, grain sizes, porosity, and flaw sizes determined from the fracture surfaces of individual fibers collected after tensile tests. The constituent phases of the fibers were identified using electron diffraction, high resolution TEM, and X-ray diffraction, XRD (Model APD 3720, Philips Electronics Instrument Co., Mt. Vernon, NY).

Fiber apparent densities were determined at 23 °C by a sink-float method (ASTM procedure D3800-79).[22] The liquids used were methylene iodide (CH_2I_2, density ~3·3 g ml^{-1}) and carbon tetrachloride (CCl_4, density ~1·6 g ml^{-1}).

Fiber tensile strengths were determined at room temperature according to ASTM procedure D3379.[23] Individual fibers were glued to paper tabs and loaded in tension (0·5 mm min^{-1} cross-head speed) until failure using a mechanical testing apparatus (Model 1122, Instron Corp. Canton MA). The gage length was 25 mm. Fiber diameters were determined prior to testing using an optical microscope equipped with a micrometer in the eyepiece.

The creep behavior of fibers was assessed using the bend stress relaxation (BSR) method of Morscher and DiCarlo.[21] In this method, stress relaxation values (designated as 'M' values) are determined based on the extent of permanent deformation that occurs when fibers are heat treated under an applied bending load. An M value which approaches 1 indicates that no permanent (creep) deformation occurred during the high temperature annealing, while an M value of 0 indicates that the stress completely relaxed. Hence, fibers are considered more thermally stable against creep as the M values increase from 0 to 1. The BSR tests were carried out using heat treatments at temperatures in the range of 1100–1850 °C for 1 h in an argon atmosphere.

3 Results and discussion

3.1 As-fabricated fibers

3.1.1 Fibers with carbon-rich composition

The normalized Si/C weight ratios for the as-pyrolyzed (< 1200 °C) UF fibers were in the range of ~59–62 wt% Si/38–41 wt% C, with an average ratio (determined from 8 samples) of ~60·5 wt% Si/~39·5 wt% C. Hence, these fibers were highly carbon-rich compared to stoichiometric SiC (~70 wt% Si/~30 wt% C). Some oxygen impurity was incorporated in the fiber during the various stages of processing,[18] but the concentrations for the fibers used in this study were limited to ~0·5–1·0 wt%. Some of the fibers were also doped with small amounts of boron (< 1 wt%). The phases present in the UF fibers were β-SiC and XRD-amorphous carbon. TEM and XRD line-broadening measurements indicated that the β-SiC crystallite sizes were < 5 nm. Sink-float measurements showed that the fiber apparent densities were in the range of ~2·5–2·7 g cm^{-3}. The relatively low densities are consistent with the presence of excess carbon in the fibers and the weakly crystalline nature of the SiC grains. (In contrast, well-crystallized, high-purity SiC has a density of ~3·21 g cm^{-3}.)

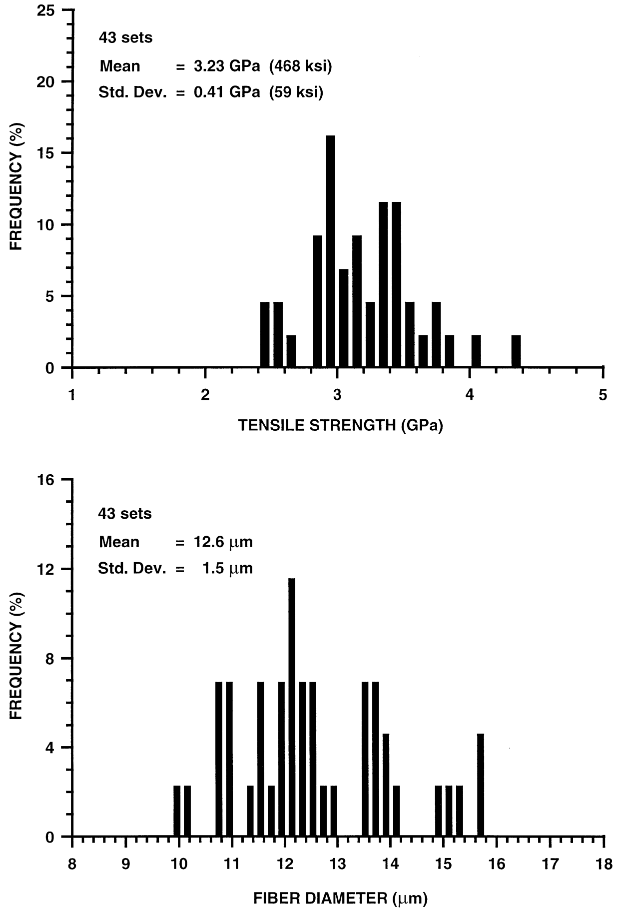

Fig. 1. Histogram plots of frequency versus average tensile strength and frequency versus average diameter for 43 sets of carbon-rich UF fibers.

Figure 1 shows histogram plots of the average room temperature tensile strengths and average diameters obtained from 43 separate sets of the UF fibers. (In most cases, ≥15 fibers were tested for each set.) The mean tensile strength was 3·23 GPa (468 ksi). The mean diameter for these test sets was 12·6 μm.

Figure 2 shows a plot of the fiber tensile strength versus the flaw size measured from the fracture surfaces of tested UF fibers. Although there is considerable scatter in the data, high-strength fibers (e.g. ~3 GPa) typically have flaws in the range of ~0·2–0·3 μm. This corresponds closely to the smallest pore sizes of the filters (nominal sizes were 0·1–0·2 μm) that were used to prepare the spinning solutions for fiber fabrication. In previous work,[18] it was observed that fibers had lower average tensile strength when the spinning solutions were prepared using filters with coarser pore sizes. Hence, it is suggested that the tensile strength of the UF fibers is controlled primarily by processing-related particulates (i.e., impurity particles, polymer 'microgel' particles, etc.) that remain in the spin dope after filtration.

