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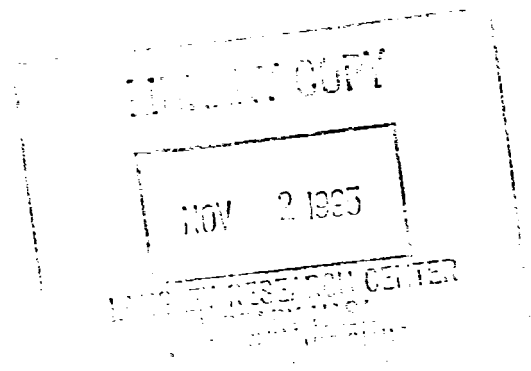
Effects of Thermal Treatment on Tensile Creep and Stress-Rupture Behavior of Hi-Nicalon SiC Fibers

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EFFECTS OF THERMAL TREATMENT ON TENSILE CREEP AND STRESS-RUPTURE BEHAVIOR OF Hi-NICALON SiC FIBERS

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ABSTRACT

Tensile creep and stress-rupture studies were conducted on Hi-Nicalon SiC fibers at 1200 and 1400 °C in argon and air. Examined were as-received fibers as well as fibers annealed from 1400 to 1800 °C for 1 hour in argon before testing. The creep and rupture results for these annealed fibers were compared to those of the as-received fibers to determine the effects of annealing temperature, test temperature, and test environment. Argon anneals up to 1500 °C degrade room temperature strength of Hi-Nicalon fibers, but improve fiber creep resistance in argon or air by as much as 100 % with no significant degradation in rupture strength. Argon anneals above 1500 °C continue to improve fiber creep resistance when tested in argon, but significantly degrade creep resistance and rupture strength when tested in air. Decrease in creep resistance in air is greater at 1200 °C than at 1400 °C. Mechanisms are suggested for the observed behavior.

INTRODUCTION

Hi-Nicalon fiber is currently of high technical interest for reinforcement of ceramic matrix composites (CMC) because of its small diameter high room temperature strength and excellent high temperature strength retention after thermal exposure [1]. In contrast to ceramic grade Nicalon, the Hi-Nicalon fiber contains a low content of oxygen (below 0.5 wt.%) which minimizes the strength degradation problem relating to decomposition of silicon oxycarbide. As-produced Hi-Nicalon fibers are also reported to have good rupture and creep strength [2,3].

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Since CMC may be fabricated and used above the maximum processing temperature for the polymer derived Hi-Nicalon fibers ($\sim 1300\text{ }^{\circ}\text{C}$), there is a need to understand the effects of these thermal excursions on the fiber key structural properties. Annealed Hi-Nicalon fibers are reported to decrease in room temperature strength [4], but little is known concerning annealing effects on fiber creep strength and rupture strength. Thus the objective of this study was to obtain an understanding of how CMC fabrication and use temperatures above $1300\text{ }^{\circ}\text{C}$ can affect Hi-Nicalon tensile strength, creep strength, and rupture strength in argon and air test environments.

