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TENSILE CREEP AND STRESS-RUPTURE BEHAVIOR OF POLYMER DERIVED SiC FIBERS

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ABSTRACT

Tensile creep and stress-rupture studies were conducted on polymer derived Nicalon, Hi-Nicalon, and SiC/BN-coated Nicalon SiC fibers. Test conditions were temperatures from 1200 to 1400 °C, stresses from 100 to 1600 MPa, stress application times up to 200 hours, and air, argon, and vacuum test environments. For all fibers, creep occurred predominantly in the primary stage. Hi-Nicalon had much higher 0.2 and 1 % creep strengths than as-produced as well as coated Nicalon fibers. The stress-rupture strength of Hi-Nicalon up to 100 hours was also higher than that of the coated and as-produced Nicalon fibers. SiC/BN coating on Nicalon increased only the short-term low-temperature rupture strength. Limited testing in argon and vacuum suggests that for all fiber types, creep and rupture resistances are reduced in comparison to the results in air. Possible mechanisms for the observed behavior are discussed.

INTRODUCTION

High temperature structural applications, such as, advanced gas turbine engines for civil transport aircraft, have generated great interest in intermetallic and ceramic composites reinforced by high strength continuous length fibers. The maximum use temperatures of these composites can depend upon key fiber properties, such as, oxidation resistance, creep resistance, and stress-rupture resistance. Because of their composition, SiC-based fibers can withstand extremely high temperatures in an oxidizing atmosphere by forming a protective silica layer [1]. However, in terms of creep resistance, polymer derived nanocrystalline SiC fibers, e.g. Nicalon and Tyranno fibers, which have high reinforcement potential because of their small diameter and high as-produced strength, have recently been shown to possess low tensile creep strengths of below 100 MPa at 1300 °C for 1 % creep strain in about 10 hours [2]. At this temperature, decomposition of their inherent Si-C-O oxycarbide phase and SiC grain growth were reported to control their creep resistance as

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well as causing weak stress-rupture behavior. Recently a low oxygen-containing nanocrystalline SiC fiber, Hi-Nicalon, has been fabricated by a radiation curing method [3,4]. Because of its reduced oxygen content (~0.5 wt. %), this fiber has greater tensile strength retention at high temperatures. However, because it contains a large content of free carbon, Hi-Nicalon creep and stress-rupture as well as oxidation resistance may not be as good as stoichiometric SiC fibers.

The primary objective of this study was to measure the tensile creep and stress-rupture behavior of newly processed Hi-Nicalon and SiC/BN-coated Nicalon fibers, and to compare this behavior to that of as-produced uncoated Nicalon in air and inert environment. The purpose was to understand whether the new Hi-Nicalon fiber with low oxygen content or Nicalon with a surface coating to prevent oxycarbide decomposition offered any creep and stress-rupture strength advantages over the as-produced Nicalon for long-term stress application at high temperature. Emphasis was placed on the low creep strain region below 1 % since this value is often quoted as the upper creep limit for structural composites. In addition, an analysis was performed to identify whether rupture strength or creep strength limits the maximum use temperature of these fibers for a 1000 hour application.

EXPERIMENTAL PROCEDURE

Typical properties of the fibers in this study are listed in Table I. The primary phase of the fibers was beta-SiC. The mole compositions of beta-SiC varied from 49 to 65 % for Nicalon and Hi-Nicalon, respectively. Other major phases were about 23 % Si-C-O and about 28 to 35 % free C for Nicalon and Hi-Nicalon, respectively. These additional phases which are a consequence of the fiber fabrication process serve as matrix for the beta-SiC nanocrystals and influence the mechanical strength of the fibers. The average diameters of these fibers were nominally 14 and 15.5 μm for both Nicalon and Hi-Nicalon, and for SiC/BN-coated Nicalon, respectively. The nominal thickness of the inner layer of BN and outer layer of SiC was about 0.4 μm. Average SiC grain sizes were about 1.7 nm and 4 nm for the Nicalon and Hi-Nicalon, respectively.