3.1.2 Fibers with near-stoichiometric composition

The normalized Si/C weight ratios for the as-sintered, near-stoichiometric UF-HM fibers were mostly in the range of ~67–70 wt% Si/30–33 wt% C, with an average composition (determined from >25 samples) of ~68·5 wt% Si/~31·5 wt% C. This indicates that the fibers typically contained a small amount of excess carbon. Residual carbon was not detected by a standard X-ray powder diffraction method, but was observed by TEM. HRTEM analysis showed the stacked hexagonal structural

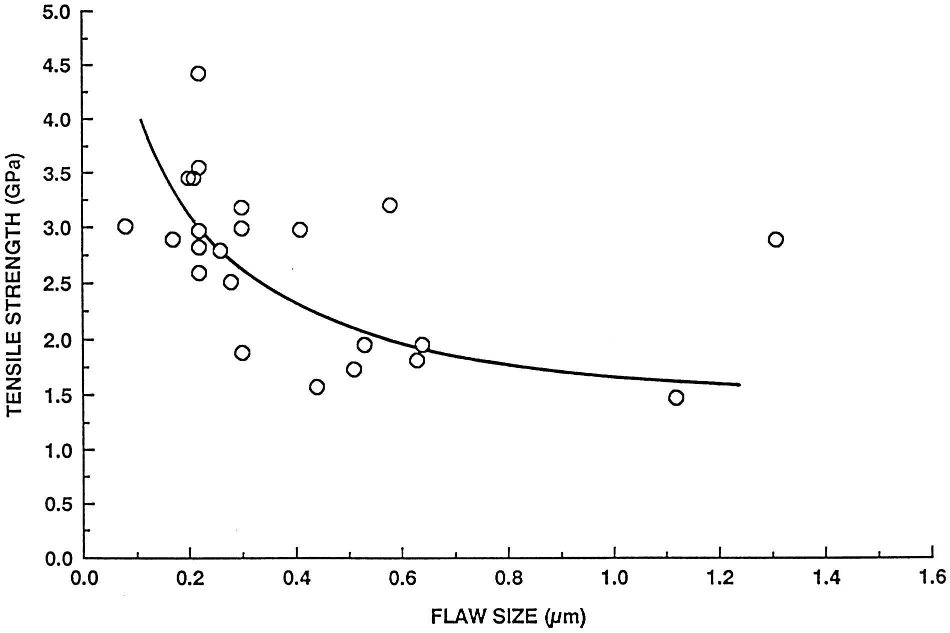

Fig. 2. Plot of tensile strength versus flaw size for individually tested UF fibers.

units with interplanar spacing of 0·34 nm that are associated with graphitic carbon. X-ray and electron diffraction analyses showed that β-SiC was the primary phase in the UF-HM fibers, although traces of the alpha phase were present in some fibers (based on electron diffraction results). EMA analysis for oxygen and nitrogen showed that concentrations were less than the resolution limit for the technique (typically $\leq$0·2 wt%). The boron concentrations were usually on the order of 1 wt%, although it was possible to prepare fibers with range of boron concentrations (i.e. ~0·1–3·0 wt%).

The apparent densities of the UF-HM fibers were usually in the range of 3·1–3·2 g cm^{-3}, with an average value of ~3·15 g cm^{-3}. The average density is lower than the theoretical value (of 3·21 g cm^{-3}) for fully dense (pore-free), stoichiometric SiC. This is attributed, in part, to the small amount of residual carbon in the fibers. In addition, TEM showed that a small amount of fine pores (usually less than 0·1 μm) was present at some grain junctions.

Figure 3 shows histogram plots of the average room temperature tensile strengths and average diameters obtained for 150 separate sets of as-sintered UF-HM fibers. (In most cases, $\geq$15 fibers were tested for each set.) The mean tensile strength was 2·85 GPa (413 ksi). The mean diameter for these test sets was 12·1 μm. A detailed fractographic analysis was not carried out for the UF-HM fibers, but it is believed that the tensile strengths were controlled mostly by larger grains at the fiber surface. Although most of the grains were generally in the range of ~0·05–0·3 μm, grains as large as ~0·5–1·0 μm were observed occasionally (see Fig. 4).

3.2 Effect of heat treatments on fiber tensile strength and BSR creep resistance

3.2.1 Fibers with carbon-rich composition

Figure 5 shows room temperature tensile strengths for UF fibers after heat treatments in argon for 1 h at temperatures in the range of 1500–1900 °C. There was no loss in strength with heat treatments up to 1700 °C and then the strength decreased rapidly with further heat treatments up to 1900 °C. Fig. 5 also shows that the UF fibers have greater retention of their original strengths after high temperature (e.g. $\geq$1600 °C) heat treatments in argon compared to the strength retention reported for carbon-rich Hi-Nicalon™ fibers.[10,11,24]

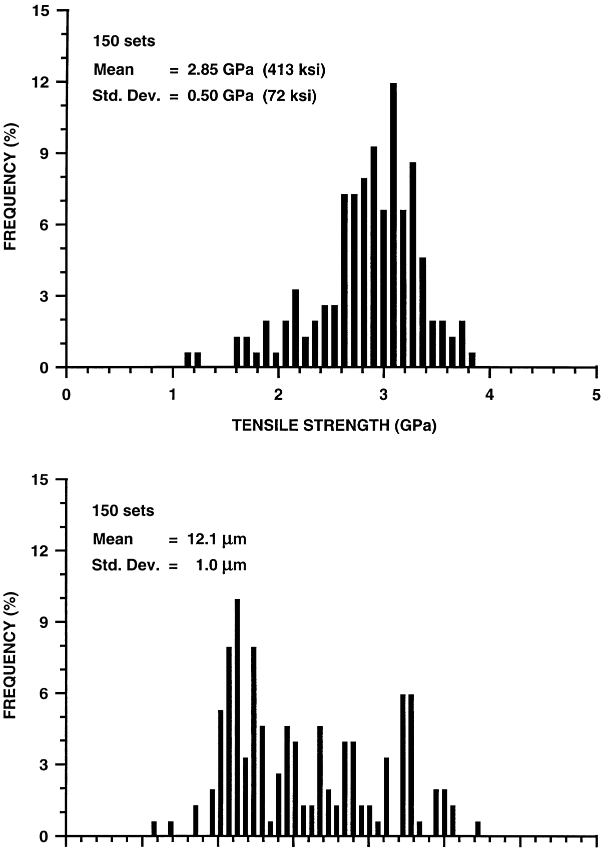

Fig. 3. Histogram plots of frequency versus average tensile strength and frequency versus average diameter for 150 sets of near-stoichiometric UF-HM fibers.