EXPERIMENTAL PROCEDURE

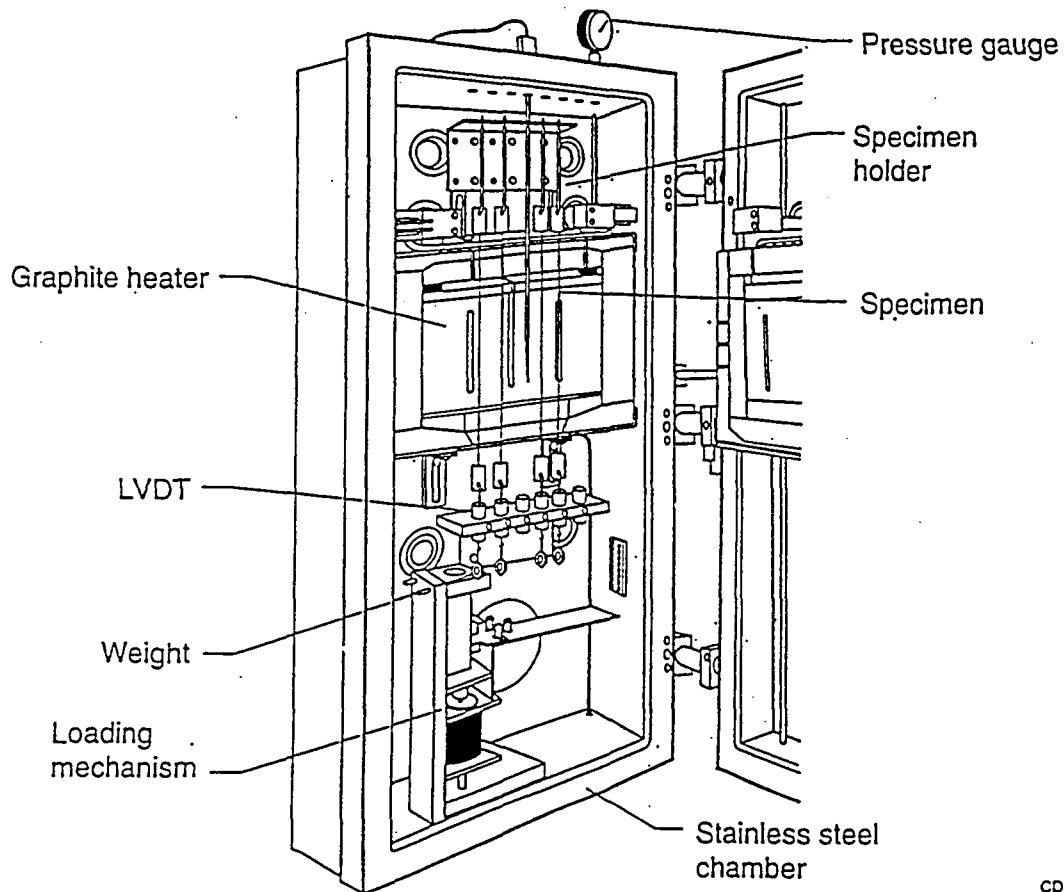
As-produced Hi-Nicalon fibers contain very fine SiC grains of about 4nm in size, a very low content of oxygen (0.5 wt.%), but a large volume fraction of free carbon ($\sim 35\text{ mol.}\%$). The maximum process temperature is $\sim 1300\text{ }^{\circ}\text{C}$, and the room temperature strength is about 2800 MPa. These and other properties of as-produced fibers are shown in Table I [3,4].

Table I. PROPERTIES OF HI-NICALON SiC FIBERS

Manufacturer	Nippon Carbon
# of Filaments(fil./yarn)	500
Composition (mol.%)	$\sim 65\%$ B SiC + $\sim 35\%$ C
Impurity (wt.%)	$\sim 0.5\%$ O
Max. Processing Temp.	$\sim 1300\text{ }^{\circ}\text{C}$
Avg. Grain Size (nm)	4
Avg. Diameter (μm)	14
Density (g/cm^3)	2.7
Elastic Modulus at RT (GPa)	~ 270
Tensile Strength at RT (MPa)	~ 2800

To determine the effects of thermal exposure above their maximum processing temperature, as-produced fibers were annealed at 1400, 1500, 1600, and $1800\text{ }^{\circ}\text{C}$ for 1 hr in a graphite heating element furnace located in a chamber filled with high purity argon at

~ 1.4 atm. pressure. The tensile strengths of as-produced and annealed fibers were measured at ~25mm gauge length using a commercial test frame. The tensile creep and stress-rupture strength of as-produced and annealed fibers were measured at 1200 and 1400 °C in air (MoSi₂ heating element) and argon (graphite heating element) at gauge lengths of ~ 25 and 112 mm, respectively. The single fiber specimens were mounted outside the furnace heating element using paper tab grips and epoxy glue. Constant stress was provided by dead weight loading in a single fiber furnace for air [5] and in a multifiber Creep Testing Frame for argon, as shown in Fig. 1. A hot grip method [6] was also utilized for air testing and the creep strains were found to be in fairly good agreement with the cold grip method. The fiber length change was monitored by an LVDT.



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Fig. 1 Multiple Fiber (Inert/Vacuum) Creep Rig

RESULTS AND DISCUSSION

- Room Temperature Strength

After annealing at 1500 and 1600 °C, Hi-Nicalon strength at room temperature decreased from 2800 MPa to 1100 MPa, as shown in Fig. 2. The Weibull modulus remained unchanged after annealing. The surfaces were clean and shiny after thermal treatment at 1600 °C (not shown). The reduction in room temperature strength may be caused by grain growth [3,4] or by flaw growth as a result of silicon oxycarbide decomposition. The strength reductions after annealing at 1500 and 1600 °C were similar to those observed by Takeda et al [4], as shown in Fig.3. The slightly larger drop in this investigation was not clear, but may be due to different fiber lots.

