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13. ABSTRACT (Maximum 200 words) The effect of non-oxidizing heat treatments on the creep resistance and strength retention for carbon-rich and near-stoichiometric SiC-based fibers was investigated. Carbon-rich fibers showed excellent strength retention and greatly improved creep resistance when heat treated at 1700°C in argon. This was attributed to the increased grain sizes and possibly more highly crystallized graphitic carbon. The measured creep resistance was comparable to or better than observed for as-prepared near-stoichiometric fibers. This result indicated that diffusion is inhibited in SiC-based fibers which contain larger amounts of excess carbon. The creep resistance of the near-stoichiometric fibers was also greatly enhanced by annealing heat treatments at 1940°C. This was attributed to increased grain size and possibly to reduced boron concentration within the bulk fiber. The combination of high strength (~3 GPa) and high creep resistance that was obtained for the annealed near-stoichiometric fibers has not been observed for other SiC based fibers.				
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**EFFECT OF MICROSTRUCTURE ON THE  
THERMOMECHANICAL PROPERTIES OF SIC FIBERS**

Final Report (12/15/98 - 12/14/00)

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## 1.0 EXECUTIVE SUMMARY

Carbon-rich and near-stoichiometric SiC fibers with fine-diameter ( $\sim 10\text{-}15\ \mu\text{m}$ ) and high tensile strength ( $\sim 3\ \text{GPa}$ ) 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 fibers showed excellent strength retention after heat treatments in argon (1 hr) up to  $1700^\circ\text{C}$  and then showed relatively 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 fibers showed excellent strength retention after heat treatments in argon (1 h) up to  $1800^\circ\text{C}$  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 ( $1950^\circ\text{C}$ ) when heat treatments were carried in nitrogen. This observation was associated with the formation of a thin BN layer ( $\sim 0.1\text{-}0.2\ \mu\text{m}$ ) 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 fibers heat treated at  $1700^\circ\text{C}$  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. 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 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.

The near-stoichiometric fibers showed excellent strength retention after heat treatment in air (1 h) at temperatures in the range of  $400\text{-}1150^\circ\text{C}$ . Interfilament adhesion occurred when the fiber bundles were heat treated at  $1250^\circ\text{C}$ , 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 fibers compared to the near-stoichiometric fibers. This was attributed to formation of porosity (and possibly other flaws) when carbon was oxidatively eliminated from the carbon-rich fibers. The strength decreases in the carbon-rich fibers occurred at substantially lower temperature for the  $1650^\circ\text{C}$  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  $1650^\circ\text{C}$  fibers.

It was demonstrated that near-stoichiometric fibers could be coated with thin layers ( $\sim 0.1\text{-}0.2\ \mu\text{m}$ ) of hexagonal BN using an in-situ processing method. The fibers prepared with the BN coatings had high strength ( $\sim 3\ \text{GPa}$ ) and excellent creep resistance. The BN coatings allowed debonding of fibers from the matrix in SiC/SiC microcomposites, but the debonding and

interfacial frictional stresses were very high. Thicker coatings are probably needed to develop suitable fiber/matrix interfaces for CMC applications.

The development of SiC fibers with high strengths is dependent on controlling each step in the fiber fabrication process, including the synthesis of the polymeric precursors. A study was initiated concerning synthesis and characterization of the polycarbosilane (PCS) polymers used to prepare the SiC fibers. It was observed that fibers prepared from less oxidation-resistant polymers had lower tensile strength.

## 2.0 RESEARCH RESULTS

### 2.1. Effect of Microstructure on Thermomechanical Properties

SiC-based fibers were fabricated with varying microstructural characteristics, such as Si/C ratio, grain size, dopant concentration, etc. Emphasis was placed on producing fibers with low oxygen content in order to minimize carbothermal reduction reactions as a potential cause for strength degradation upon heat treatment at elevated temperatures. The effects of processing variables and heat treatment conditions on microstructure development and thermomechanical properties were investigated. The research progress is summarized below. Additional details are provided in attachments in the Appendix.

#### 2.1.1 As-Fabricated Fibers

##### *Fibers with Carbon-Rich Composition*

SiC-based fibers with carbon-rich composition ("UF fibers") were prepared initially. The as-fabricated UF fibers had an average composition (determined using electron microprobe analysis, EMA) of  $\sim 60.5$  wt% Si/ $\sim 39.5$  wt% C. (Hence, these fibers were highly carbon-rich relative to stoichiometric SiC which has a composition of 70 wt% Si/30 wt% C.) Oxygen concentrations were relatively low, i.e., typically in the range of  $\sim 0.5$ -1.0 wt%. XRD and TEM studies indicated that the phases present in the UF fibers were  $\beta$ -SiC and XRD-amorphous carbon. TEM and XRD line-broadening measurements indicated that the  $\beta$ -SiC crystallite sizes in the as-fabricated fibers were less than 5 nm. Sink-float measurements showed that the fiber apparent densities were in the range of  $\sim 2.5$ -2.7 g/cm<sup>3</sup>. The relatively low densities were 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, near-stoichiometric SiC has a density of  $\sim 3.21$  g/cm<sup>3</sup>.) The fibers had an average tensile strength of  $\sim 3.2$  GPa and diameters were typically in the range of  $\sim 10$ -15  $\mu$ m. Fractography studies indicated that the strength-controlling flaw sizes were mostly in the range of  $\sim 0.2$ -0.3  $\mu$ m. This corresponds closely to the smallest pore sizes of the filters (nominal sizes were 0.1-0.2  $\mu$ m) that were used to prepare the spinning solutions for fiber fabrication. Hence, it is believed that the tensile strength of the UF fibers is controlled primarily by processing-related particulates (i.e., impurity particles, polymer "microgel" particles, etc.).

##### *Fibers with Near-Stoichiometric Composition*

Near-stoichiometric SiC fibers were prepared by sintering using boron as a sintering aid. The normalized Si/C weight ratios in the fibers were mostly in the range of  $\sim 67$ -70 wt% Si/30-33 wt% C, with an average composition (determined from  $>25$  samples) of  $\sim 68.5$  wt% Si/ $\sim 31.5$  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 units with interplanar spacing of 0.34 nm that are associated with graphitic carbon. X-ray and electron

diffraction analyses showed that  $\beta$ -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). Electron microprobe analyses for oxygen and nitrogen showed that concentrations were less than the resolution limit for the technique (typically  $\leq 0.2$  wt%). The residual boron concentrations were usually on the order of 1 wt%, although it was possible to prepare fibers with a range of boron concentrations (i.e.,  $\sim 0.1 - 3.0$  wt%). The apparent densities of the were typically in the range of  $3.1-3.2$  g/cm<sup>3</sup>, with an average value of  $\sim 3.15$  g/cm<sup>3</sup>. The average density is lower than the theoretical value (of  $3.21$  g/cm<sup>3</sup>) 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  $0.1$   $\mu\text{m}$ ) was present at some grain junctions. The tensile strengths of the as-prepared fibers were typically  $\sim 3$  GPa and the fiber diameters were mostly in the range of  $\sim 10-14$   $\mu\text{m}$ . 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  $\sim 0.05 - 0.3$   $\mu\text{m}$ , grains as large as  $\sim 0.5-1.0$   $\mu\text{m}$  were observed occasionally.

### 2.1.2 Effect of Heat Treatments on Fiber Tensile Strength and BSR Creep Resistance

#### *Fibers with Carbon-Rich Composition*

The carbon-rich UF fibers were given heat treatments in argon for 1 h at temperatures in the range of  $1500-1900^\circ\text{C}$ . The fibers showed no loss in strength with heat treatments up to  $1700^\circ\text{C}$  and then showed relatively sharp decreases in strength with further heat treatments up to  $1900^\circ\text{C}$ . The fibers show greater retention of their original strengths after high temperature (e.g.,  $\geq 1600^\circ\text{C}$ ) heat treatments in argon compared to the strength retention reported for carbon-rich Hi-Nicalon<sup>TM</sup> fibers and near-stoichiometric Hi-Nicalon<sup>TM</sup> Type S fibers, respectively.[1,2] However, the UF fibers decreased in tensile strength at lower heat treatment temperature (and decreased more sharply with increasing temperature) compared to the near-stoichiometric SiC fibers (UF-HM fibers). The reason for the latter behavior is unclear. One possible explanation is that carbothermal reduction reactions occurred due to a higher amount of residual oxygen in the carbon-rich fibers. Carbothermal reduction reactions could create strength-degrading flaws (e.g., pores or large grains). However, supporting evidence for this explanation is lacking. Scanning electron microscope (SEM) observations of the fibers (including the fracture surfaces) did not reveal the development of any obvious flaws which would account for the rapid decrease in strength with heat treatments above  $1700^\circ\text{C}$ . In addition, TEM observations showed that the grain sizes remained much smaller than those observed in near-stoichiometric UF-HM fibers. For example, carbon-rich UF fiber heat treated for 1 h at  $1900^\circ\text{C}$  (in argon) had a considerably smaller average grain size compared to the near-stoichiometric UF-HM fibers heat treated for only 0.2 h at  $1840^\circ\text{C}$  (in argon). (The relatively slow grain growth in the UF fibers can be attributed to the much larger amount of excess carbon. This is expected to inhibit the Si diffusional transport that is required for SiC grain coarsening.) A possible explanation for the rapid decay in tensile strength for the carbon-rich UF fibers at temperatures above  $1700^\circ\text{C}$  is the presence of residual tensile stresses at the fiber surface. Such stress might arise due to the mismatch in thermal expansion coefficients between SiC and C. These stresses could become more severe as the SiC/C structure coarsens during heat treatment at higher temperatures. (In

addition to growth of the  $\beta$ -SiC grains, the carbon regions grow into larger and more highly ordered domains when PCS-derived carbon-rich SiC fibers are heat treated at temperatures above the original fabrication temperature.[3,4] The growth of the graphitic carbon regions also has significance because graphite has a very large difference in the thermal expansion coefficients for the directions parallel and normal to the hexagonal basal planes.)

The creep resistance of the carbon-rich UF fibers was assessed under argon-atmosphere heat-treatment conditions using the bend stress relaxation (BSR) method of Morscher and DiCarlo.[5] Bend stress relaxation ratios,  $M$ , as a function of the heat treatment temperature were obtained 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 significantly 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.[4,6] 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.

BSR data were also compared to values reported [4,7-9] for Hi-Nicalon™ and Hi-Nicalon™ Type S fibers. The Hi-Nicalon™ fibers had higher  $M$  values (for a given BSR test temperature) compared to the as-prepared carbon-rich 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 1700°C heat-treated UF fibers had  $M$  values comparable or better (for a given BSR test temperature) than various near-stoichiometric SiC fibers, such as Hi-Nicalon™ Type S fibers and as-fabricated UF-HM fibers. This occurred despite the fact that the grain sizes were much larger for the latter two near-stoichiometric SiC fibers. This observation again suggests that Si 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, but also in the improved creep resistance of the fibers.)

As-pyrolyzed, carbon-rich 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. The room temperature tensile strengths were then determined. Strength decreases were observed above ~950°C for the as-pyrolyzed fibers and above ~550°C for the 1650°C argon-treated fibers. 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. The SiC/C fiber microstructure coarsens significantly during the argon annealing heat treatment at 1650°C and the coarser microstructure in these fibers allows oxygen to react with the carbon phase more readily. Hence, the strength decrease in these fibers occurs at a similar temperature (above ~550°C) at which significant reaction occurs when bulk carbon is heat treated to air. The tensile strengths for these fibers also level off at ~1.8 GPa after a 900°C air heat treatment. This apparently 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 and, hence, the strength decreases are not observed air heat treatment temperatures above ~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.

### *Fibers with Near-Stoichiometric Composition*

The room temperature tensile strengths for the near-stoichiometric UF-HM fibers were determined after heat treatments in argon for 1 h at temperatures in the range of 1400-1950°C. These 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 carbon-rich 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 near-stoichiometric 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 near-stoichiometric 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.[10] The improved strength retention may result from restricting the flaw size at the fiber surface to the approximate thickness of the BN layer.

BSR data was obtained for as-prepared and nitrogen-annealed near-stoichiometric UF-HM fibers. Annealing results in significant improvements in creep resistance. In fact, the annealed fibers show comparable BSR behavior to that reported [7-9] 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.[11] The coarser grain sizes results in fibers which have excellent creep resistance, but relatively low tensile strength.) The improved creep resistance of the near-stoichiometric 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.[4] 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. Near-stoichiometric UF-HM fibers could be prepared which had 1400°C BSR M values of ~0.9 and 1600°C BSR M values of ~0.45, while still retaining tensile strengths of ~3 GPa in both cases. In contrast, 1400°C and 1600°C BSR

M values of only  $\sim 0.6$  and  $\sim 0.05$ , respectively, were possible in Hi-Nicalon™ Type S fibers which retained tensile strengths of  $\sim 3$  GPa.

Room temperature tensile strengths were measured 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. A slight decrease in tensile strength was observed for samples in which the heat treatment temperature increased from 500 to 600°C. The strength then remained nearly constant for samples which had higher heat treatment temperatures, i.e., as high as 1200°C. Another slight decrease in strength was observed for the samples that were heat treated at 1250°C. Scanning auger microprobe (SAM) measurements showed that heat treatment in air above 500°C removes a thin (typically  $\sim 10$ -20 nm) carbon-rich layer from the near-stoichiometric 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 have resulted in an increased concentration and/or size of surface flaws, thereby accounting for the slight decrease in tensile strength observed in fibers heat treated at 600°C. The fibers are expected to develop silica surface layers of increasing thickness 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.

### 2.1.3 In-Situ BN-Coated SiC Fibers

As noted earlier, BN coatings could be prepared on the near-stoichiometric SiC UF-HM fibers by an in-situ process in which boron that was initially present in the fiber (as a sintering aid) was reacted with nitrogen in the annealing atmosphere.<sup>30</sup> TEM studies show that the coatings were comprised of the hexagonal polymorph of BN and that the layer thicknesses were typically on the order of  $\sim 0.10$ - $0.15$   $\mu\text{m}$ .

In collaboration with Greg Morscher at NASA Lewis Research Center, SiC/SiC microcomposites were prepared with these fibers by CVI infiltration of SiC into small fiber bundles. The microcomposite samples were characterized at NASA using indentation push-out tests. It was demonstrated that the BN-coated SiC fibers debonded from the matrix phase during indentation push-out tests. However, the debonding stresses and the interfacial frictional stresses were very high (average values of  $\sim 3.5$  GPa and  $\sim 0.5$  GPa, respectively). This is primarily attributed to the relatively small thickness of the BN coatings (i.e.,  $\sim 0.1$ - $0.2$   $\mu\text{m}$ ). Another contributing factor may have been the orientation of the BN coating on the fibers. TEM studies showed that the BN was preferentially oriented such that the hexagonal planes were perpendicular to the long axis of the SiC fibers.