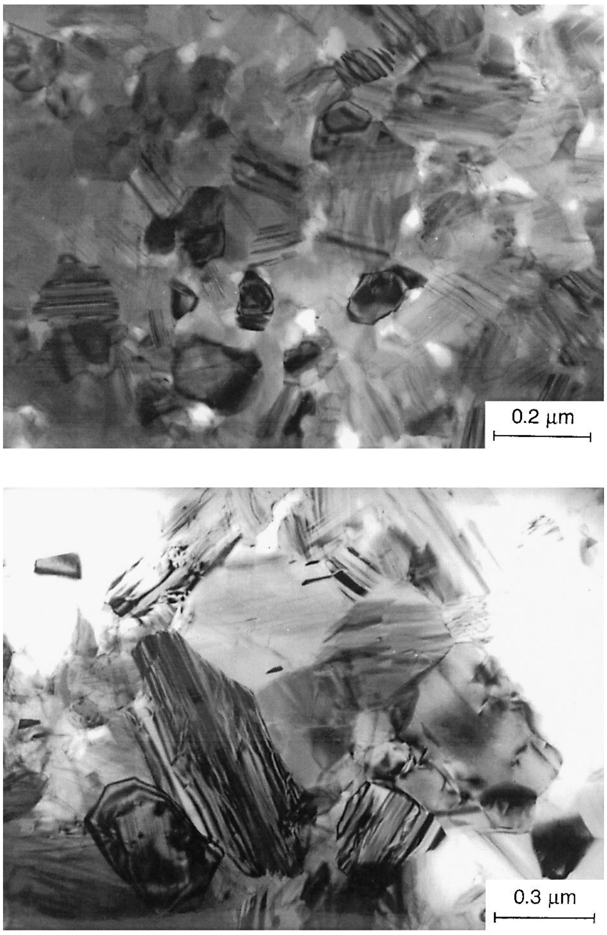

Fig. 4. TEM micrographs showing the grains in a near-stoichiometric UF-HM fiber.

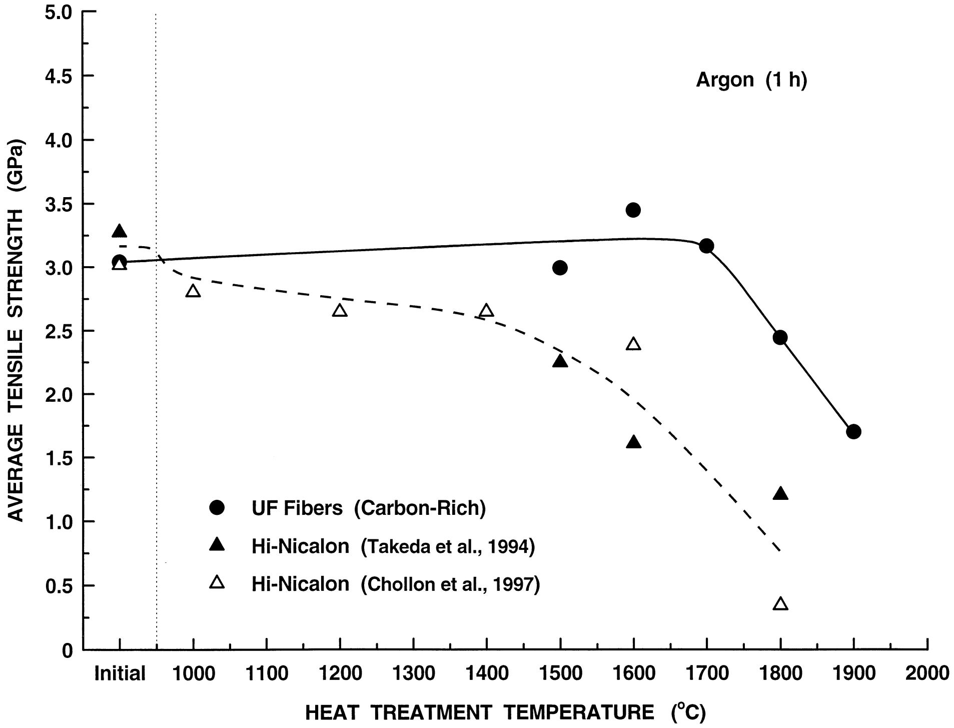

Fig. 5. Plot of average tensile strength versus heat treatment temperature (in argon for 1 h) for carbon-rich UF fibers. Data reported by other researchers for Hi-Nicalon™ fibers are also shown.