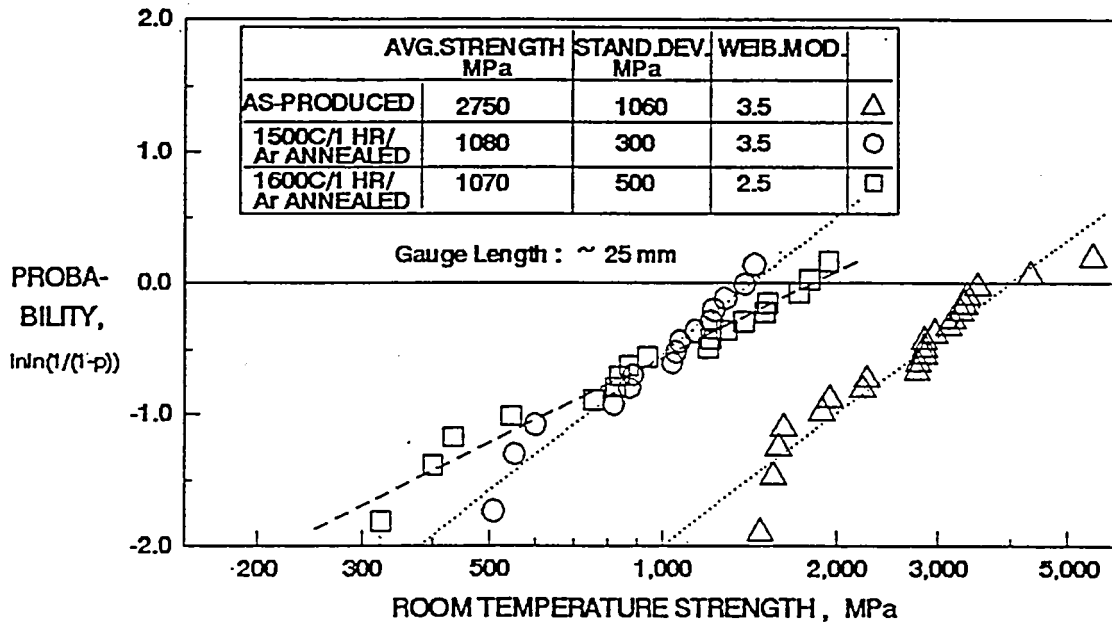


Fig.2 WEIBULL PLOTS FOR ROOM TEMPERATURE STRENGTH OF AS-PRODUCED AND ANNEALED HI-NICALON SiC FIBERS

- Creep

Representative creep curves are shown in Fig. 4 for as-received and annealed Hi-Nicalon fibers tested at 1400 °C and 140 MPa in argon (Fig. 4 a) and in air (Fig. 4 b). For annealing at 1500 °C