## 2.2 Synthesis and Characterization of Polymeric Precursor for SiC Fibers

The development of SiC fibers with high tensile strength is dependent on controlling each step in the fiber fabrication process, including the synthesis of the polymeric precursors. A study was initiated concerning synthesis and characterization of the polycarbosilane (PCS) polymeric precursor used to prepare the SiC fibers. PCS polymers were synthesized by pressure pyrolysis of polydimethylsilane (PDMS) using a stainless steel autoclave (1-liter or 3-gallon capacity) under a nitrogen atmosphere. Selected polymers were characterized by gel permeation chromatography, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy, and weight gain measurements. In addition, selected polymers were used to prepare SiC fibers which were subsequently tested for tensile strength.

PCS polymers with weight-average molecular weights ( $M_w$ ) ranging from ~2,000-25,000 were prepared by varying several processing parameters including temperature, time, pressure, and the amount of PDMS in the autoclave. Available evidence indicated that PCS characteristics were affected by temperature gradients within the reactor. The magnitude of the temperature gradients depended on the equipment set-up and processing conditions. PCS polymers produced in the 3-gallon reactor were less oxidation-resistant compared to polymers synthesized in the 1-liter reactor. This suggested that the PCS to PDMS reaction had not gone to completion for some portions of the 3-gallon reaction product (i.e., due to the temperature gradients). However, this could not be confirmed by FTIR spectroscopy or liquid-phase  $^{29}\text{Si}$  NMR spectroscopy. This suggested that the fraction of incompletely reacted product was too small for detection. Nevertheless, these PCS polymers produced fibers which had lower tensile strength compared to the more oxidation-resistant polymers produced in the 1-liter reactor. The specific reason why the oxidation sensitivity of the PCS polymer affected the final fiber tensile strength has not yet been identified.

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### 3.0 PUBLICATIONS

#### Scientific Publications

M.D. Sacks, G.W. Scheiffele, L. Zhang, Y. Yang, and J.J. Brennan, "Polymer-Derived SiC-Based Fibers with High Tensile Strength and Improved Creep Resistance," *Ceram. Eng. Sci. Proc.*, 19 (3) 73-86 (1998).

M.D. Sacks, "Effect of Composition and Heat Treatment Conditions on the Tensile Strength and Creep Resistance of SiC-Based Fibers," *J. Eur. Ceram. Soc.*, 19 2305-2315 (1999).

M.D. Sacks and J.J. Brennan, "Silicon Carbide Fibers with Boron Nitride Coatings," *Ceram. Eng. Sci. Proc.*, Vol. 21 (4) 275-281 (2000).

M.D. Sacks and G.A. Staab, "Creep Behavior of Polymer-Derived SiC-Based Fibers," *Ceram. Eng. Sci. Proc.*, Vol. 21 (4) 331-338 (2000).

#### Patents

M.D. Sacks, "Silicon Carbide Fibers with Boron Nitride Coatings," U.S. Patent No. 6,040,008, March 21, 2000.

M.D. Sacks, "Creep-Resistant, High-Strength Silicon Carbide Fibers," U.S. Patent No. 6,069,102, May 30, 2000.

M.D. Sacks, "Creep-Resistant, High-Strength Silicon Carbide Fibers," U.S. Patent No. 6,187,705, February 13, 2001.

M.D. Sacks, "Silicon Carbide Fibers with Boron Nitride Coatings," U.S. Patent No. to be issued in 2001.

#### Graduate Student Thesis

M. Sillick, "Synthesis and Characterization of Polycarbosilane Polymers for SiC-Based Fiber Fabrication," M.S. thesis. Expected completion in May 2001.

## 4.0 APPENDIX

### Appended Publications

"Polymer-Derived SiC-Based Fibers with High Tensile Strength and Improved Creep Resistance," *Ceram. Eng. Sci. Proc.*, 19 (3) 73-86 (1998).

"Effect of Composition and Heat Treatment Conditions on the Tensile Strength and Creep Resistance of SiC-Based Fibers," *J. Eur. Ceram. Soc.*, 19 2305-2315 (1999).

"Silicon Carbide Fibers with Boron Nitride Coatings," *Ceram. Eng. Sci. Proc.*, Vol. 21 (4) 275-281 (2000).

"Creep Behavior of Polymer-Derived SiC-Based Fibers," *Ceram. Eng. Sci. Proc.*, Vol. 21 (4) 331-338 (2000).

## **POLYMER-DERIVED SiC-BASED FIBERS WITH HIGH TENSILE STRENGTH AND IMPROVED CREEP RESISTANCE**

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### **ABSTRACT**

Fine-diameter ( $\sim 10\text{-}15\ \mu\text{m}$ ), polymer-derived, SiC-based fibers with carbon-rich and near-stoichiometric compositions were prepared and characterized. Tensile strengths and creep resistance were evaluated for as-fabricated fibers and for fibers given heat treatments at temperatures up to  $1950^\circ\text{C}$ . The creep resistance was assessed using the bend stress relaxation (BSR) method developed by Morscher and DiCarlo. Fibers showed excellent strength retention after heat treatments in argon (for 1 h) at temperatures up to  $1700^\circ\text{C}$  for the carbon-rich ("UF") fibers and up to  $1800^\circ\text{C}$  for the near-stoichiometric ("UF-HM") fibers. Creep resistance of the as-fabricated fibers was greatly improved by high temperature annealing treatments. Heat-treated UF fibers could be prepared with  $\sim 3\ \text{GPa}$  tensile strengths and BSR creep behavior which was similar to that reported for Hi-Nicalon<sup>TM</sup> Type S fibers. Heat-treated UF-HM fibers were also prepared with  $\sim 3\ \text{GPa}$  tensile strengths, while BSR results showed that the creep resistance was significantly better than that reported for Hi-Nicalon<sup>TM</sup> Type S fibers. It was also shown that the UF-HM fibers could be coated with hexagonal BN using an in-situ processing method.

### **INTRODUCTION**

There has been considerable interest in recent years in producing SiC-based fibers with improved thermomechanical properties. Much of the effort in this area has been directed toward fabrication of fine-diameter, high-strength, polymer-derived fibers which have low oxygen content.[1-14] The development of such fibers with both carbon-rich and near-stoichiometric compositions have been reported by several research groups, including those at Nippon Carbon Co. (Hi-Nicalon<sup>TM</sup> and Hi-Nicalon<sup>TM</sup> Type S fibers)[1-6], Dow Corning Co. (Sylramic<sup>TM</sup> fibers)[7-10], and the University of Florida (UF and

UF-HM fibers).[11-14] All of these fibers show significantly improved thermomechanical properties compared to fibers which contain large amounts of oxygen, such as Nicalon™ and Tyranno™ fibers.

In this study, the tensile strength and creep resistance of carbon-rich UF fibers and near-stoichiometric UF-HM fibers were evaluated before and after heat treatments at temperatures up to 1950°C. The creep resistance was assessed using the bend stress relaxation (BSR) method of Morscher and DiCarlo.[15]

This study also reports the development of boron nitride (BN) coatings on the UF-HM SiC fibers. Well-crystallized hexagonal BN layers were formed by an in-situ processing method.

## EXPERIMENTAL

The development of polymer-derived UF and UF-HM fibers has been reported previously.[11-14] Fibers were fabricated using a high-molecular-weight polycarbosilane (PCS) polymer as the primary ceramic precursor. (The infusible PCS polymers were prepared by pressure pyrolysis of polydimethylsilane.) Fine-diameter fibers were formed by dry spinning of concentrated PCS-based polymer solutions. The polymeric fibers were decomposed to SiC-based ceramics by pyrolysis in an inert atmosphere. Carbon-rich fibers (designated "UF fibers") were initially processed at temperatures in range of 1000-1200°C, while the near-stoichiometric fibers (designated "UF-HM fibers") were fabricated at higher temperatures ( $\geq 1750^\circ\text{C}$ ). Boron additions were used in the latter fibers, both as a sintering aid and as the boron source for the formation of BN coatings by in-situ processing.

Conventional and high resolution transmission electron microscopy (TEM and HRTEM) were used to characterize the fiber microstructure. The phases present were determined by X-ray diffraction (XRD) and electron diffraction. Elemental analyses for Si, C, O, and N were carried out using electron microprobe analysis (EMA). Oxygen concentrations were also determined by neutron activation analysis, NAA, (Nicolet Electron Services, San Diego, CA). NAA was also used to determine boron concentrations (University of Missouri Research Reactor, Columbia, MO). Fiber apparent densities were determined by a sink-float method (ASTM procedure D3800-79).[16]

Single-filament tensile strengths were determined at room temperature according to ASTM procedure D3379.[17] The fiber gage length was 25 mm. The creep behavior of fibers was assessed using the bend stress relaxation (BSR) method.[15] 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.

## RESULTS AND DISCUSSION

### High-Strength, Creep-Resistant UF Fibers and UF-HM Fibers

Table 1 summarizes the characteristics of typical as-fabricated UF fibers (carbon-rich) and UF-HM (near-stoichiometric) fibers.

The as-pyrolyzed UF fibers had normalized Si/C weight ratios 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 are highly carbon-rich relative to stoichiometric SiC (~70 wt% Si/~30 wt% C). Oxygen was present in the fiber as an impurity picked up during various stages of processing.[12] The concentrations usually did not exceed 1.5 wt% and were more typically in the range of ~0.5-1.0 wt%. Some of the fibers were doped with small amounts of boron. The phases present in the UF fibers were  $\beta$ -SiC and XRD-amorphous carbon. TEM and XRD line-broadening measurements indicated that the  $\beta$ -SiC crystallite sizes were less than 5 nm. Fiber apparent densities were in the range of ~2.5-2.7 g/cm<sup>3</sup>. The relatively low densities are consistent with the large amount of carbon present in the fibers and the weakly crystalline nature of the SiC grains. (Well-crystallized, high purity SiC has a density of ~3.21 g/cm<sup>3</sup>.)

Figure 1A shows a histogram plot of the average room temperature tensile strengths obtained for 43 separate sets of UF fibers. (In most cases,  $\geq 15$  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  $\mu\text{m}$  (std. dev. = 1.5  $\mu\text{m}$ ). Previous fractography studies on similar fibers indicated that the strength-controlling flaw sizes were mostly in the range of ~0.2-0.3  $\mu\text{m}$ . [18] This corresponds closely to the smallest pore sizes of the filters (nominal sizes were 0.1-0.2  $\mu\text{m}$ ) that were used to prepare the spinning solutions for fiber fabrication. Hence, it is possible that the tensile strength of the UF fibers is controlled primarily by processing-related particulates (i.e., impurity particles, polymer "microgel" particles, etc.).

The near-stoichiometric UF-HM fibers had normalized Si/C weight ratios 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 usually contained a small amount of excess carbon. X-ray and electron diffraction analyses of the UF-HM fibers showed that  $\beta$ -SiC was the primary phase in the fibers, although traces of the alpha phase were observed in some fibers. The SiC grain sizes were generally in the range of ~0.05 - 0.3  $\mu\text{m}$ , although grains as large as ~0.5-1.0  $\mu\text{m}$  were occasionally observed. Residual carbon was not detected by a standard XRD powder diffraction method, but was observed by TEM. HRTEM analysis showed the stacked hexagonal structural units with interplanar spacing of 0.34 nm that are associated with graphitic carbon. 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 fibers with range of boron concentrations (i.e., ~0.1 - 3.0 wt%) were also prepared.

The apparent densities of the UF-HM fibers were usually in the range of 3.1-3.2

**TABLE 1. TYPICAL FIBER CHARACTERISTICS**

**UF Fibers (Carbon-Rich Composition)**

Elemental Analysis:	Si/C ratio: ~59-62 wt% Si/ ~38-41 wt% C
	Oxygen: ~0.5 - 1.5 wt%
	Boron: ~0-1 wt%
Phases:	weakly-crystalline $\beta$ -SiC, XRD-amorphous Carbon
SiC Grain Size:	$\leq 5$ nm
Apparent Density:	~2.5-2.7 g/cm <sup>3</sup>
Diameter:	~10-15 $\mu$ m
Tensile Strength:	~400-500 ksi (~2.8-3.5 GPa)

**UF-HM Fibers (Near-Stoichiometric Composition)**

Elemental Analysis:	Si/C ratio: ~67-70 wt% Si/ ~30-33 wt% C
	Boron: ~0.1 - 3.0 wt%
	Oxygen: $\leq 0.2$ wt%
	Nitrogen: $\leq 0.2$ wt%
Phases:	well-crystallized $\beta$ -SiC trace amounts of graphitic Carbon, $\alpha$ -SiC
SiC Grain Size:	mostly ~0.05-0.3 $\mu$ m
Apparent Density:	~3.1-3.2 g/cm <sup>3</sup>
Diameter:	~10-15 $\mu$ m
Tensile Strength:	~300-500 ksi (~2.1-3.5 GPa)

g/cm<sup>3</sup>, with an average value of ~3.15 g/cm<sup>3</sup>. The latter value is 98% of the theoretical value of 3.21 g/cm<sup>3</sup> for fully dense (pore-free), stoichiometric SiC. The density is lower than the theoretical value, at least in part, because of the small amount of residual carbon. In addition, small amounts of fine pores (usually less than 0.1  $\mu$ m) were occasionally observed (by TEM) at some grain junctions.

Figure 1B shows a histogram plot of the average room temperature tensile strengths 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  $\mu$ m (std. dev. = 1.0  $\mu$ m). The tensile strengths

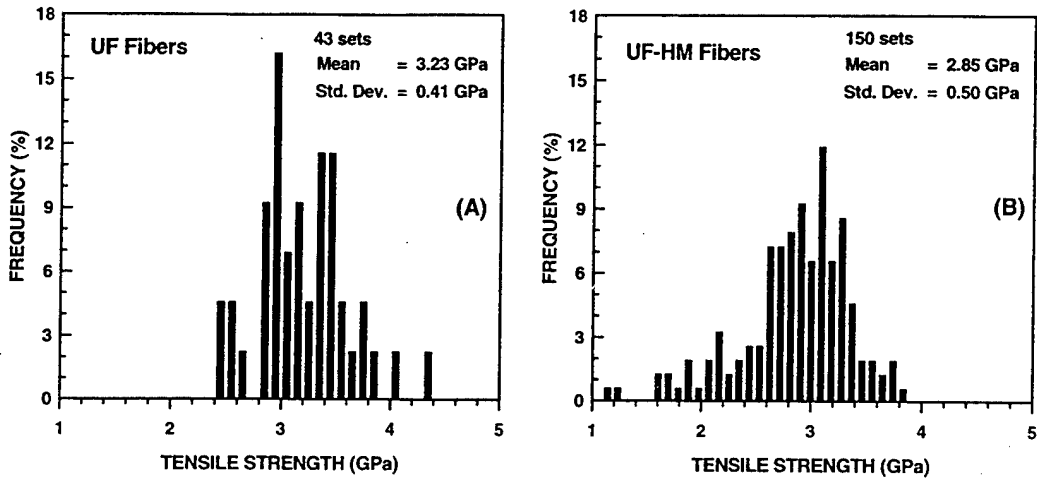


Fig. 1. Histogram plots of frequency vs. tensile strength for (A) UF fibers and (B) UF-HM fibers.