For Hi-Nicalon™ fibers, strength decreases upon heat treatment in inert atmospheres have been attributed to a combination of coarsening of SiC grains and flaw formation resulting from thermochemical degradation reactions.[24] SEM observations of the fracture surfaces of the UF fibers heat treated at 1700 °C and 1900 °C did not reveal any obvious differences in the flaw populations. TEM observations (Fig. 6) did show that the SiC grains coarsened with increasing heat treatment temperature. However, even after heat treatment at 1900°C for 1 h in argon, the grains are still relatively small (e.g. compared to the high-strength UF-HM fibers shown in Fig. 4). Hence, it is unlikely that coarser grains act directly as strength-controlling flaws responsible for the lower strength in the 1900 °C heat-treated UF fibers. A possible explanation for the rapid decrease in strength for the 1900 °C heat-treated fibers is the presence of residual tensile stresses at the fiber surface. Residual tensile stresses might develop as a result of the mismatch in thermal expansion coefficients between SiC and C. These stresses would become larger as the SiC/C structure coarsens during heat treatment at higher temperatures. Fig. 6 shows that both the β-SiC grains and the carbon regions grow to larger size with increasing heat treatment temperature. It is also known that the carbon-rich regions in PCS-derived SiC fibers become more highly ordered (i.e. more graphitic) as fibers are heat treated above the original fabrication temperature.[24,25] This is significant because graphite has a very large difference in the thermal expansion coefficients for the directions parallel and normal to the hexagonal basal planes and, hence, higher thermal expansion mismatch stresses might be expected.

It is not understood why the UF fibers show improved strength retention upon heat treatment in argon compared to the Hi-Nicalon™ fibers. The fibers have similar chemical and phase compositions and similar grain sizes. The differences in strength retention could be due to minor differences in impurities in the fibers. For example, it has been observed that strength retention is highly sensitive to low levels of oxygen impurities.[8,18] In addition, the purity of the atmosphere and the presence of contaminants during the heat treatments of the fibers can have a significant effect on the strength retention of these fibers. (For example, oxygen impurities in an otherwise inert heat treatment atmosphere have been observed to cause significant decreases in the fiber strength.)

Figure 7 shows plots of the bend stress relaxation ratios, M, as a function of the heat treatment temperature for as-pyrolyzed (1200 °C) UF fibers and for UF fibers which were given heat treatments for 1 h (in argon) at 1700 °C and 1900 °C. Heat treatment of the UF fibers results in improved BSR creep resistance. This is consistent with reports from other researchers that Hi-Nicalon™ and Hi-Nicalon™ Type S fibers become more creep-resistant after annealing heat treatments above the original processing temperature.[12,26] This may be attributed to the increased grain sizes and/or the more highly crystallized graphitic carbon. Both microstructural changes are expected to inhibit diffusion-controlled creep processes.

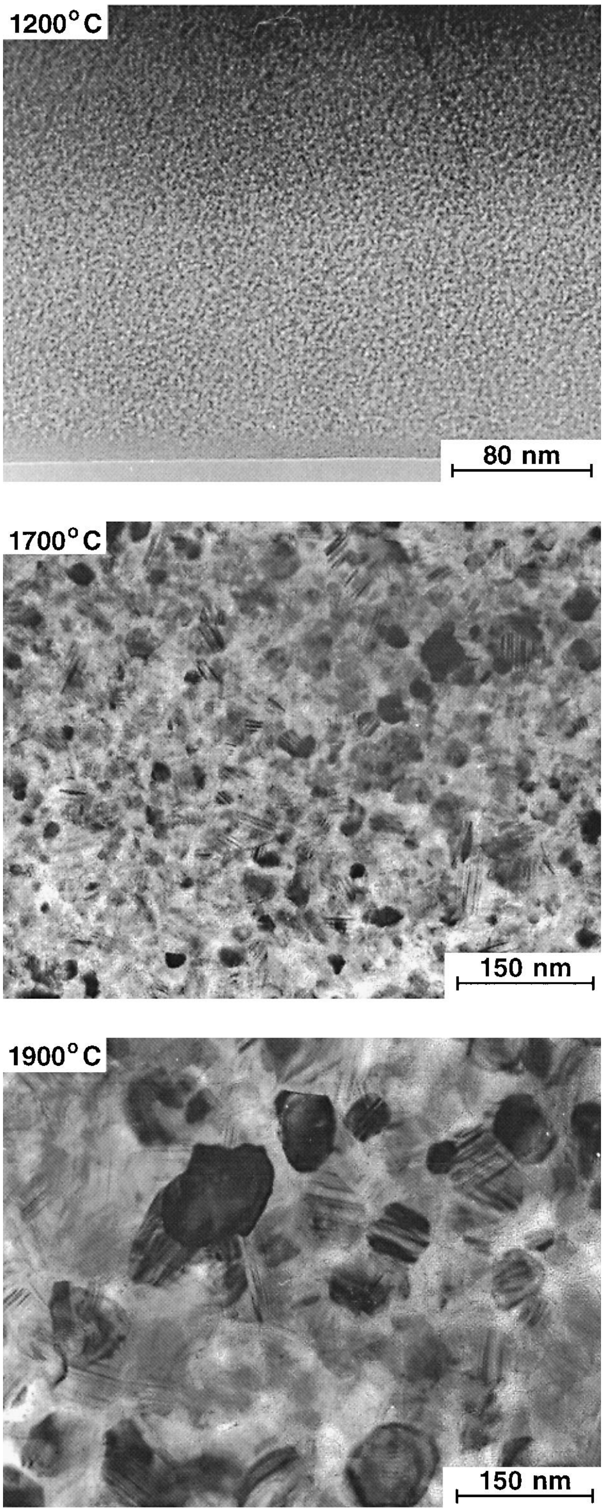

Fig. 6. TEM micrographs for as-pyrolyzed carbon-rich UF fibers (1200 °C) and for UF fibers heat treated in argon for 1 h at 1700 and 1900 °C.