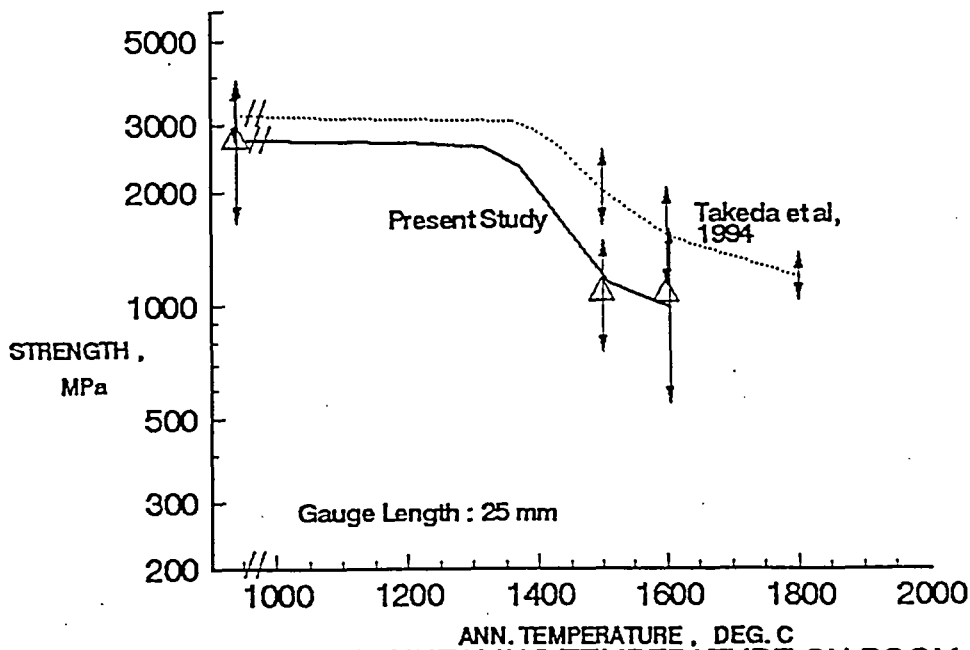


Fig.3 EFFECT OF ANNEALING TEMPERATURE ON ROOM TEMPERATURE STRENGTH OF HI-NICALON FIBERS

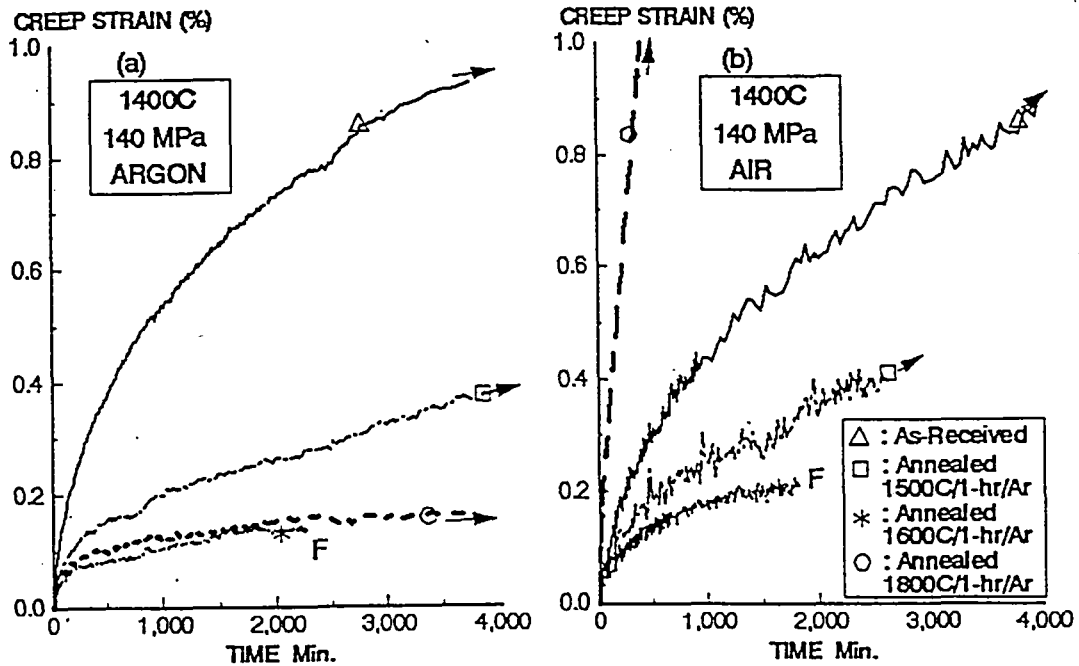


Fig. 4 REPRESENTATIVE CREEP-RUPTURE CURVES AT 1400 C FOR AS-RECEIVED AND 1 - HR ARGON ANNEALED HI-NICALON

and above, creep in argon decreased significantly and leveled off for anneals from 1600 to 1800 °C. For anneals up to 1600 °C, creep in air also decreased, but after the 1800 °C anneal, creep drastically increased (failure strain of 12 % at 140 MPa) and rupture time decreased. The drastic increase in air creep after 1800 °C annealing was also observed at 1200 °C (failure strain above 15 % at 140 MPa).

A similar influence of testing environment has also been reported for reaction-bonded silicon nitride (RBSN); that is, low creep in argon and more creep at lower temperatures in air than at higher temperatures [7,8]. This was related to the open porosity of the RBSN and the formation of internal SiO₂. It is believed that the Hi-Nicalon creep increase in air may also be caused by open porosity, perhaps formed with annealing temperatures above 1600 °C. Porosity could be formed by decomposition of the small amount of the silicon-oxycarbide phase or by densification and restructuring of the free carbon. This porosity effect may be enhanced during air creep testing by oxygen penetration into the fiber and removal of the free carbon. This, in turn, could allow easier internal oxidation of the remaining SiC and enhanced creep by SiO₂ formation. The decrease in creep observed for anneals up to 1500 °C is probably related to SiC grain growth or to carbon restructuring with little open porosity formation. Similar creep resistance improvement in argon was reported by Bodet et al [3] after 1 - hr 1600 °C anneals.