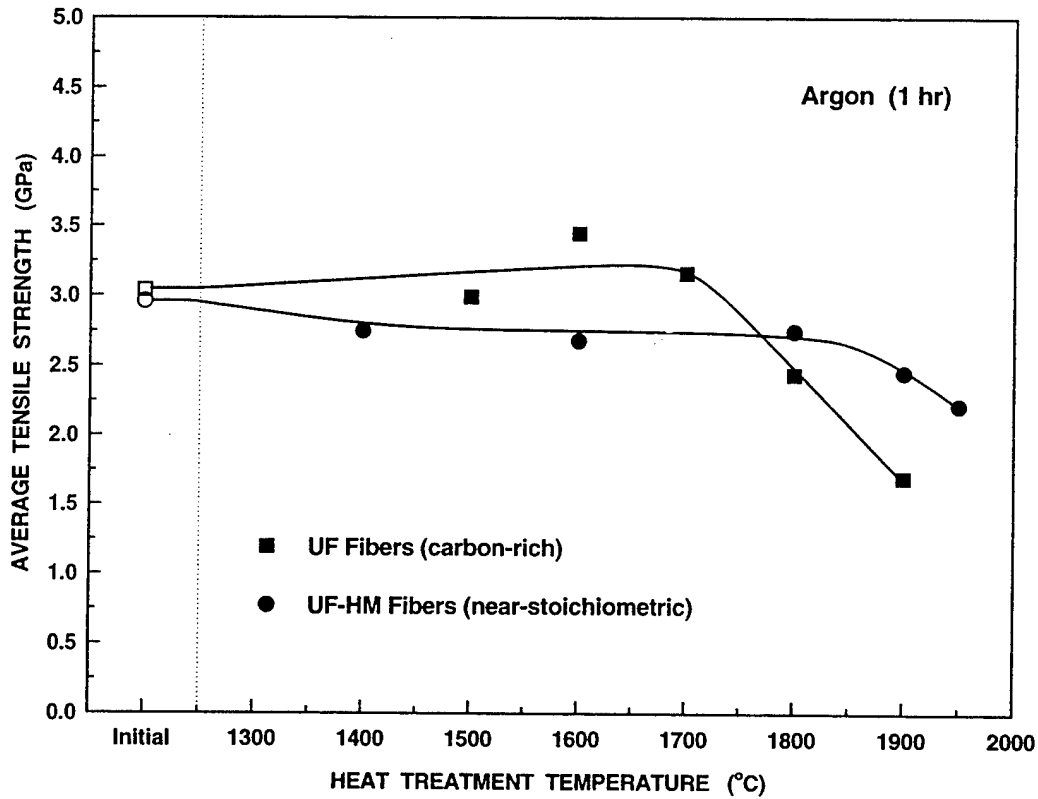


Fig. 2. Plots of average tensile strength vs. heat treatment temperature for UF fibers and UF-HM fibers.

of the UF-HM fibers were probably controlled primarily by larger grains at the fiber surface. (Fracture was generally initiated at the surface, but it was difficult to identify the specific flaws responsible for failure.)

Figure 2 shows room temperature tensile strengths for UF and UF-HM 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). The UF fibers showed no loss in strength with heat treatments up to 1700°C and then showed sharper decreases in strength (compared to the UF-HM fibers) with further heat treatments up to 1900°C. Despite these differences, both the UF fibers and the UF-HM fibers show greater retention of their original strengths after high temperature (e.g.,  $\geq 1600^\circ\text{C}$ ) heat treatments in argon compared to the strength retention reported for carbon-rich Hi-Nicalon<sup>TM</sup> fibers and near-stoichiometric Hi-Nicalon<sup>TM</sup> Type S fibers, respectively.[4,5,19]

As noted earlier, it is believed that the strength-controlling flaws for the as-prepared UF-HM fibers are larger grains at the fiber surfaces. Therefore, the gradual decrease in tensile strength in the UF-HM fibers after heat treatment in argon at higher temperatures is attributed to grain growth. A small increase in the grain sizes was confirmed by TEM observations on a 1950°C heat-treated sample.[20]

It is not clear why the UF fibers decrease in tensile strength at lower heat treatment temperature (and decrease more sharply with increasing temperature) compared to the UF-HM fibers. For Hi-Nicalon<sup>TM</sup> fibers, it has been suggested that the strength decreases upon heat treatment in inert atmospheres because of a combination of coarsening of SiC grains and flaw formation resulting from thermochemical degradation reactions.[19] (The presence of small amounts of residual oxygen in the Hi-Nicalon<sup>TM</sup> fibers is expected to result in the same type of carbothermal reduction reactions that occur in conventional Nicalon<sup>TM</sup> fibers.[21-24] Such reactions result in weight losses, formation of porosity, and coarsening of SiC grains.[21-24] However, in the case of Hi-Nicalon<sup>TM</sup> fibers, these effects are much less extensive due to the much lower oxygen content.) Although these strength-degradation mechanisms are not implausible, they do not appear to be the likely cause of the strength decay that is observed in Fig. 2 for the UF fibers. This is suggested for the following reasons:

- (1) UF fibers undergo SiC grain coarsening during heat treatment which is similar to that observed in Hi-Nicalon[24]; however, the grains remain smaller than the grains observed in the UF-HM fibers. Figures 3A and 3B show TEM micrographs for a UF fiber heat treated for 1 h at 1900°C (in argon) and a UF-HM fiber heat treated for 0.2 h at 1840°C (in argon), respectively. Despite heat treatment at the higher temperature and longer time, the UF fibers have a considerably smaller average grain size compared to the UF-HM fibers. (The relatively slow grain growth in the UF fibers can be attributed to the much larger amount of excess carbon. This is expected to inhibit the Si diffusional transport that is required for SiC grain coarsening.)
- (2) The carbothermal degradation reactions arising from the small amounts of residual oxygen are expected to begin at temperatures below 1700°C.[21-24] If these

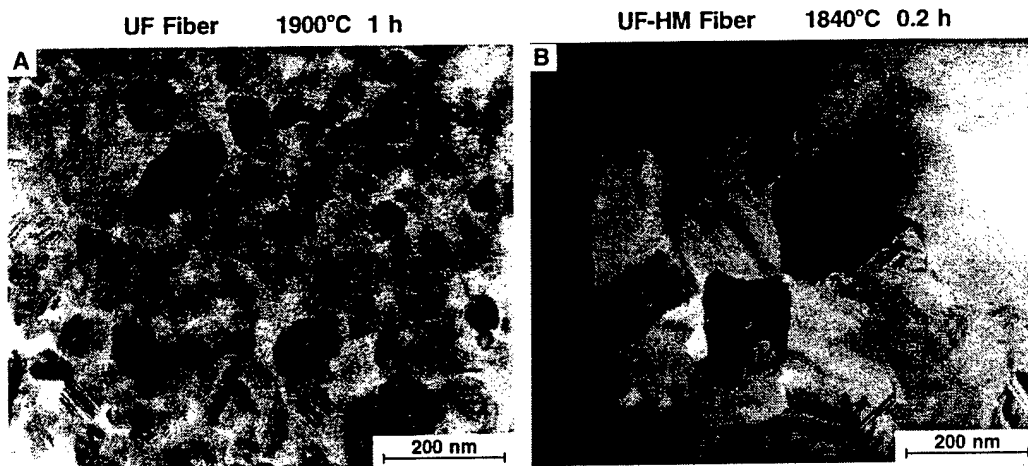


Fig. 3. TEM micrographs for (A) a UF fiber heat treated for 1 h at 1900°C and (B) a UF-HM fiber heat treated for 0.2 h at 1840°C.

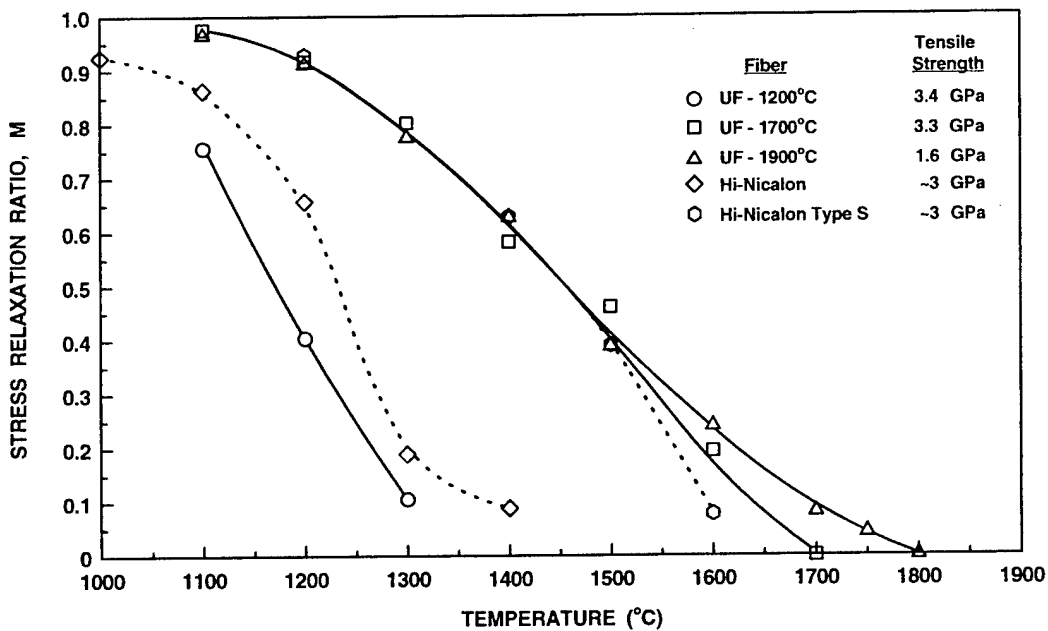


Fig. 4. Plots of stress relaxation ratio,  $M$ , vs. heat treatment temperature for as-prepared UF fibers (1200°C), heat-treated UF fibers (1700 and 1900°C), Hi-Nicalon fibers, and Hi-Nicalon Type S fibers.

reactions caused significant flaw formation in the UF fibers, then the strength decreases would be expected to begin at lower heat treatment temperatures. Furthermore, scanning electron microscope (SEM) observations of the fibers (including the fracture surfaces) did not reveal the development of any obvious flaws which could account for the sharp decreases in strength with heat treatments above 1700°C.

A possible explanation for the more rapid decay in strength of the UF fibers with heat treatment is the presence of residual tensile stresses at the fiber surface. Such stress might arise due to the mismatch in thermal expansion coefficients between SiC and C. These stresses could become more severe as the SiC/C structure coarsens during heat treatment at higher temperatures. (In addition to growth of the  $\beta$ -SiC grains, the carbon regions grow into larger and more highly ordered domains when PCS-derived carbon-rich SiC fibers are heat treated at temperatures above the original fabrication temperature.[19,25] The growth of the graphitic carbon regions also has significance because graphite has a very large difference in the thermal expansion coefficients for the directions parallel and normal to the hexagonal basal planes.)

The excellent strength retention of the UF and UF-HM fibers after high temperature heat treatments (e.g., compared to fibers such as Hi-Nicalon™ and Hi-Nicalon™ Type S) offers the possibility for improved high-temperature strength retention in ceramic-matrix composites (CMC's) that are fabricated with such fibers. Furthermore, two other advantages can be realized. First, higher temperatures can be used during the processing of CMC's (e.g., to produce matrices with higher relative density) without degradation of the properties of the fibers. Second, it is possible to prepare fibers with improved creep resistance, while still retaining high tensile strength. In regard to the latter consideration, it has been shown that Hi-Nicalon™ and Hi-Nicalon™ Type S fibers become more creep-resistant after annealing heat treatments above the original processing temperature.[6,26] (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.) The same effect (i.e., improved creep resistance in annealed fibers) was observed in the present study for the UF and UF-HM fibers. Figure 4 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. As expected, substantial increases in  $M$  values were obtained for the heat-treated UF fibers. The 1700°C heat-treated UF fibers not only show greatly improved creep resistance (based on the BSR test results), but also retain high tensile strength.

Figure 4 also includes BSR data reported [6,27-29] for Hi-Nicalon™ and Hi-Nicalon™ Type S fibers. The Hi-Nicalon™ fibers have 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 1700°C heat-treated UF fibers have  $M$  values comparable or better (for a given BSR test temperature) than the Hi-Nicalon™ Type S fibers. This occurs despite the fact that the grain sizes are larger for the latter fibers.[6] This observation again suggests 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, but also in the improved creep resistance of the fibers.)

Figure 5 shows that the creep resistance (as assessed by the BSR method) for the near-stoichiometric UF-HM fibers can also be improved by annealing heat treatments. In fact, the annealed UF-HM 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.[30] This resulted in fibers with considerably larger grain sizes, larger diameters, and rougher surfaces compared to typical polymer-derived SiC fibers. The coarser grain sizes result in fibers with excellent creep resistance, but relatively low tensile strength.)

Takeda et al.[6] have reported that annealing heat treatments can be used to improve the creep resistance of the Hi-Nicalon™ Type S fibers (as assessed by the BSR test). However, these fibers do not retain tensile strengths as high as the UF-HM fibers after the annealing heat treatments. This is illustrated in Fig. 6 which shows plots of tensile strengths vs.  $M$  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). It was possible to produce UF-HM fibers which had 1400°C BSR  $M$  values of  $\sim 0.9$ , while still retaining tensile strengths of  $\sim 3$  GPa. In contrast, 1400°C BSR  $M$  values of only  $\sim 0.6$  were possible in Hi-Nicalon™ Type S fibers which retained tensile strengths of  $\sim 3$  GPa.

### BN-Coated UF-HM fibers

UF-HM fibers with BN surface coatings were prepared by an in-situ process which is schematically illustrated in Fig. 7 (top). Boron-doped fibers were heat treated in a nitrogen-containing atmosphere. BN forms by reaction of boron at the surface with nitrogen in the atmosphere. After the initial reaction at the original SiC fiber surface, it is presumed that the increases in thickness of the coating occur by diffusion of boron from the interior of the fiber to the reaction layer, followed by chemical interdiffusion of boron and nitrogen through the growing BN layer.

Figure 7 (bottom left) shows a TEM micrograph of the BN coatings formed on the UF-HM fibers. Typical coating thicknesses were  $\sim 0.1$ - $0.2 \mu\text{m}$ , although it may be possible to increase the thickness by using SiC fibers with higher initial boron content. Figure 7 (bottom right) shows an HRTEM micrograph of the BN layer. Electron diffraction analysis and the lattice spacing value (0.346 nm) show that the layer is hexagonal BN. The HRTEM micrograph also shows that the coating grows such that the hexagonal BN basal planes are oriented mostly perpendicular to the long axis of the UF-HM fibers.

UF-HM fibers prepared with the BN coatings retained high strength ( $\sim 3$  GPa) and excellent creep resistance. The effectiveness of the BN coatings for developing weak fiber/matrix interfaces in CMC's has not yet been evaluated.