Figure 7 also shows the BSR data that has been reported[12,27–29] for Hi-Nicalon™ and Hi-Nicalon™ Type S fibers. The Hi-Nicalon™ fibers have somewhat higher M values (for a given BSR test temperature) compared to the as-prepared UF fibers. This is attributed to a slightly higher initial processing temperature for the Hi-Nicalon™ fibers which, in turn, results in slightly coarser microstructures (including larger SiC crystallite sizes). The Hi-Nicalon™ Type S fiber have significantly higher M values (for a given BSR test temperature) compared to the Hi-Nicalon™ fibers and the as-pyrolyzed UF fibers. This is attributed to the much larger grain sizes of the Hi-Nicalon™ Type S fiber.[12]

The 1700 °C heat-treated UF fibers not only show greatly improved creep resistance, but also retain high tensile strength. The creep resistance of these fibers (based on the BSR test results) is comparable to or better than the Hi-Nicalon™ Type S fibers. This occurs despite the fact that the grain sizes are much larger for the latter fibers.[12] These observations again indicate that diffusion is inhibited in SiC-based fibers with larger amounts of excess carbon. This manifests itself not only in the slower coarsening of SiC grains upon heat treatment (as indicated by comparing the grain sizes in Figs. 4 and 6 for carbon-rich and near-stoichiometric fibers), but also in the improved creep resistance of the fibers.

As-pyrolyzed UF fibers and UF fibers heat treated in argon at 1650 °C were subsequently given heat treatments in air for 1 h at temperatures in the range of 500–1150 °C. Figure 8 shows the room temperature tensile strengths for these fibers after the air heat treatments. The decreases in strength are attributed to the formation of porosity (and possibly other flaws) resulting from the oxidative combustion of the carbon phase in the fibers. As noted from Fig. 6, the SiC/C fiber microstructure coarsens significantly during the argon annealing heat treatment. The coarser microstructure in the 1650 °C fibers evidently allows oxygen to react with the carbon phase more readily. The fiber strength begins to decrease in the range of only 500–600 °C, i.e. at similar temperatures for which significant reaction occurs when bulk carbon is heat treated to air. Figure 8 also shows that the tensile strengths for the 1650 °C fibers level off after the 900 °C air heat treatment. It is presumed that this correlates with the removal of most of the excess carbon from the fiber. In contrast to these results, the oxidative removal of carbon from the as-pyrolyzed UF fibers occurs at considerably higher temperatures. Strength decreases are not observed until the air heat treatment temperature is greater than ~950 °C. This is attributed to the development of a thin siliceous surface layer on the fibers during air heat treatment which would inhibit oxidative removal of the carbon at the lower temperatures.

3.2.2 Fibers with near-stoichiometric composition

Figure 9 shows a direct comparison of the room temperature tensile strengths for the carbon-rich UF fibers and the near-stoichiometric UF-HM

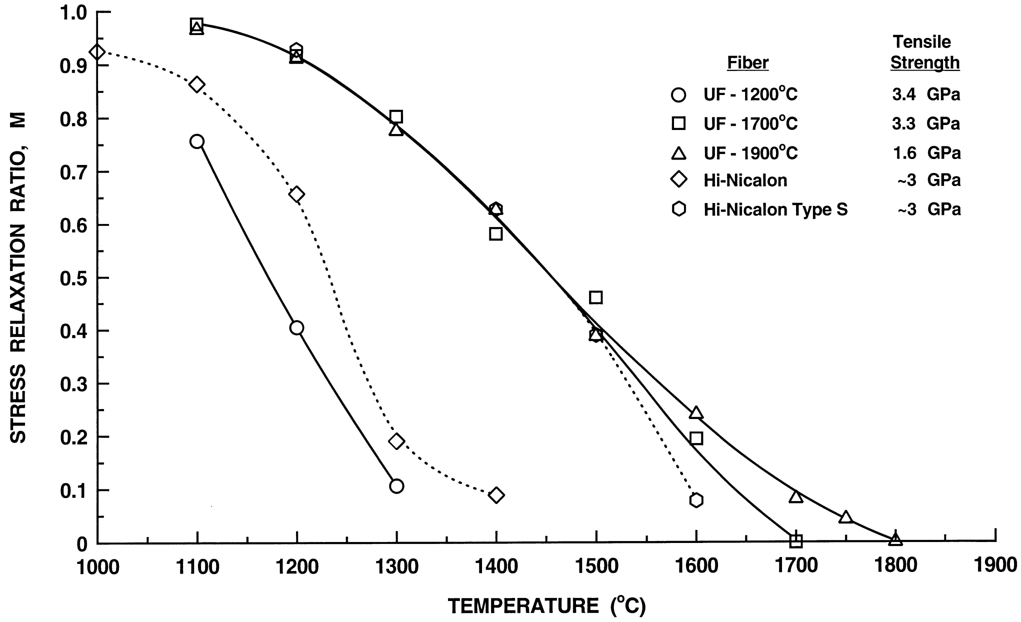

Fig. 7. Plots of stress relaxation ratio, *M*, versus heat treatment temperature for as-pyrolyzed carbon-rich UF fibers (1200 °C), argon heat-treated (1700 and 1900 °C) UF fibers, Hi-Nicalon® fibers, and Hi-Nicalon® Type S fibers.