- Creep and Rupture Strength

By measuring creep and rupture time at many stresses, the effects of annealing on Hi-Nicalon creep strength and rupture strength were also determined. The creep strength results for reaching 0.1 % in 10 hours are shown in Fig. 5 as a function of annealing temperature, test environment, and test temperature. At 1200 and 1400 °C, the 0.1 % creep strength in argon steadily increased until anneals up to 1800 °C; whereas the creep strength in air maximized after anneals at 1500 °C and then decreased dramatically. Comparatively the creep strength degradation in air for anneals above 1500 °C was greater at 1200 °C than at 1400 °C. This may be explained by the rapid formation of a silica layer overcoating of the fiber at 1400 °C which inhibited oxygen

ingress into the fiber.

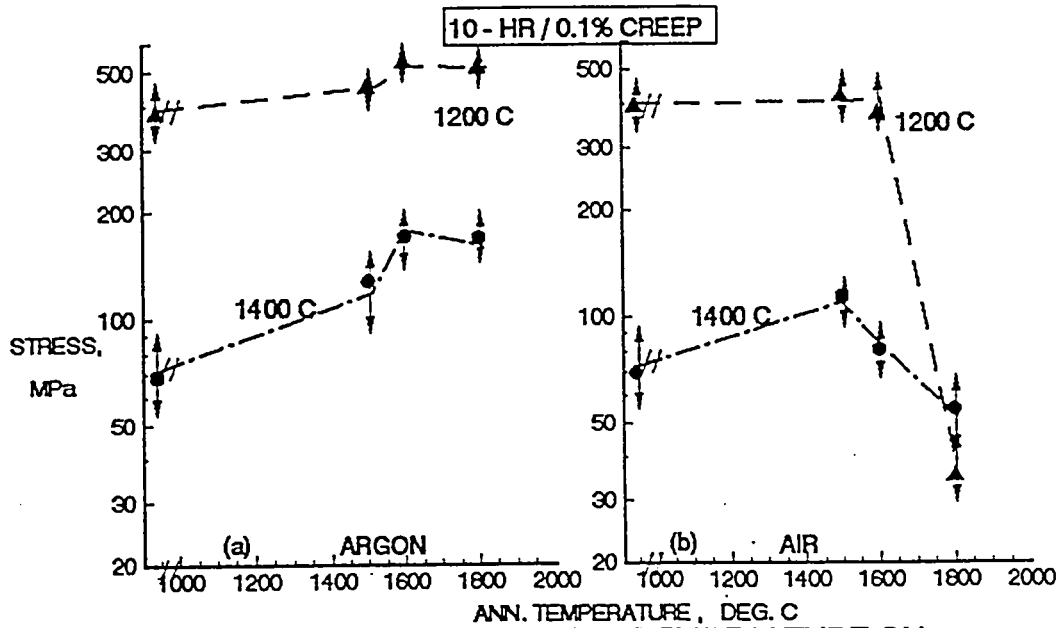


Fig.5 EFFECT OF ANNEALING TEMPERATURE ON 0.1% CREEP STRENGTH OF HI-NICALON FIBERS

The 10 hr rupture strength was also determined at 1200 and 1400 °C as a function of annealing temperature and test environment. The results are shown in Figs. 6a and 6b for argon and air, respectively. The rupture strength was not degraded significantly after anneals at 1500 °C for both air and argon test environments. Above 1600 °C the rupture strength decreased for the air tests, while the change was not significant up to 1800 °C for the argon tests.

SEM photomicrographs of creep-ruptured fibers annealed at 1600 °C for 1 hr and tested at 275 MPa and 1400 °C for ~ 20 hrs are shown in Fig. 7. The surface of the air tested fiber was fully coated by a silica layer, while that of argon tested fiber indicated the formation of ridges which may be related to the inter-connected porosity formed during annealing. The apparent damage on the fracture surface edge in the air tested specimen may be formed because of silica layer at the fiber surface, often reported as oxidation pitting.