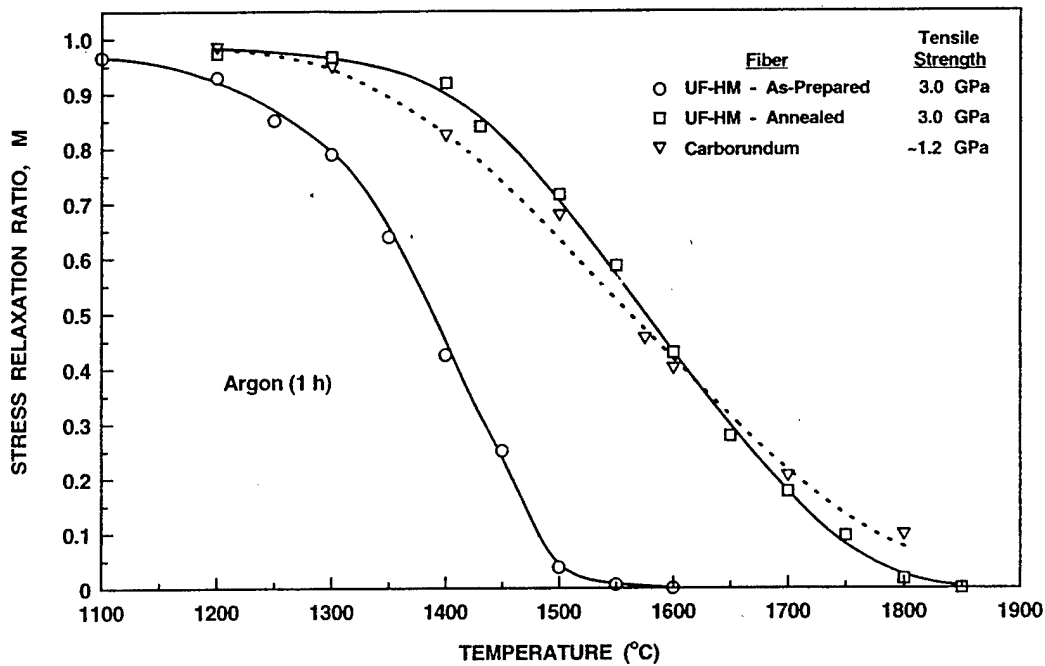


Fig. 5. Plots of stress relaxation ratio,  $M$ , vs. heat treatment temperature for as-prepared UF-HM fibers, heat-treated UF-HM fibers, and Carborundum fibers.

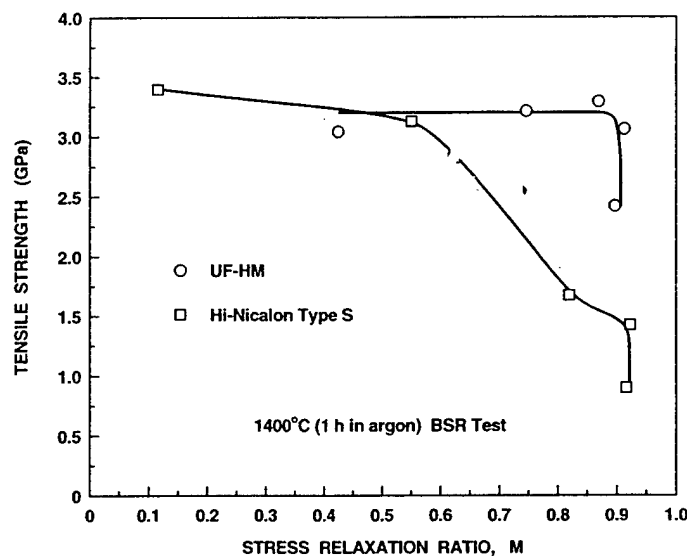


Fig. 6. Plots of tensile strength vs. stress relaxation ratio,  $M$ , for UF-HM fibers and Hi-Nicalon Type S fibers which were given varying annealing treatments in order to alter the  $M$  values. The BSR test temperature was  $1400^{\circ}\text{C}$ .

## IN-SITU PROCESSING OF BN COATINGS

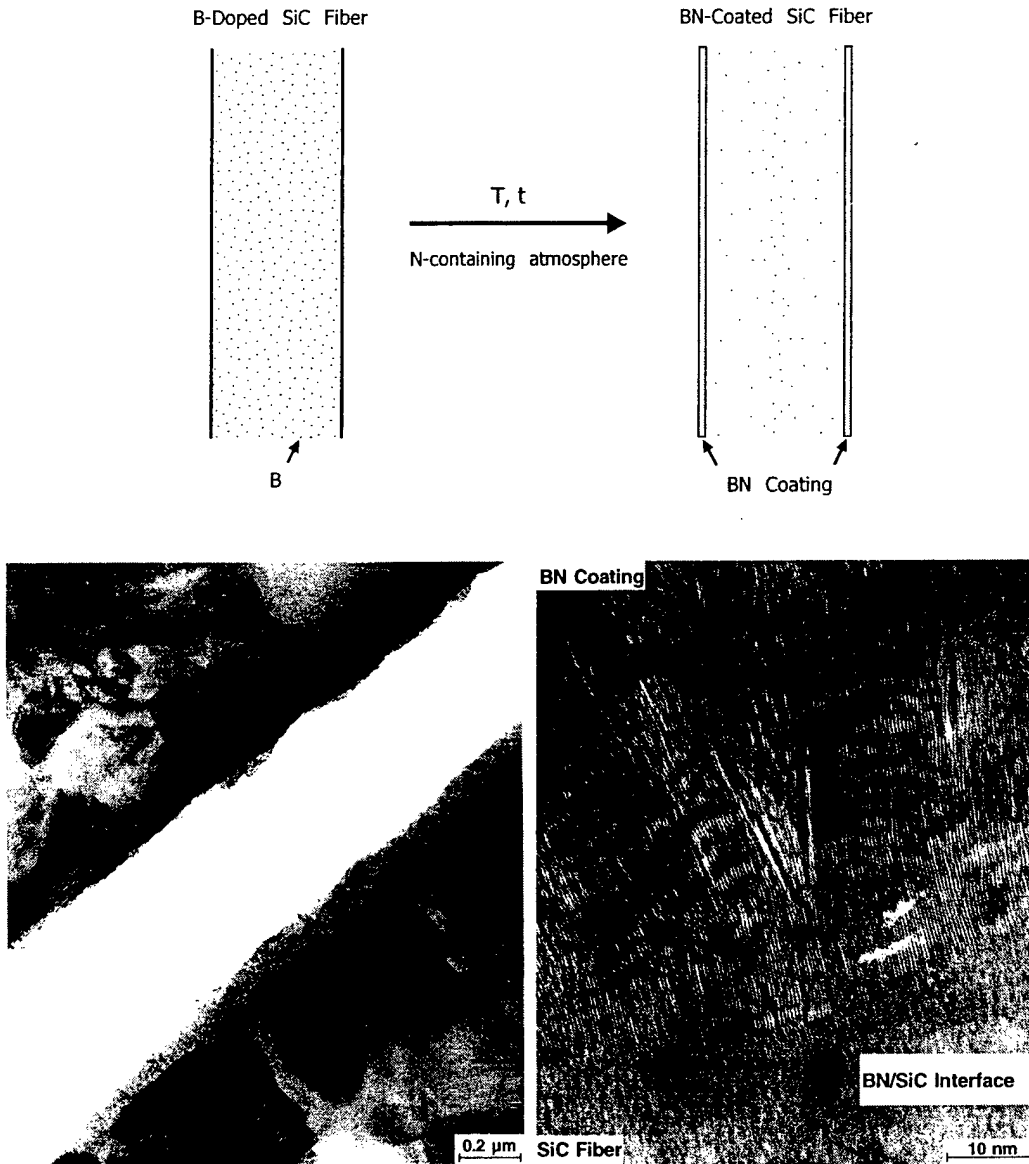


Fig. 7. Top: Schematic illustration of the formation of a BN coating on a SiC fiber by in-situ processing. Bottom left: TEM micrograph showing BN coatings and SiC fiber grains. Bottom right: HRTEM micrograph showing the BN coating/SiC fiber interface and the lattice planes of the BN coating. The BN basal planes grow with an orientation that is mostly perpendicular to the long axis of the SiC fiber.

## CONCLUSION

Polymer-derived, SiC-based fibers with high tensile strength ( $\sim 3$  GPa) and fine diameter ( $\sim 10$ - $15$   $\mu\text{m}$ ) were fabricated with carbon-rich (UF) and near-stoichiometric (UF-HM) compositions. UF fibers retained tensile strengths of  $\sim 3$  GPa after heat treatments in argon (for 1 h) at temperatures up to  $1700^\circ\text{C}$ . Heat treatments resulted in significant improvements in creep resistance as assessed by bend stress relaxation (BSR) measurements. UF fibers heat treated at  $1700^\circ\text{C}$  showed BSR creep behavior similar to that reported for Hi-Nicalon<sup>TM</sup> Type S fibers. The near-stoichiometric UF-HM fibers showed even better strength retention than the carbon-rich UF fibers after high temperature heat treatments. In addition, heat-treated UF-HM fibers showed BSR creep resistance which was significantly better than that reported for Hi Nicalon<sup>TM</sup> Type S fibers and was similar to that reported for the relatively low-strength Carborundum fibers. The near-stoichiometric UF-HM fibers were also prepared with hexagonal BN coatings using an in-situ processing method. These fibers retained high strength and excellent BSR creep resistance.

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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.<sup>1,2</sup> 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.<sup>3–6</sup> To minimize this problem, there has been considerable effort in recent years to prepare organosilicon polymer-derived SiC fibers with low oxygen content.<sup>7–20</sup> 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),<sup>7–12</sup> Dow Corning Co. (near-stoichiometric Sylramic™ fibers),<sup>13–16</sup> and the University of Florida (carbon-rich UF and near-stoichiometric UF-HM fibers).<sup>17–20</sup> These SiC-based fibers show significantly improved thermo-mechanical 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.<sup>21</sup>

## 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.<sup>17–20</sup> The infusible PCS polymers were prepared by pressure pyrolysis of polydimethylsilane.<sup>18,19</sup> 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.<sup>18,19</sup> 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  $\sim 1000$ – $1200$  °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 ( $\sim 100$ – $200$  °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<sub>x</sub>O<sub>y</sub> ceramic (at  $< 1200$  °C) and to subsequently effect the carbothermal reduction reductions (at  $\sim 1400$ – $1600$  °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  $\geq 1750$  °C) in inert atmosphere. Boron additions (typically  $\sim 1$  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).<sup>22</sup> The liquids used were methylene iodide (CH<sub>2</sub>I<sub>2</sub>, density  $\sim 3.3$  g ml<sup>-1</sup>) and carbon tetrachloride (CCl<sub>4</sub>, density  $\sim 1.6$  g ml<sup>-1</sup>).

Fiber tensile strengths were determined at room temperature according to ASTM procedure D3379.<sup>23</sup> Individual fibers were glued to paper tabs and loaded in tension ( $0.5$  mm min<sup>-1</sup> 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.<sup>21</sup> 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  $\sim 59$ – $62$  wt% Si/ $38$ – $41$  wt% C, with an average ratio (determined from 8 samples) of  $\sim 60.5$  wt% Si/ $\sim 39.5$  wt% C. Hence, these fibers were highly carbon-rich compared to stoichiometric SiC ( $\sim 70$  wt% Si/ $\sim 30$  wt% C). Some oxygen impurity was incorporated in the fiber during the various stages of processing,<sup>18</sup> but the concentrations for the fibers used in this study were limited to  $\sim 0.5$ – $1.0$  wt%. Some of the fibers were also doped with small amounts of boron ( $< 1$  wt%). The phases present in the UF fibers were  $\beta$ -SiC and XRD-amorphous carbon. TEM and XRD line-broadening measurements indicated that the  $\beta$ -SiC crystallite sizes were  $< 5$  nm. Sink-float measurements showed that the

fiber apparent densities were in the range of  $\sim 2.5$ – $2.7 \text{ g cm}^{-3}$ . 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  $\sim 3.21 \text{ g cm}^{-3}$ .)

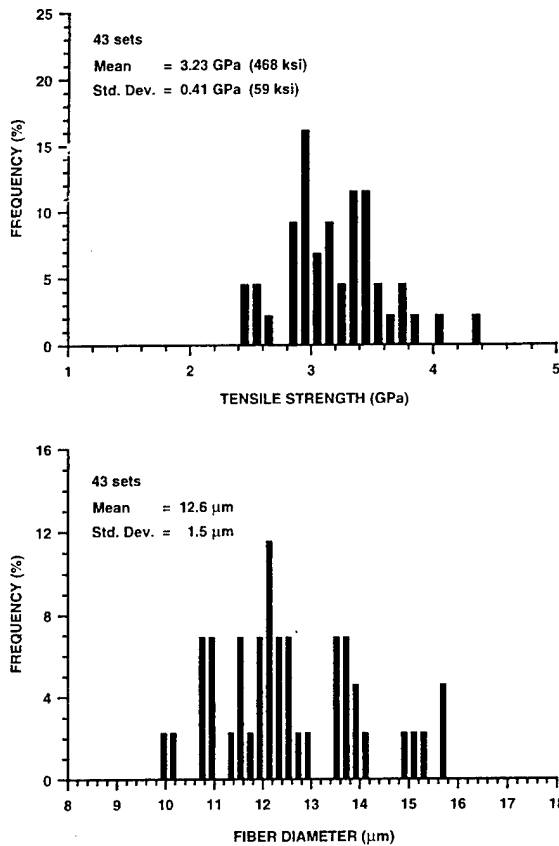


Fig. 1. Histogram plots of frequency versus average tensile strength and frequency versus average diameter for 43 sets of carbon-rich UF fibers.

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,  $\geq 15$  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  $\mu\text{m}$ .