For this investigation, tensile creep and stress-rupture measurements were made by dead weight loading. The test temperatures were in the range of 1200 to 1400 °C with loading up to about 200 hours. The tests were done mostly in air, but some experiments were done in argon and in vacuum of 10^{-5} Pa to determine possible environmental effects. Before starting the creep

rupture experiments at constant temperature, fibers were dead-weight loaded at various stresses at room temperature, and then subjected to a constant warm-up rate to ~1500°C. Temperatures for fiber fracture were recorded for each stress level. The results of this "warm-up" test allowed determination of the maximum stresses that the fibers could withstand during the long-time constant temperature tests.

TABLE I. NOMINAL PROPERTIES OF POLYMER DERIVED SiC FIBERS

Fiber / Property	NICALON NL202	Hi-NICALON	COATED NICALON (SiC/BN)
Manufacturer	Nippon Carbon	Nippon Carbon	Nippon Carbon (3M Coating)
# of Filaments	500	500	500
Composition (mol.%)	~49% β SiC + ~23% Si-O-C + ~28% C	~65% β SiC + ~35% C	~49% β SiC + ~23% Si-O-C + ~28% C ~0.4μm BN : ~0.2μm SiC
Avg. Grain Size (nm)	1.7	4	1.7
Avg. Diameter (μm)	14	14	15.5
Density (g/cm^3)	2.6	2.7	2.6
Elastic Modulus at RT (GPa)	~ 200	~ 270	~ 200
Tensile Strength at RT (MPa)	~2400	~2800	~2400

In preparation for the elevated temperature creep and stress-rupture tests, 250 mm long fiber specimens were first separated from as-received multifilament tows and then glued on paper tab grips for air testing. The fibers were inserted through a slit in the furnace and hooks were attached to the paper grips (Fig. 1). For argon and vacuum testing a similar rig was used. The uniform temperature regions of the furnace (hot zone) were determined to be 1 and 4 " for two types of $MoSi_2$ heating element furnaces. The hot zone length for the argon (graphite heating element) and vacuum (tungsten heating element) furnaces was 4". The creep deformation was calculated by assuming the main creep deformation occurred only in the hot zone lengths. A hot-grip method [5] was also used and the creep strains were found to be in fairly good agreement with the cold grip method. The fiber length change was monitored by a free floating cored LVDT (Schaevitz Engineering, Pennsauken, NJ). The

displacement sensor was interfaced with a computer to record the data. The maximum temperature gradient along the hot zone of the furnace (1" and 4" hot zone) was within 6 °C. A Pt-Rh (for the air and vacuum furnace) and W-Re (for the argon furnace) thermocouple electronic controller provided a constant temperature at center of the hot zone (± 2 °C).