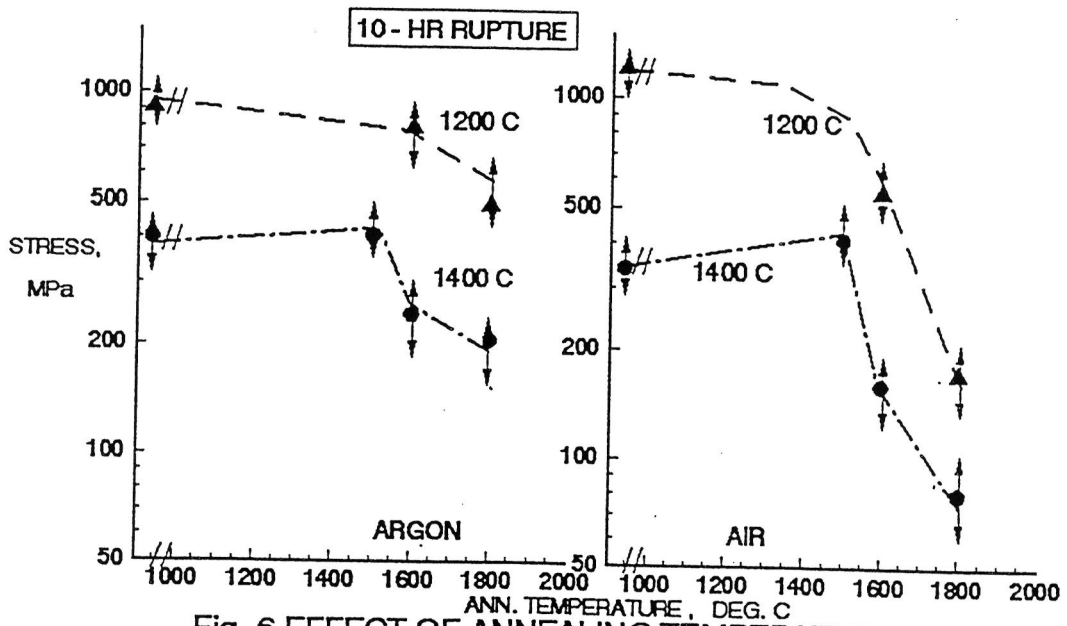
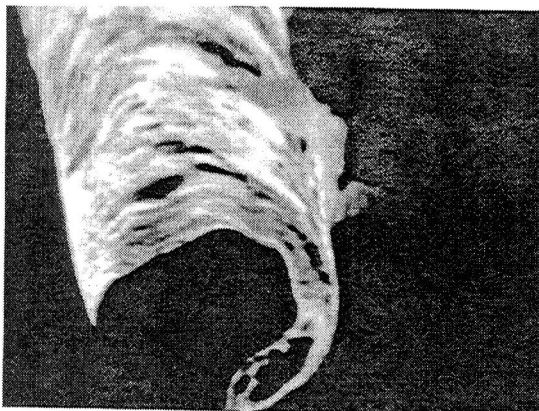
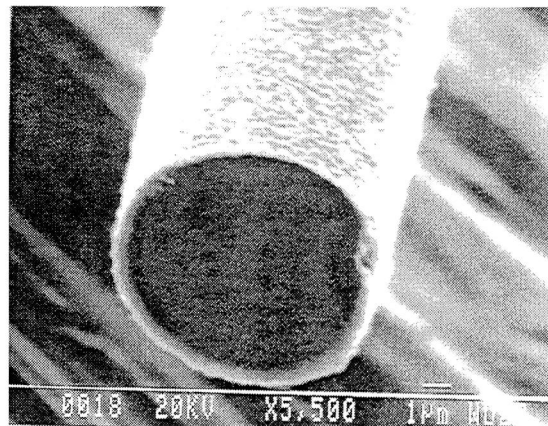


Fig. 6 EFFECT OF ANNEALING TEMPERATURE ON RUPTURE STRENGTH OF Hi-NICALON FIBERS



ARGON CREEP TESTED
(1400 C/275 MPa/20 hr)



AIR CREEP TESTED
(1400 C/275 MPa/20 hr)

Fig. 7 SEM PHOTOMICROGRAPHS OF CREEP AND RUPTURED Hi-NICALON FIBERS, ANNEALED AT 1600°C

CONCLUSIONS

For Hi-Nicalon fibers, the results of this study indicate that short-time thermal exposures from 1200 to 1500 °C can improve fiber creep strength in argon or air, but may degrade low temperature tensile strength. This suggests that if improved high temperature structural performance is required, CMC processing conditions up to 1500 °C can be used. Alternatively low temperature CMC fabrication conditions could include a short-term post-processing thermal treatment to ~ 1400 °C.

For thermal exposure above 1500 °C, the Hi-Nicalon creep and rupture strength degrade significantly in air tests. The large decrease in 1200 °C creep resistance may be related to open porosity formation during the thermal exposure, carbon removal during testing in air, and SiO₂ formation in grain boundaries. Reduced degradation effects at 1400 °C may be related to the formation of a protective silica overcoating.

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