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.  $\sim 3 \text{ GPa}$ ) typically have flaws in the range of  $\sim 0.2$ – $0.3 \mu\text{m}$ . This corresponds closely to the smallest pore sizes of the filters (nominal sizes were  $0.1$ – $0.2 \mu\text{m}$ ) that were used to prepare the spinning solutions for fiber fabrication. In previous work,<sup>18</sup> 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  $\sim 67$ – $70 \text{ wt}\%$  Si/ $30$ – $33 \text{ wt}\%$  C, with an average composition (determined from  $> 25$  samples) of  $\sim 68.5 \text{ wt}\%$  Si/ $\sim 31.5 \text{ wt}\%$  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

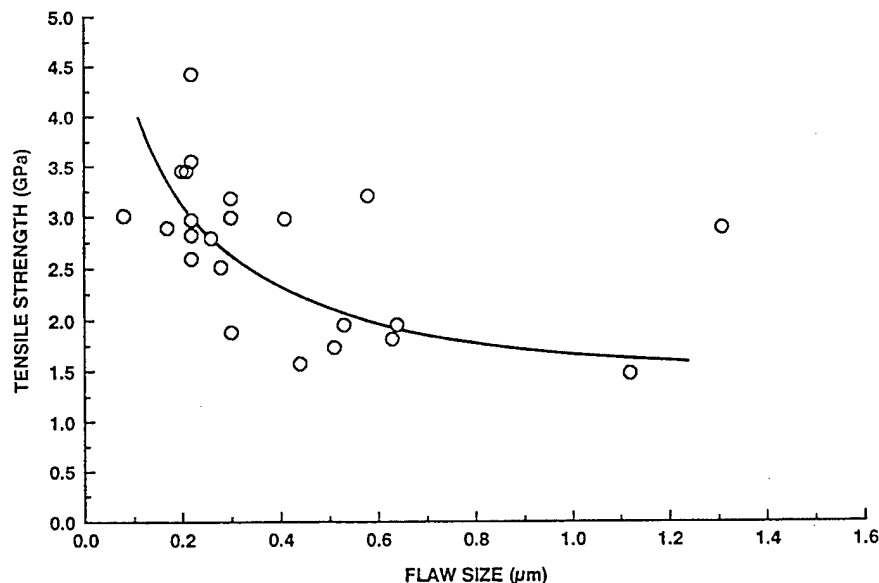


Fig. 2. Plot of tensile strength versus flaw size for individually tested UF fibers.

units with interplanar spacing of 0.34 nm that are associated with graphitic carbon. X-ray and electron diffraction analyses showed that  $\beta$ -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.  $\sim 0.1$ – $3.0$  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  $\sim 3.15$  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  $0.1$   $\mu$ m) 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  $12.1$   $\mu$ m. 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  $\sim 0.05$ – $0.3$   $\mu$ m, grains as large as  $\sim 0.5$ – $1.0$   $\mu$ m 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  $1500$ – $1900$   $^{\circ}$ C. There was no loss in strength with heat treatments up to  $1700$   $^{\circ}$ C and then the strength decreased rapidly with further heat treatments up to  $1900$   $^{\circ}$ C. Fig. 5 also shows that the UF fibers have greater retention of their original strengths after high temperature (e.g.  $\geq 1600$   $^{\circ}$ C) heat treatments in argon compared to the strength retention reported for carbon-rich Hi-Nicalon<sup>®</sup> fibers.<sup>10,11,24</sup>

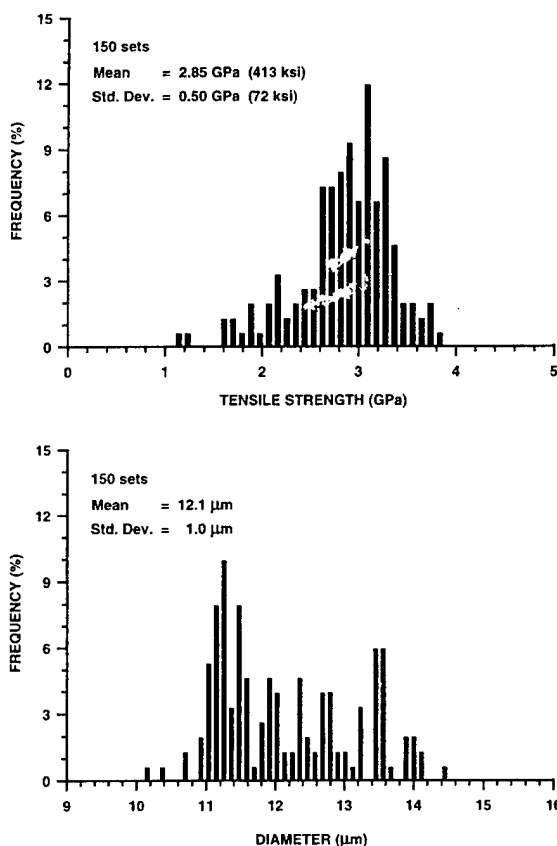


Fig. 3. Histogram plots of frequency versus average tensile strength and frequency versus average diameter for 150 sets of near-stoichiometric UF-HM fibers.



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

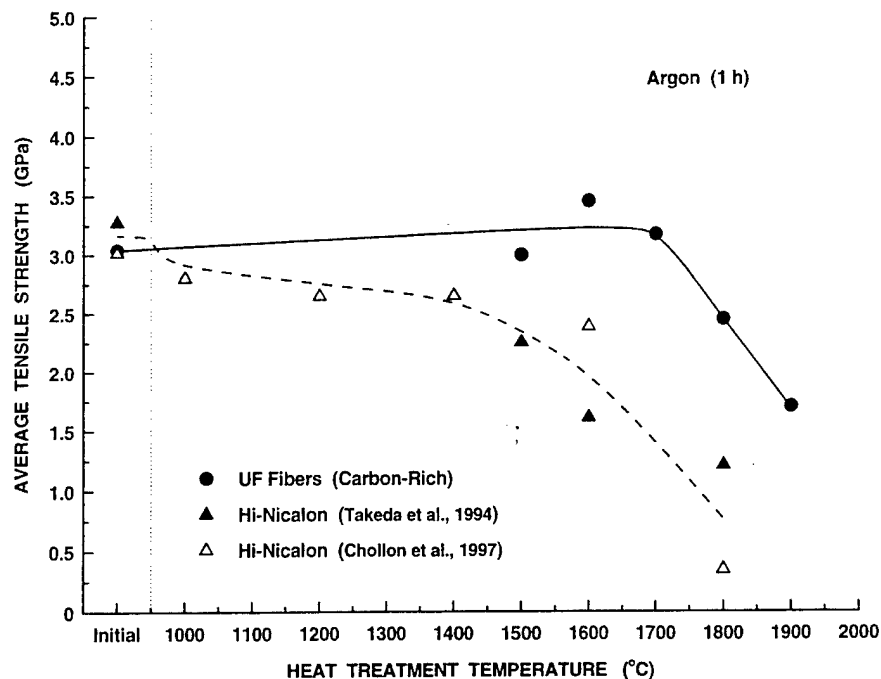


Fig. 5. Plot of average tensile strength versus heat treatment temperature (in argon for 1 h) for carbon-rich UF fibers. Data reported by other researchers for Hi-Nicalon<sup>®</sup> fibers are also shown.

For Hi-Nicalon<sup>®</sup> 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.<sup>24</sup> 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  $\beta$ -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.<sup>24,25</sup> 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<sup>®</sup> 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.<sup>8,18</sup> 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<sup>®</sup> and Hi-Nicalon<sup>®</sup> Type S fibers become more creep-resistant after annealing heat treatments above the original processing temperature.<sup>12,26</sup> 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.

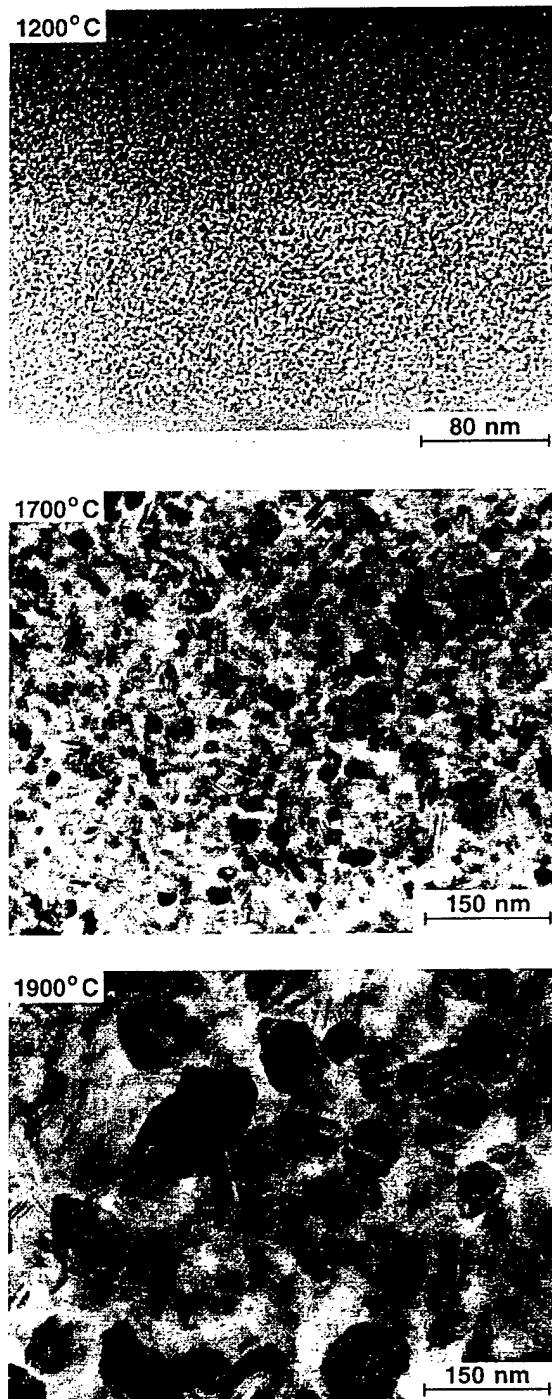


Fig. 6. TEM micrographs for as-pyrolyzed carbon-rich UF fibers (1200°C) and for UF fibers heat treated in argon for 1 h at 1700 and 1900°C.

Figure 7 also shows the BSR data that has been reported<sup>12,27-29</sup> for Hi-Nicalon<sup>®</sup> and Hi-Nicalon<sup>®</sup> Type S fibers. The Hi-Nicalon<sup>®</sup> 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<sup>®</sup> fibers

which, in turn, results in slightly coarser microstructures (including larger SiC crystallite sizes). The Hi-Nicalon<sup>®</sup> Type S fibers have significantly higher  $M$  values (for a given BSR test temperature) compared to the Hi-Nicalon<sup>®</sup> fibers and the as-pyrolyzed UF fibers. This is attributed to the much larger grain sizes of the Hi-Nicalon<sup>®</sup> Type S fiber.<sup>12</sup>

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<sup>®</sup> Type S fibers. This occurs despite the fact that the grain sizes are much larger for the latter fibers.<sup>12</sup> 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

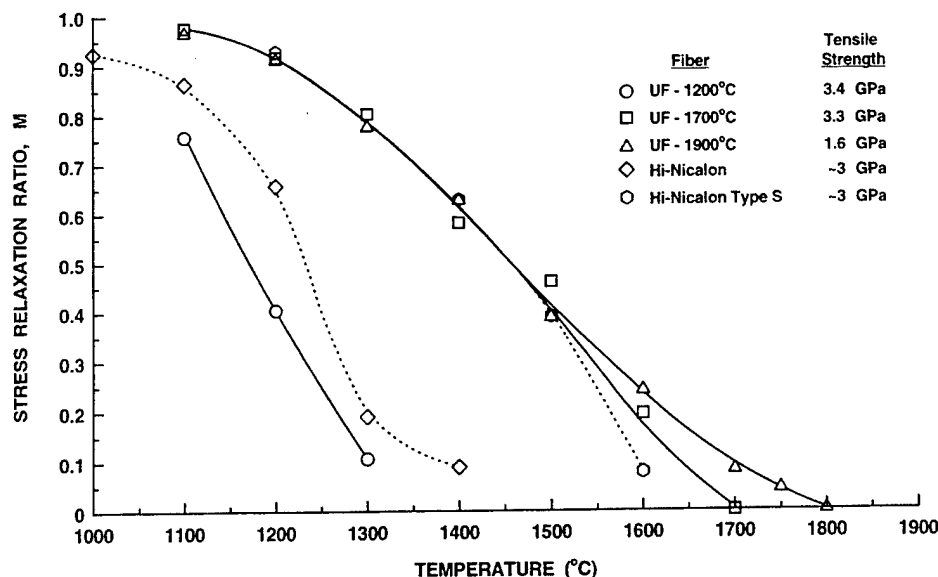


Fig. 7. Plots of stress relaxation ratio,  $M$ , versus heat treatment temperature for as-pyrolyzed carbon-rich UF fibers (1200°C), argon heat-treated (1700 and 1900°C) UF fibers, Hi-Nicalon<sup>®</sup> fibers, and Hi-Nicalon<sup>®</sup> Type S fibers.

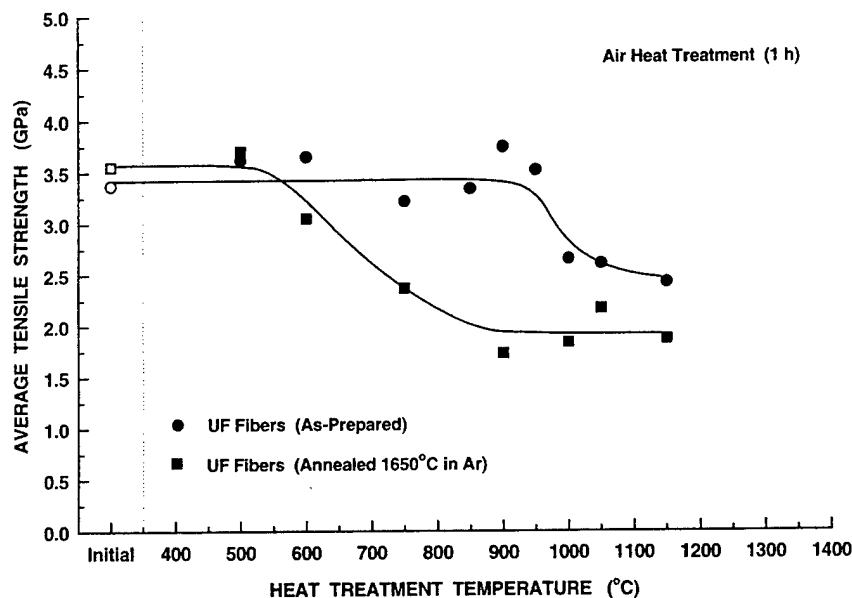


Fig. 8. Plots of average tensile strength versus heat treatment temperature (in air for 1 h) for as-pyrolyzed carbon-rich UF fibers and for argon heat-treated (1650°C) UF fibers.

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  $\sim 1950^\circ\text{C}$ . The reason for this behavior is

unclear, but it is believed to be associated with the formation of a thin BN layer ( $\sim 0.1\text{--}0.2\ \mu\text{m}$ ) 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.<sup>30</sup> 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.

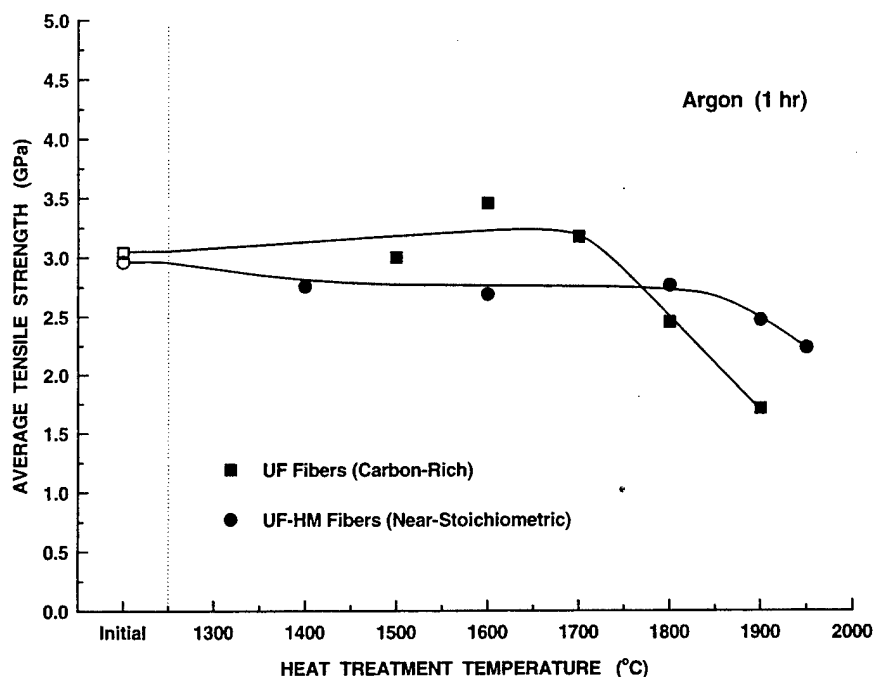


Fig. 9. Plots of average tensile strength versus heat treatment temperature (in argon for 1 h) for carbon-rich UF fibers and near-stoichiometric UF-HM fibers.