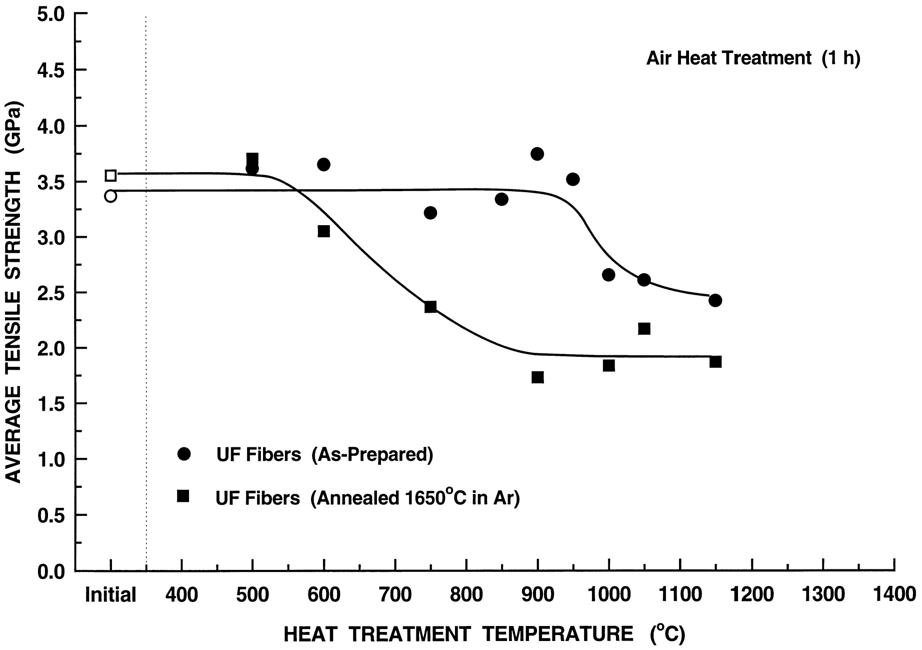

Fig. 8. Plots of average tensile strength versus heat treatment temperature (in air for 1 h) for as-pyrolyzed carbon-rich UF fibers and for argon heat-treated (1650 °C) UF fibers.

fibers after heat treatments in argon for 1 h at temperatures in the range of 1400–1950 °C. The UF-HM fibers retained most of their original strength through heat treatments up to 1800 °C and then the strength gradually decreased with heat treatments at higher temperatures (up to 1950 °C). As noted earlier, the UF fibers showed a relatively rapid decrease in the tensile strength after heat treatments above 1700 °C.

The strength-controlling flaws for the as-sintered UF-HM fibers are believed to be larger grains at the fiber surfaces. Hence, the gradual decrease in tensile strength for the UF-HM fibers after heat treatment in argon at higher temperatures is attributed to grain growth. Although quantitative measurements have not been made, TEM observations did show that larger grains were more prevalent in the 1950 °C heat-treated fibers compared to the as-sintered fibers.

The near-stoichiometric UF-HM fibers retained most of their initial strength to higher temperature than the carbon-rich UF fibers, despite the considerably larger grain sizes of the former fibers. Hence, the relatively rapid decrease in strength in UF fibers heat treated above 1700 °C cannot be attributed to larger grains acting directly as strength-controlling flaws. As noted earlier, it is instead suggested that the strength decay results from larger residual stresses arising from the mismatch in the SiC/C thermal expansion coefficients.

The UF-HM fibers show even better strength retention when heat treated in nitrogen-containing atmosphere instead of argon. The as-fabricated tensile strengths were retained after heat treatments up to ~1950 °C. The reason for this behavior is unclear, but it is believed to be associated with the formation of a thin BN layer (~0·1–0·2 μm) on the fiber surface. The BN forms *in situ* (i.e. during heat treatment) by the reaction of boron that is initially present in the fiber (as a sintering aid) and nitrogen in the annealing atmosphere.[30] The improved strength retention is believed to result from restricting the flaw size at the fiber surface to the approximate thickness of the BN layer.

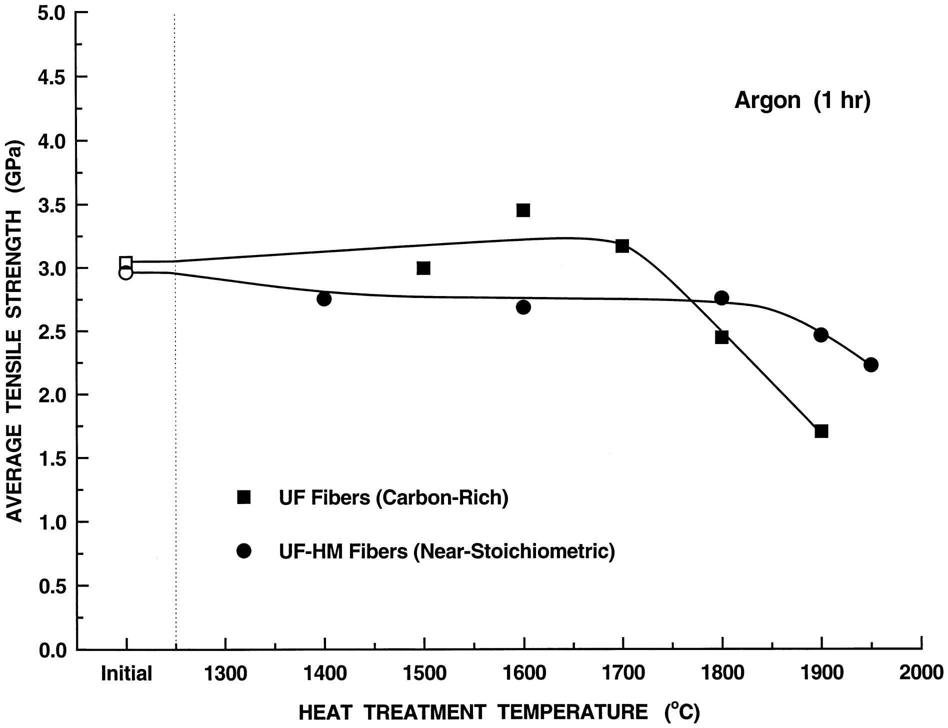

Fig. 9. Plots of average tensile strength versus heat treatment temperature (in argon for 1 h) for carbon-rich UF fibers and near-stoichiometric UF-HM fibers.