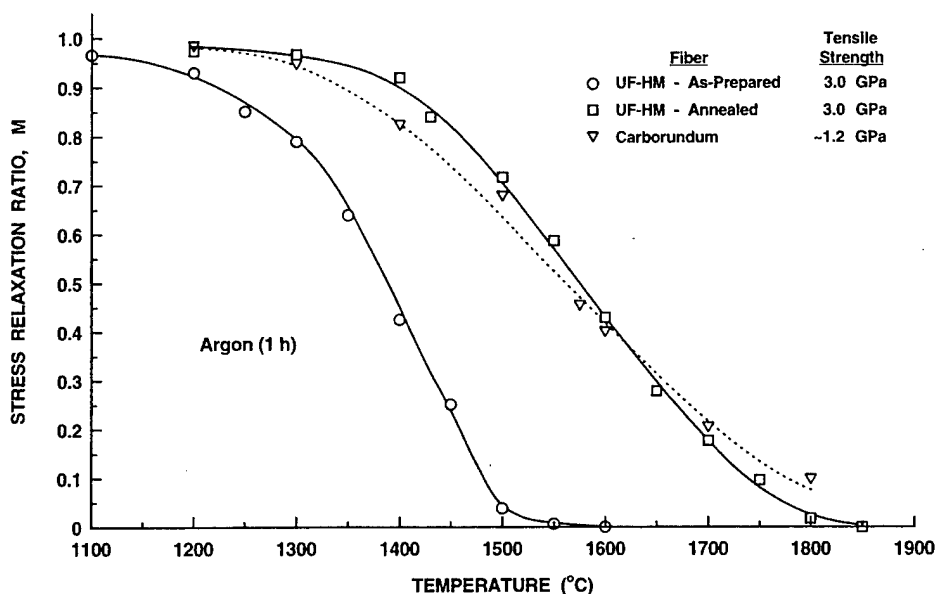


Fig. 10. Plots of stress relaxation ratio,  $M$ , versus heat treatment temperature for as-sintered near-stoichiometric UF-HM fibers, heat-treated UF-HM fibers, and Carborundum fibers.

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<sup>27-29</sup> 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.<sup>31</sup> 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.*<sup>12</sup> reported that annealing heat treatments improved the creep resistance of Hi-Nicalon<sup>®</sup> 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<sup>®</sup> 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  $\sim 0.9$ , while still retaining tensile strengths of  $\sim 3$  GPa. In contrast, 1400°C BSR  $M$  values of only  $\sim 0.6$  were possible in Hi-Nicalon<sup>®</sup> Type S fibers which retained tensile strengths of  $\sim 3$  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  $\pm 1$  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  $\sim 10$ – $20$  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.

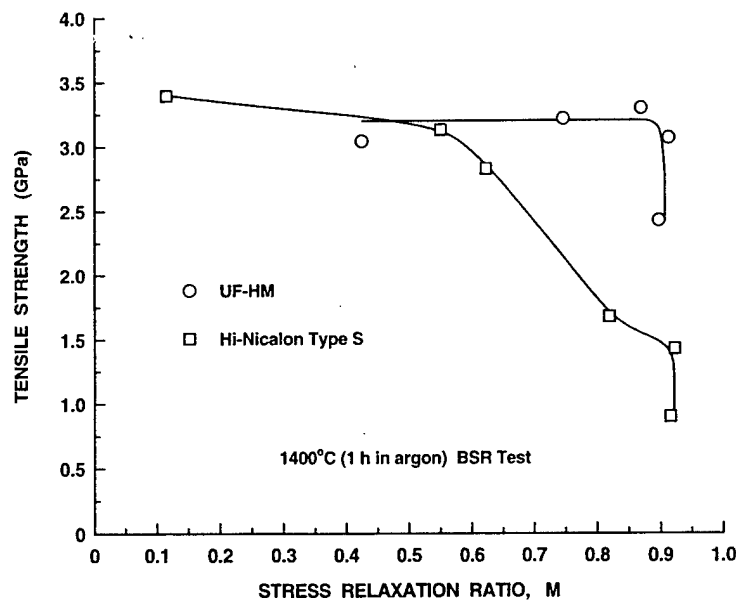


Fig. 11. Plots of tensile strength versus stress relaxation ratio,  $M$ , for near-stoichiometric UF-HM fibers and Hi-Nicalon Type S fibers which were given varying annealing treatments in order to alter the  $M$  values. The BSR tests were carried out at 1400°C.

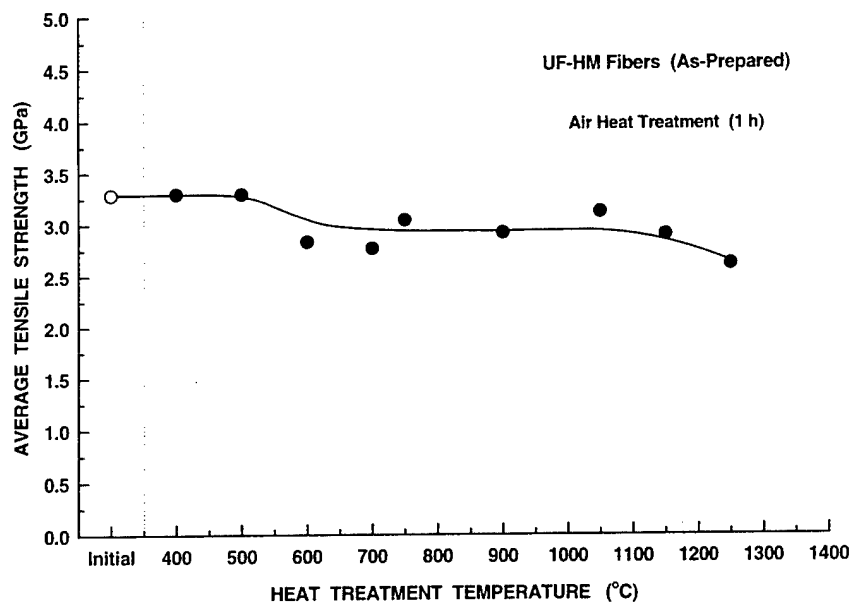


Fig. 12. Plot of average tensile strength versus heat treatment temperature (in air for 1 h) for near-stoichiometric UF-HM fibers.

#### 4 Conclusions

Carbon-rich and near-stoichiometric SiC fibers with fine-diameter ( $\sim 10\text{--}15\ \mu\text{m}$ ) and high tensile strength ( $\sim 3\ \text{GPa}$ ) 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  $1700^\circ\text{C}$  and then showed relatively a sharp decrease 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  $1800^\circ\text{C}$  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 ( $1950^\circ\text{C}$ ) when heat treatments were carried in nitrogen. This observation was associated with the formation of a thin BN layer ( $\sim 0.1\text{--}0.2\ \mu\text{m}$ ) 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  $1700^\circ\text{C}$  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<sup>®</sup> 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  $400\text{--}1150^\circ\text{C}$ . Interfilament adhesion occurred when the fiber bundles were heat treated at  $1250^\circ\text{C}$ , 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  $1650^\circ\text{C}$  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  $1650^\circ\text{C}$  fibers.

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## SILICON CARBIDE FIBERS WITH BORON NITRIDE COATINGS

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### ABSTRACT

SiC fibers were prepared with boron nitride (BN) coatings using an in-situ processing method. Scanning Auger electron spectroscopy, X-ray photoelectron spectroscopy, and transmission electron microscopy showed that the coatings were uniformly distributed, well-crystallized, hexagonal BN. The coated fibers had high strength ( $\sim 3$  GPa) and excellent creep resistance based on bend stress relaxation tests.

### INTRODUCTION

Boron nitride is a common interphase material in fiber-reinforced ceramic-matrix composites (CMC's).[1-3] In particular, it has been shown that thin BN interfacial layers can be used to produce relatively weak bonding between the fiber and matrix phases and thereby allow the development of toughened (damage-tolerant) CMC's. Chemical vapor deposition is the most commonly used to produce BN coatings on fibers, especially for SiC-based fibers.[1-4] Another method is to dip-coat the fibers with a boron precursor (e.g., boric acid) and subsequently heat treat the fibers in ammonia at elevated temperature to form a BN reaction product.[5] The formation of "in-situ" BN coatings on Nextel 312<sup>TM</sup> boroaluminum silicate fibers has also been reported.[6] In this method, the BN is formed at the fiber surface by high temperature reaction between boria in the fibers and ammonia in the gas atmosphere. The aforementioned methods for forming BN coatings on fibers each have one or more disadvantages: (i) difficulty in forming uniform coatings throughout fiber tows, (ii) use of gas-phase reactants and by-products which are corrosive and/or toxic, and (iii) high cost. In the present study, an in-situ method was developed for producing uniform, low-cost BN coatings on near-stoichiometric SiC fibers without the use of hazardous gases.

## EXPERIMENTAL

The starting material used in this study was fine-diameter, high-strength, near-stoichiometric SiC fibers which are homogeneously doped with boron. The fabrication methods for producing these fibers has been described in detail previously.[7-9] The fibers were prepared by dry spinning of concentrated polymer solutions which contained high-molecular-weight polycarbosilane (PCS) as the primary ceramic precursor.[7-9] The spinning solutions contained soluble boron hydride in order to incorporate boron in the fibers. Boron is used both as a sintering aid for SiC and as a reactant for the formation of BN coatings by in-situ processing. After spinning, the polymeric fibers were dried and subsequently given several heat treatments [8,9] in order to produce near-stoichiometric SiC fibers with high relative density and a homogeneous distribution of boron.

The properties of the as-prepared (sintered) near-stoichiometric SiC fibers have been described previously [9] and are summarized as follows: (i)  $\sim 10\text{-}15\ \mu\text{m}$  diameter, (ii)  $\sim 3\ \text{GPa}$  tensile strength, (iii)  $\sim 3.15\ \text{g/cm}^3$  apparent density (determined by a sink-float method, ASTM procedure D3800-79 [10]), (iv) near-stoichiometric (but carbon-rich) chemical composition with an average normalized Si/C ratio of  $\sim 68.5\ \text{wt}\% \text{ Si}/\sim 31.5\ \text{wt}\% \text{ C}$  (based on electron microprobe analysis, EMA); residual oxygen and nitrogen contents below the resolution limit of EMA ( $\leq 0.2\ \text{wt}\%$ ); boron concentrations in the range of  $\sim 0.75\text{-}2.5\ \text{wt}\%$  (based on neutron activation analysis); (v) phase composition consisting mostly of  $\beta\text{-SiC}$  (based on X-ray diffraction and electron diffraction); some graphitic carbon (observed by TEM); traces of  $\alpha\text{-SiC}$  (observed in some fibers by electron diffraction).

BN surface coatings were formed on the SiC fibers by an in-situ process which is schematically illustrated in Fig. 1. The boron-doped SiC fibers were heat treated in a nitrogen-containing atmosphere. BN forms by reaction of boron at the surface with nitrogen in the atmosphere. After the initial reaction at the original SiC fiber surface, it is presumed that the increases in thickness of the coating occur by diffusion of boron from the interior of the fiber to the reaction layer, followed by chemical interdiffusion of boron and nitrogen through the growing BN layer.

Surface chemical analysis of the coated fibers was carried out using X-ray photoelectron spectroscopy, XPS, (XSAM 800, Kratos Analytical) and scanning Auger microprobe analysis, SAM, (PHI 660, Perkin-Elmer Corp). The XPS data were collected from a group of fibers, while the SAM analysis was carried out on individual fibers. Conventional and high resolution transmission electron microscopy (TEM and HRTEM) were used to characterize the coated fiber microstructure.

Single-filament tensile strengths were determined at room temperature according to

ASTM procedure D3379.[11] The fiber gage length was 25 mm. The creep behavior of fibers was assessed using the bend stress relaxation (BSR) method.[12] 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.

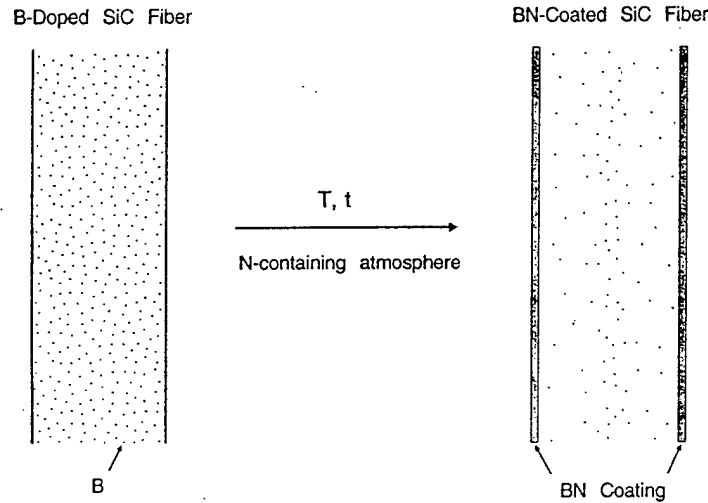


Fig. 1. Schematic illustration of the formation of a BN coating on a SiC fiber by in-situ processing.

## RESULTS AND DISCUSSION

The formation of BN coatings on the SiC fibers was shown by surface chemical analyses. Figure 2A shows a SAM survey scan for the initial (uncoated) sintered SiC fiber. The surface composition of this fiber is dominated primarily by carbon. This is due to preferential evaporation of Si from the SiC at the surface during the high temperature sintering treatment under an argon atmosphere. The small oxygen peak observed in Fig. 2A is probably due adventitious contamination during the SAM sample preparation and/or analysis. (This is suggested by observations that (i) the oxygen peak is reduced or eliminated by carrying out argon ion sputtering (for 1 min) to remove an  $\sim 10$  nm surface layer and (ii) oxygen was not detected by electron microprobe analyses on polished fiber cross-sections.) Figure 2B shows a SAM survey scan for the SiC fiber after the heat treatment to form the in-situ BN coating. It is evident that the surface of the fiber is now dominated by B and N.

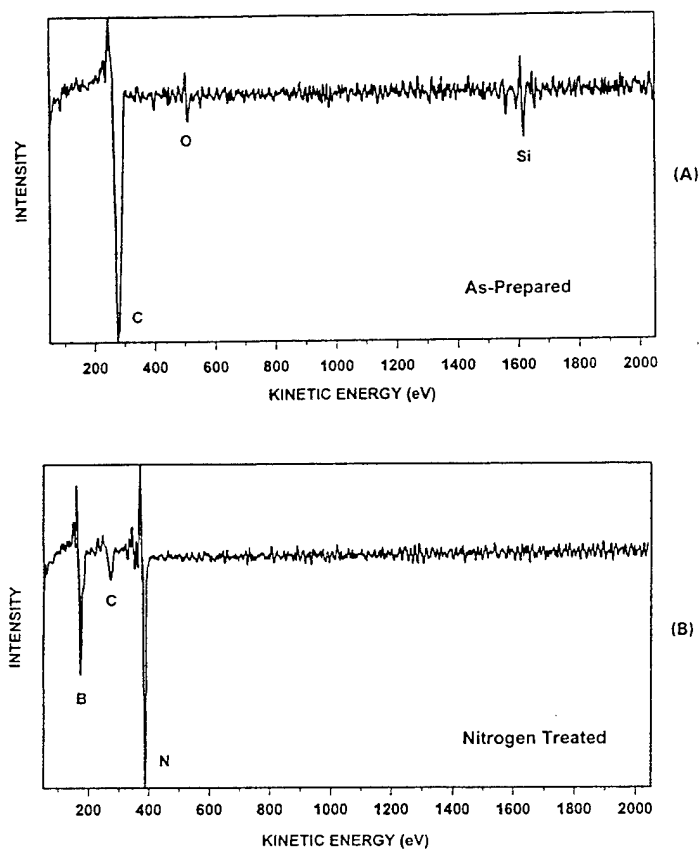


Fig. 2. SAM survey scans for (A) uncoated SiC fiber (sintered in argon) and (B) SiC fiber with in-situ BN coating (nitrogen heat treatment).

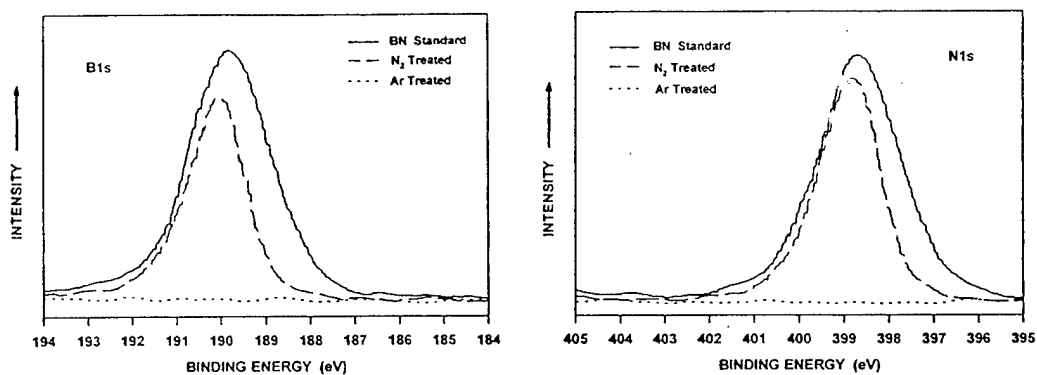


Fig. 3. XPS spectral regions for boron (left) and nitrogen (right) for three samples: as-prepared (uncoated) SiC fibers (sintered in argon), SiC fibers with an in-situ BN coating (nitrogen treatment), and hexagonal BN powder.

The formation of the BN coating was also confirmed by XPS. Figure 3 shows high resolution scans in regions specific to boron and nitrogen for three different samples: as-prepared SiC fibers (sintered in argon), SiC fibers after heat treatment to form the in-situ BN coating (nitrogen treatment), and hexagonal BN powder (UBN-C, Ube Co.). It is evident that the spectra obtained from the BN coatings on the fibers are very similar to those of the BN powder "standard."

Figure 4 (left side) shows a TEM micrograph of the BN coatings formed on the SiC fibers. Typical coating thicknesses were  $\sim 0.1-0.2 \mu\text{m}$ . Electron diffraction analysis showed that the BN was the hexagonal phase. High resolution TEM (right side) showed a lattice spacing value of 0.346 nm which is close to the expected value for hexagonal BN. The HRTEM micrograph also shows that the coating grows such that the hexagonal BN basal planes are oriented mostly perpendicular to the long axis of the SiC fibers.

Fibers prepared with the BN coatings had the same high tensile strength ( $\sim 3$  GPa) as the original fibers and also showed excellent creep resistance. Figure 5 shows a plot of the bend stress relaxation  $M$  value vs. temperature for BN-coated fibers. The  $M$  values at elevated temperatures ( $\geq 1300^\circ\text{C}$ ) are higher than reported for other fine-diameter near-stoichiometric SiC fibers with comparable tensile strength.[13-16]

## CONCLUSION

Fine-diameter ( $\sim 10-12 \mu\text{m}$ ), high-strength ( $\sim 3$  GPa), near-stoichiometric SiC fibers were prepared with boron nitride (BN) coatings by an in-situ processing method. Characterization by TEM, XPS, and SAM showed that the coatings were uniformly distributed on the fiber surfaces with a thickness of  $\sim 0.1-0.2 \mu\text{m}$  and consisted of well-crystallized hexagonal BN. The coated fibers had high tensile strength ( $\sim 3$  GPa) and excellent BSR creep resistance.

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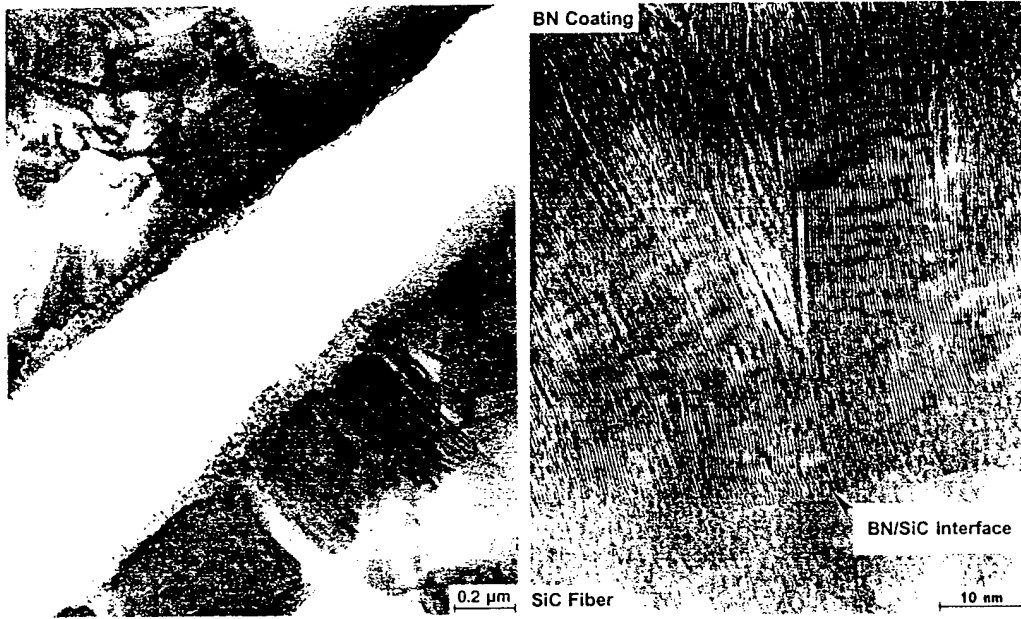


Fig. 4. Left: TEM micrograph showing BN coatings and SiC fiber grains. Right: HRTEM micrograph showing the BN coating/SiC fiber interface and the lattice planes of the BN coating. The BN basal planes grow with an orientation that is mostly perpendicular to the long axis of the SiC fiber.

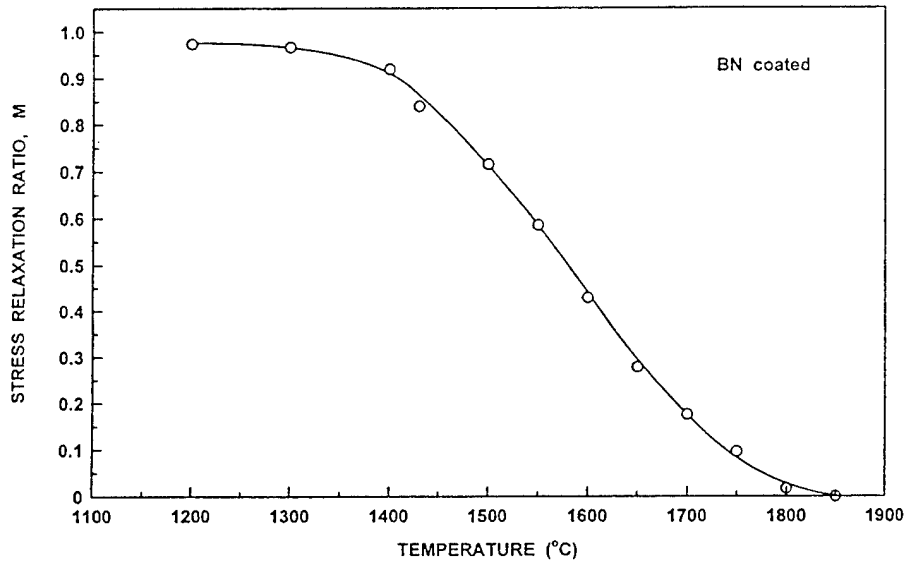


Fig. 5. Plot of stress relaxation ratio,  $M$ , vs. heat treatment temperature for BN-coated fibers.

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## CREEP BEHAVIOR OF POLYMER-DERIVED SiC-BASED FIBERS

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### ABSTRACT

Polymer-derived SiC-based fibers with fine-diameter ( $\sim 10\text{-}15\ \mu\text{m}$ ) and high strength ( $\sim 3\ \text{GPa}$ ) were prepared with carbon-rich and near-stoichiometric compositions. The creep resistance of these fibers (as assessed by bend stress relaxation, BSR, measurements) could be improved significantly by annealing heat treatments in nonoxidizing atmospheres. Fibers also showed excellent strength retention after annealing heat treatments up to  $1700^\circ\text{C}$  for the carbon-rich fibers and up to  $1950^\circ\text{C}$  for the near-stoichiometric fibers. The near-stoichiometric fibers could be prepared with  $\sim 3\ \text{GPa}$  tensile strength and BSR creep behavior which was significantly better than previously reported for other types of polymer-derived SiC-based fibers.

### INTRODUCTION

There has been considerable effort in recent years to prepare organosilicon polymer-derived SiC-based fibers with fine-diameter, high tensile strength, and improved thermomechanical stability.[1-11] The development of such fibers with both carbon-rich and near-stoichiometric compositions has been reported by various researchers, including those at Nippon Carbon Co. (carbon-rich Hi-Nicalon<sup>TM</sup> and near-stoichiometric Hi-Nicalon<sup>TM</sup> Type S fibers)[1-4], Dow Corning Co. (near-stoichiometric Sylramic<sup>TM</sup> fibers)[5-7], Ube Industries Ltd. (near-stoichiometric Tyranno<sup>TM</sup> SA fibers)[8], and the University of Florida (carbon-rich UF and near-stoichiometric UF-HM fibers).[9-11] All of these SiC-based fibers have low oxygen contents and show significantly improved thermomechanical properties compared to fibers containing much larger amounts of oxygen, such as Nicalon<sup>TM</sup> and Tyranno<sup>TM</sup> Lox fibers. In this study, the creep resistance and the tensile strength of both carbon-rich UF SiC fibers and near-stoichiometric UF-HM SiC fibers were determined before and after heat treatments in non-oxidizing atmospheres. The creep resistance was assessed using the bend stress relaxation (BSR) method of Morscher and DiCarlo.[12]

## EXPERIMENTAL

The fabrication procedures for producing fine-diameter, high strength, SiC-based fibers with variable Si/C ratio have been described previously.[9-11] Fibers were prepared by dry spinning of concentrated polymer solutions which contained high-molecular-weight polycarbosilane (PCS) as the primary ceramic precursor.[9-11] The as-spun polymeric fibers were dried and subsequently given different heat treatments depending on the composition. Carbon-rich fibers (designated "UF fibers") were prepared by directly pyrolyzing the dried fibers at temperatures in the range of  $\sim 1000$ - $1200^\circ\text{C}$  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, followed by sintering at higher temperature.[11] Boron (typically  $\sim 1$  wt%) was used as a sintering aid. (It was incorporated in the fibers by adding soluble boron hydride to the initial spinning solutions.)

The as-prepared carbon-rich (UF) and near-stoichiometric (UF-HM) fibers both had diameters in the range of  $\sim 10$ - $15 \mu\text{m}$  and average tensile strengths of  $\sim 3$  GPa. The average normalized Si/C ratios (based on electron microprobe analysis, EMA) were  $\sim 68.5$  wt% Si/ $\sim 31.5$  wt% C and  $\sim 60.5$  wt% Si/ $\sim 39.5$  wt% C for the UF-HM and UF fibers, respectively. The UF-HM fibers had residual oxygen and nitrogen contents below the resolution limit of EMA ( $\leq 0.2$  wt%), while the UF fibers typically contained a higher oxygen content ( $\sim 0.5$ - $1.0$  wt%) as a result of the lower final processing temperature. X-ray diffraction (XRD) and transmission electron microscopy (TEM) showed that the UF-HM fibers consisted primarily of  $\beta$ -SiC grains (mostly in the range of  $0.05$ - $0.3 \mu\text{m}$ ). TEM showed that some graphitic carbon (which was XRD-amorphous) was always present in the fibers which is consistent with the slightly carbon-rich composition of the UF-HM fibers (i.e., relative to stoichiometric SiC). Selected area (electron) diffraction also showed that traces of  $\alpha$ -SiC were present in some UF-HM fibers. In contrast, the UF fibers consisted of weakly-crystalline  $\beta$ -SiC (crystallite size  $< 5$  nm) and much larger amounts of carbon. The high carbon content resulted in a lower apparent density for the UF fibers (i.e.,  $\sim 2.5$ - $2.7$  g/cm<sup>3</sup> compared to  $\sim 3.1$ - $3.2$  g/cm<sup>3</sup> for the UF-HM fibers).

The as-fabricated fibers were given annealing heat treatments in argon- or nitrogen-containing atmospheres at temperatures up to  $\sim 1950^\circ\text{C}$ . After heat treatment, single-filament tensile strengths were determined at room temperature according to ASTM procedure D3379.[13] The fiber gage length was 25 mm. The BSR method was used to assess the creep behavior.[12] Stress relaxation values (designated as "M" values) were determined based on the extent of permanent deformation that occurred when fibers were 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 treatment temperatures in the range of  $1100$ - $1850^\circ\text{C}$  for 1 h in an argon atmosphere.

## RESULTS AND DISCUSSION

Figure 1 shows plots of the bend stress relaxation ratios,  $M$ , as a function of the heat treatment temperature for as-pyrolyzed (1200°C) carbon-rich UF fibers and for fibers which were given heat treatments for 1 h (in argon) at 1700°C and 1900°C. The heat treatment significantly improved the BSR creep resistance. The 1700°C heat-treated UF fibers also retained high tensile strength ( $\sim 3$  GPa), while a strength degradation (to  $\sim 1.6$  GPa) was observed for the 1900°C heat-treated fibers. The improved creep resistance upon heat treatment in inert atmosphere 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.[4,14] The effect is attributed to increased SiC grain sizes (see Figs. 3A-3C) and/or more highly crystallized graphitic carbon. Both microstructural changes are expected to inhibit diffusion-controlled creep processes.