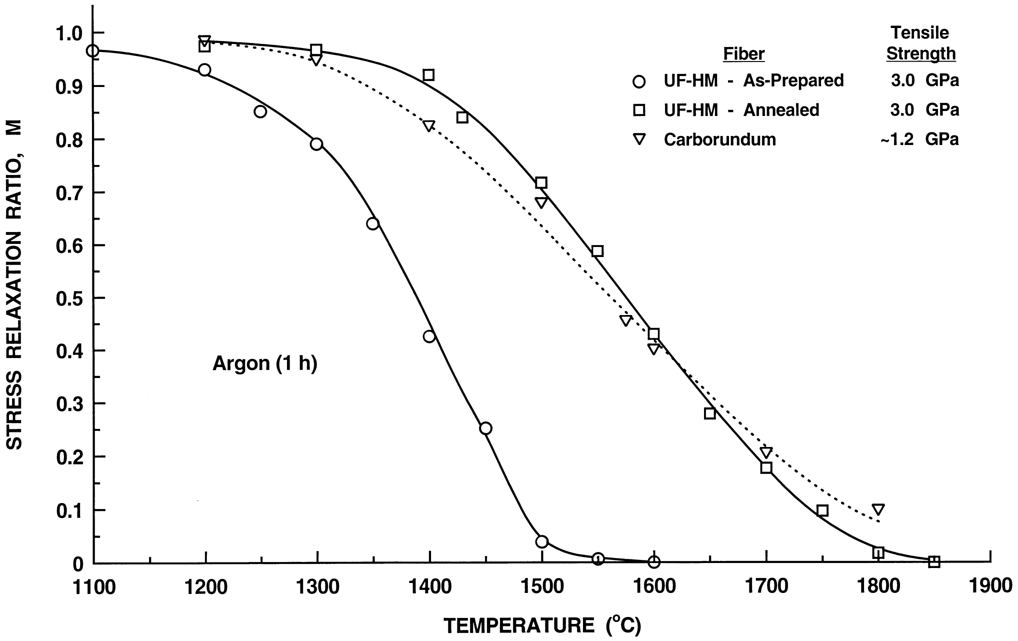

Fig. 10. Plots of stress relaxation ratio, *M*, versus heat treatment temperature for as-sintered near-stoichiometric UF-HM fibers, heat-treated UF-HM fibers, and Carborundum fibers.

Figure 10 shows BSR data for the as-sintered and nitrogen-annealed UF-HM fibers. Annealing results in significant improvements in creep resistance. In fact, the annealed fibers show comparable BSR behavior to that reported[27–29] for much weaker, coarse-grained Carborundum fibers. (The latter fibers were prepared by sintering of SiC powders and have considerably larger grain sizes, larger diameters, and rougher surfaces compared to typical polymer-derived SiC fibers.[31] The coarser grain sizes results in fibers which have excellent creep resistance, but relatively low tensile strength.) The improved creep resistance of the UF-HM fibers after the annealing treatment is attributed, at least in part, to increased grain sizes. It is also possible that boron removal from the bulk of the fiber (i.e. due to migration to the fiber surface) decreases SiC self-diffusion coefficients and thereby decreases the creep rate.

Takeda *et al.*[12] reported that annealing heat treatments improved the creep resistance of Hi-Nicalon™ Type S fibers. However, these fibers did not retain tensile strengths as high as the UF-HM fibers after the annealing heat treatments. This is illustrated in Fig. 11 which shows plots of tensile strengths versus M values for Hi-Nicalon™ Type S and UF-HM fibers which were subjected to various annealing heat treatments prior to BSR tests at 1400 °C (for 1 h argon). UF-HM fibers could be prepared which had 1400 °C BSR M values of ~0·9, while still retaining tensile strengths of ~3 GPa. In contrast, 1400 °C BSR M values of only ~0·6 were possible in Hi-Nicalon™ Type S fibers which retained tensile strengths of ~3 GPa.

Figure 12 shows the room temperature tensile strengths for as-sintered UF-HM fibers after they were heat treated in air for 1 h at temperatures in the range of 400–1250 °C. The fibers show excellent strength retention under these heat treatment conditions. The curve drawn in Fig. 12 suggests that there is a small initial decrease in strength as the heat treatment temperature is increased from 500 to 600 °C and another small decrease in strength after heat treatment at 1250 °C. It could be argued that the differences in strength values for various points shown in Fig. 12 are not statistically significant since all the values are within ± 1 standard deviation of the average value. However, the trends suggested for the curve drawn in Fig. 10 are supported by other observations: (1) Scanning auger microprobe (SAM) measurements show that heat treatment in air above 500 °C removes a thin (typically ~10–20 nm) carbon-rich layer from the UF-HM fiber surfaces. (It is well known that Si tends to evaporate preferentially from the surface of SiC during high temperature heat treatment in inert or vacuum atmospheres. SAM measurements showed that the as-sintered UF-HM fibers have a thin carbon layer on the surface.) The oxidative elimination of the carbon surface layer may lead to increased concentration and/or size of surface flaws. (2) The fibers are expected to develop thicker silica surface layers as the oxidation temperature increases. After the 1250 °C heat treatment in air, it was evident that the individual fibers were beginning to stick together (i.e. presumably due to viscous flow of the silica surface layers). It is likely that surface damage was introduced when these fibers were separated for the tensile tests.

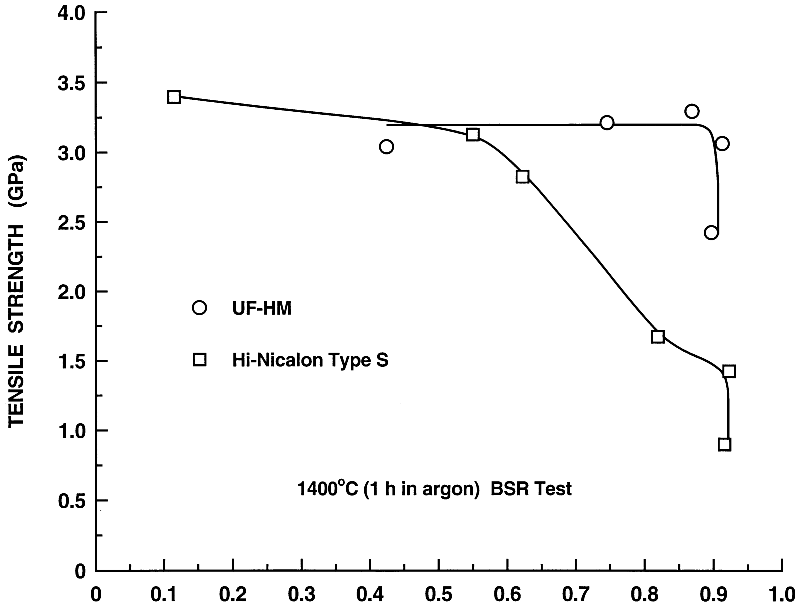

Fig. 11. Plots of tensile strength versus stress relaxation ratio, M, for near-stoichiometric UF-HM fibers and Hi-Nicalon Type S fibers which were given varying annealing treatments in order to alter the M values. The BSR tests were carried out at 1400 °C.

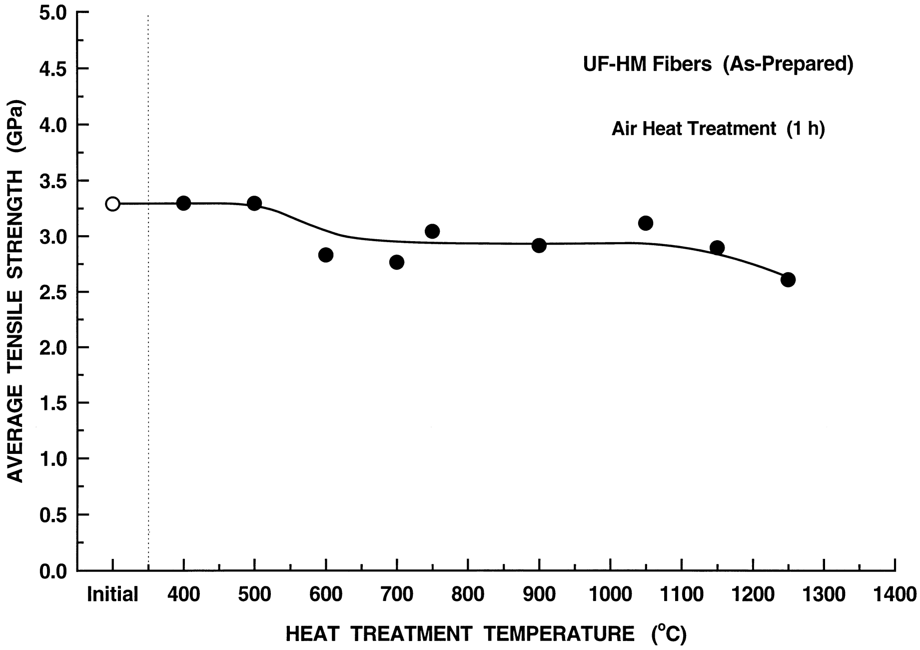

Fig. 12. Plot of average tensile strength versus heat treatment temperature (in air for 1 h) for near-stoichiometric UF-HM fibers.

4 Conclusions

Carbon-rich and near-stoichiometric SiC fibers with fine-diameter (~10–15 μm) and high tensile strength (~3 GPa) were prepared by dry spinning of polycarbosilane-based polymer solutions. The effects of heat treatments in oxidizing and non-oxidizing atmospheres on the thermomechanical properties of the carbon-rich and near-stoichiometric SiC fibers were investigated.

The carbon-rich UF fibers showed excellent strength retention after heat treatments in argon (1 h) up to 1700 °C and then showed relatively a sharp decreases in strength. The strength decrease at higher temperatures may be due to increasing residual stresses arising from mismatches in the thermal expansion coefficients in the SiC/C fibers. The near-stoichiometric UF-HM fibers showed excellent strength retention after heat treatments in argon (1 h) up to 1800 °C and then showed a relatively gradual decrease in strength. The strength decrease was attributed to increased grain sizes as a result of grain growth. The near-stoichiometric fibers were able to retain their initial tensile strengths to even higher temperature (1950 °C) when heat treatments were carried in nitrogen. This observation was associated with the formation of a thin BN layer (~0·1–0·2 μm) at the fiber surface which was believed to restrict the size of the strength-degrading flaws at the fiber surface.

The as-prepared carbon-rich UF fibers showed significant improvements in creep resistance (as assessed by the bend stress relaxation, BSR, method) when heat treated at elevated temperatures in argon. This was attributed to the increased grain sizes and possibly more highly crystallized graphitic carbon. Despite finer SiC grain sizes, the carbon-rich UF fibers heat treated at 1700 °C in argon showed creep resistance (based on the BSR test results) which was comparable to or better than that observed for the as-prepared near-stoichiometric fibers (both UF-HM fibers and Hi-Nicalon™ Type S fibers). This result indicated that diffusion is inhibited in SiC-based fibers which contain larger amounts of excess carbon. The BSR creep resistance of the near-stoichiometric UF-HM fibers was also enhanced significantly by annealing heat treatments in nitrogen. This was attributed to increased grain size and reduced boron concentration within the bulk fiber. UF-HM fibers showed excellent strength retention after heat treatment in air (1 h) at temperatures in the range of 400–1150 °C. Interfilament adhesion occurred when the fiber bundles were heat treated at 1250 °C, presumably due to viscous flow of siliceous material that had formed at the fiber surface. Strengths decreased after heat treatments in air at much lower temperatures for the carbon-rich UF fibers compared to the near-stoichiometric UF-HM fibers. This was attributed to formation of porosity (and possibly other flaws) when carbon was oxidatively eliminated from the UF fibers. The strength decreases in the carbon-rich fibers occurred at substantially lower temperature for the 1650 °C argon heat-treated fibers compared to the as-pyrolyzed fibers. This was attributed to an enhanced oxidative attack of the carbon due to the considerably coarser SiC/C microstructure of the 1650 °C fibers.

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