Figure 2 shows that the BSR creep resistance of the 1700°C-annealed carbon-rich UF fibers is better than that observed for the as-sintered near-stoichiometric UF-HM fibers. This occurs despite the fact that the grain sizes are much larger for the latter fibers (see Figs. 3B and 3D). These observations indicate that diffusion is inhibited in SiC-based fibers with larger amounts of excess carbon. Slower diffusion rates in the carbon-rich fibers would account for both the slower coarsening of SiC grains upon heat treatment and the better creep resistance.

Figure 2 also shows a comparison of BSR data for as-sintered and heat-treated ( $\sim 1940^\circ\text{C}$ ) near-stoichiometric UF-HM fibers. The heat treatment results in a significant improvement in the creep resistance without any decrease in the tensile strength. Figure 4 shows that the annealed UF-HM fibers also have much better BSR creep resistance than reported [27-29] for other polymer-derived fibers with fine-diameter, high strength, and near-stoichiometric composition (i.e., Hi-Nicalon™ Type S and Sylramic fibers). In addition, Fig. 4 shows that the annealed UF-HM fibers have comparable BSR creep behavior to that reported [27-29] for the much weaker, coarse-grained Carborundum fibers. (The latter fibers were prepared by powder processing.[15]) The improved creep resistance of the UF-HM fibers after the annealing treatment is attributed, at least in part, to increased grain sizes (see Figs. 3D and 3E). In addition, chemical analyses indicate that the overall concentration of boron in the fibers is reduced by the annealing heat treatment (i.e., via diffusion to the fiber surface). It is possible that this could decrease the SiC self-diffusion coefficients and thereby decrease the creep rate.

Takeda et al. showed that annealing heat treatments improved the creep resistance of Hi-Nicalon™ Type S fibers.[4] However, the annealed fibers did not retain tensile strengths as high as observed for the annealed UF-HM fibers. This is illustrated in Fig. 5 which shows plots of tensile strengths vs.  $M$  values for Hi-Nicalon™ Type S [4] and UF-HM fibers which were subjected to various annealing heat treatments prior to BSR tests at 1600°C (1 h argon). It was possible to produce UF-HM fibers with 1600°C BSR  $M$  values of  $\sim 0.45$ , while still retaining a tensile

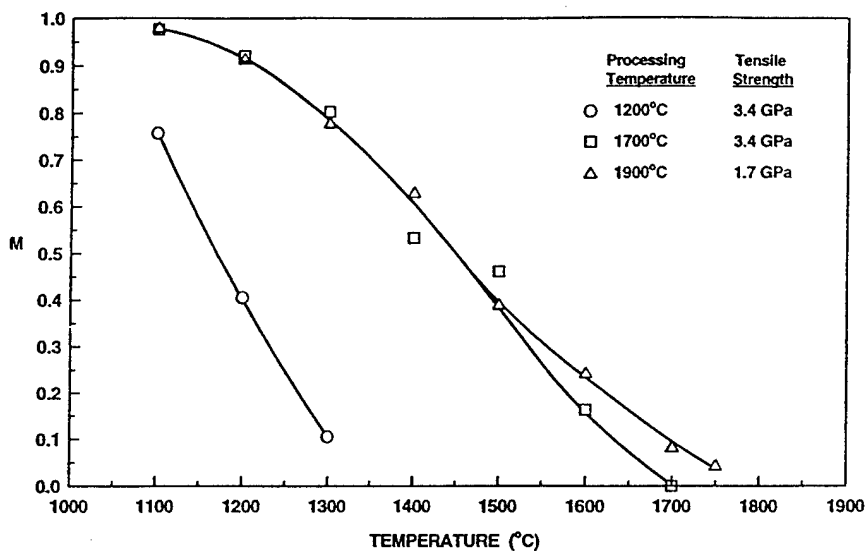


Fig. 1. Plots of stress relaxation ratio,  $M$ , vs. heat treatment temperature for as-prepared carbon-rich UF fibers (1200°C) and heat-treated UF fibers (1700°C and 1900°C).

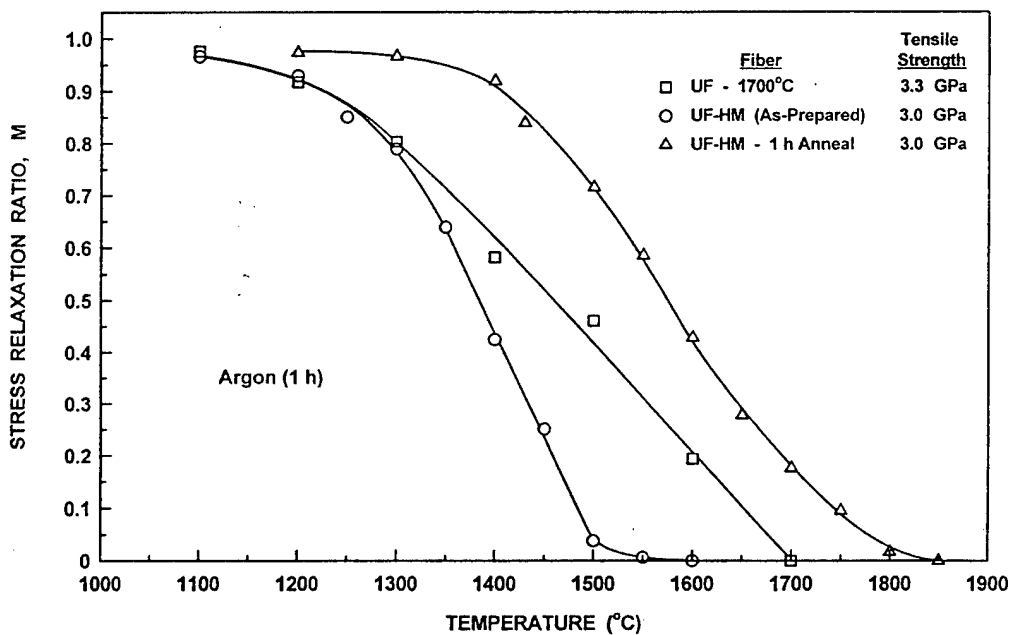


Fig. 2. Plots of stress relaxation ratio,  $M$ , vs. heat treatment temperature for as-prepared near-stoichiometric UF-HM fibers, heat-treated (1940°C) UF-HM fibers, and heat-treated (1700°C) carbon-rich UF fibers.

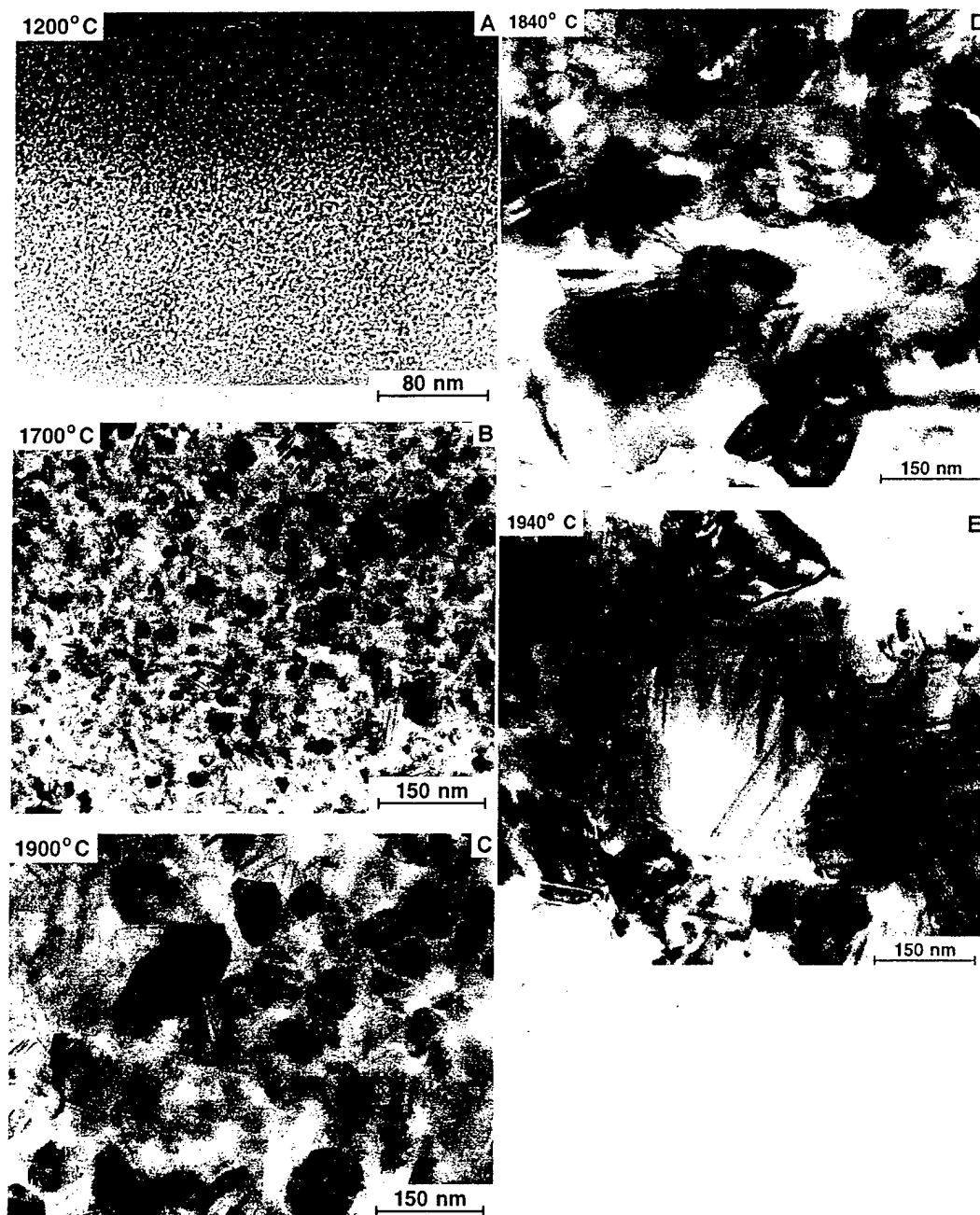


Fig. 3. TEM micrographs for (A) as-pyrolyzed carbon-rich UF fibers (1200°C), (B) 1700°C-heat treated UF fibers 1700°C, (C) 1900°C-heat treated UF fibers, (D) as-sintered near-stoichiometric UF-HM fibers (1840°C), and (E) 1940°C-heat treated UF-HM fibers.

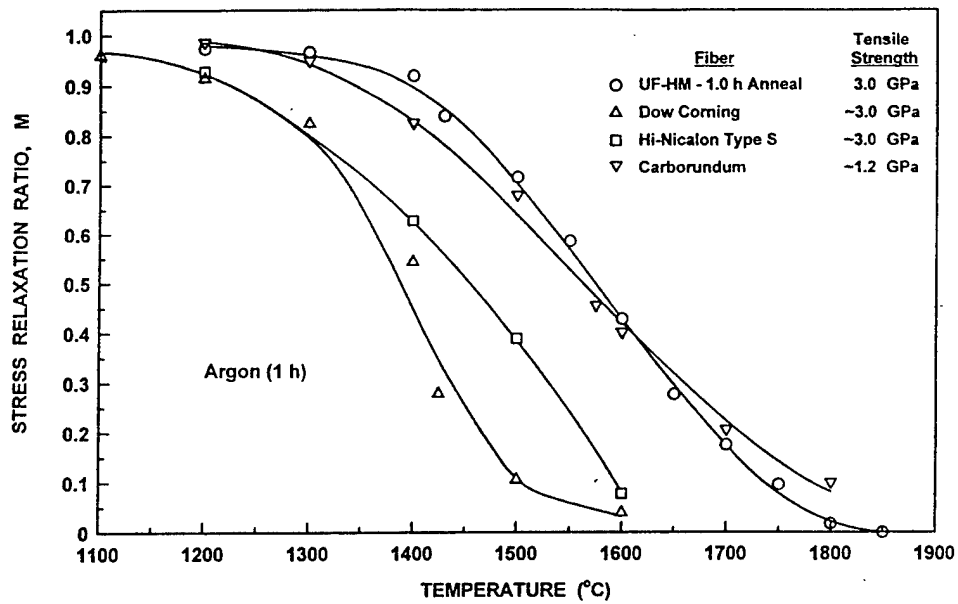


Fig. 4. Plots of stress relaxation ratio,  $M$ , vs. heat treatment temperature for heat-treated ( $1940^{\circ}\text{C}$ ) UF-HM, Hi-Nicalon<sup>TM</sup> Type S, Sylramic<sup>TM</sup>, and Carborundum fibers.

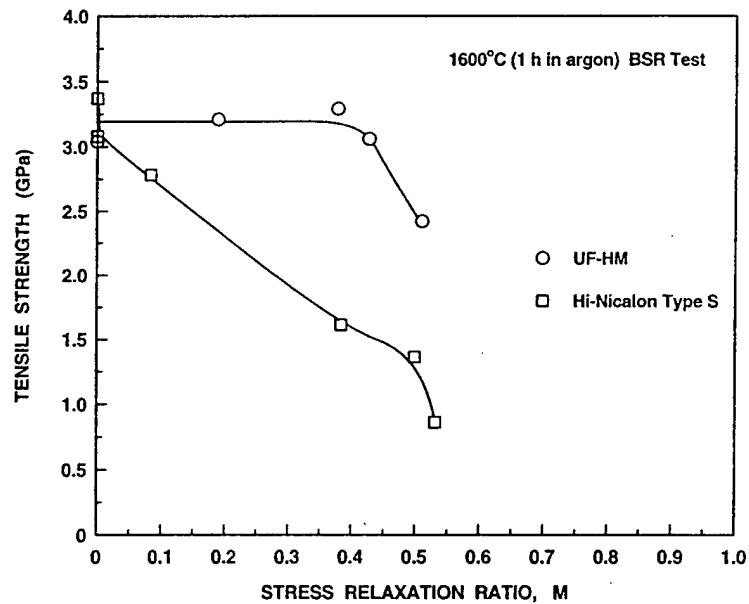


Fig. 5. Plots of tensile strength vs. stress relaxation ratio,  $M$ , for Hi-Nicalon<sup>TM</sup> Type S and UF-HM fibers which were given varying annealing treatments in order to alter the  $M$  values. The BSR test temperature was  $1600^{\circ}\text{C}$ .

strength of  $\sim 3$  GPa. In contrast, much lower 1600°C BSR M values ( $\leq 0.05$ ) were reported for Hi-Nicalon™ Type S fibers which retained tensile strengths of  $\sim 3$  GPa.

## CONCLUSION

The effect of non-oxidizing heat treatments on the BSR creep resistance and strength retention for carbon-rich and near-stoichiometric SiC-based fibers was investigated. Carbon-rich UF fibers showed excellent strength retention and greatly improved BSR creep resistance when heat treated at 1700°C in argon. This was attributed to the increased grain sizes and possibly more highly crystallized graphitic carbon. The BSR creep resistance was comparable to or better than that observed for as-prepared near-stoichiometric fibers (UF-HM, Hi-Nicalon™ Type S, and Sylramic™ 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 greatly enhanced by annealing heat treatments at 1940°C. This was attributed to increased grain size and possibly to reduced boron concentration within the bulk fiber. The combination of high strength ( $\sim 3$  GPa) and high BSR creep resistance that was obtained for the annealed UF-HM fibers has not been observed previously for other SiC-based fibers.

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