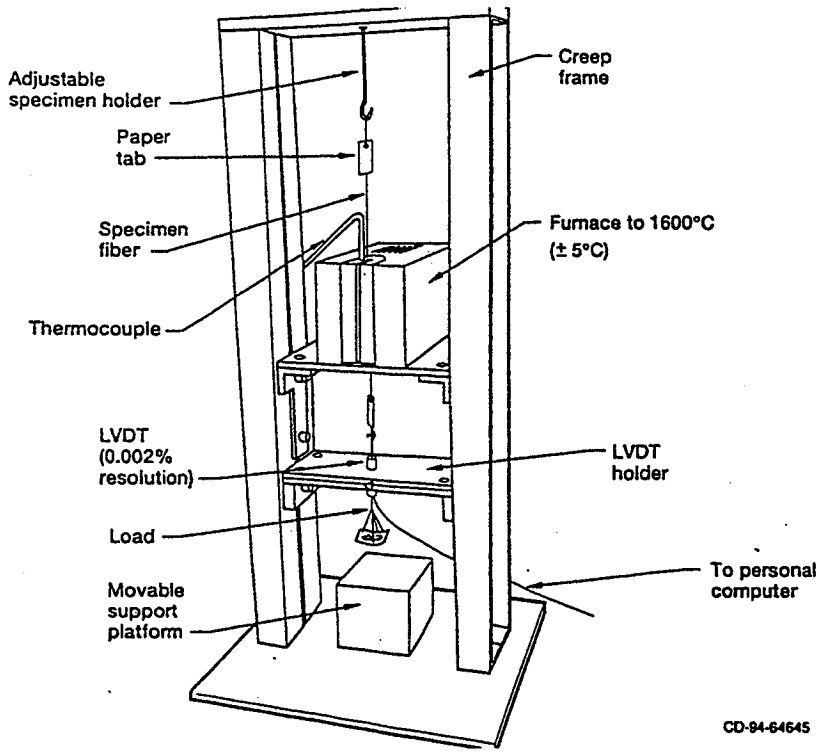


FIG.1. SINGLE FILAMENT CREEP AND STRESS-RUPTURE RIG.

RESULTS

Typical rupture strength versus temperature results for the warm-up test are shown in Fig. 2. As shown in this figure, for rupture temperatures from 1000 to 1600 °C for the SiC fibers, the required stresses were in the range from 100 to 1600 MPa. The general ranking of the fibers in terms of maximum rupture temperature at a given stress were Hi-Nicalon, coated Nicalon, and uncoated Nicalon. The coated Nicalon data indicated higher rupture temperatures in argon than the as-produced Nicalon, suggesting that the coating on Nicalon delays the decomposition of the Si-C-O phase. Generally, the rupture temperatures in air for the Hi-Nicalon were higher than those measured for the same fiber in argon and vacuum.

For the constant temperature tests, Fig. 3 illustrates the stress-rupture strength versus time for Hi-Nicalon (a), and coated & as-produced Nicalon (b) as a function of testing temperature. At 1200 to 1315 °C and stresses below 500 MPa, most fibers did not rupture in less than 100 hours. Therefore it was not possible to use these results to draw best fit lines for rupture time.

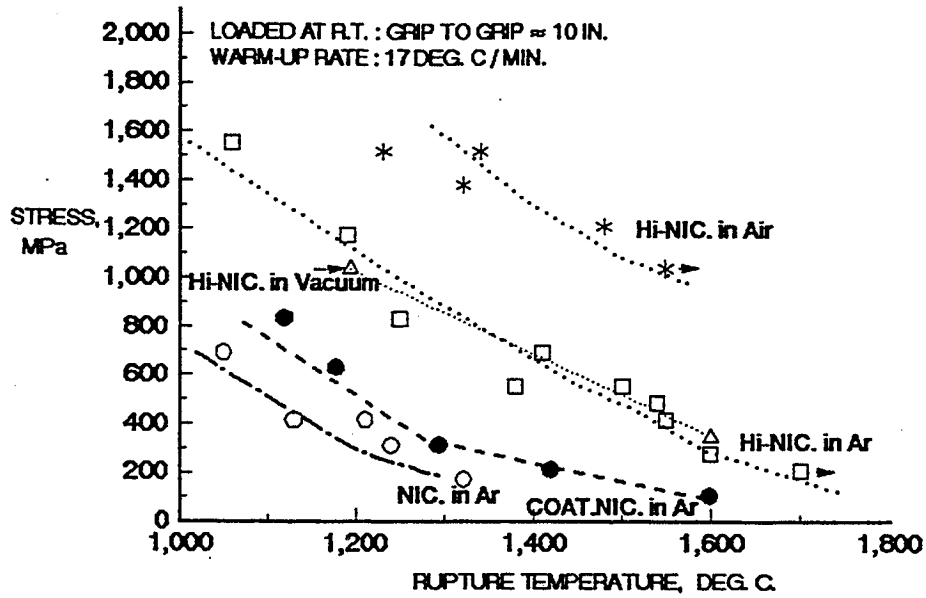


FIG.2. WARM-UP RUPTURE STRENGTH OF Hi-NICALON, NICALON, AND SiC/BN-COATED NICALON FIBERS

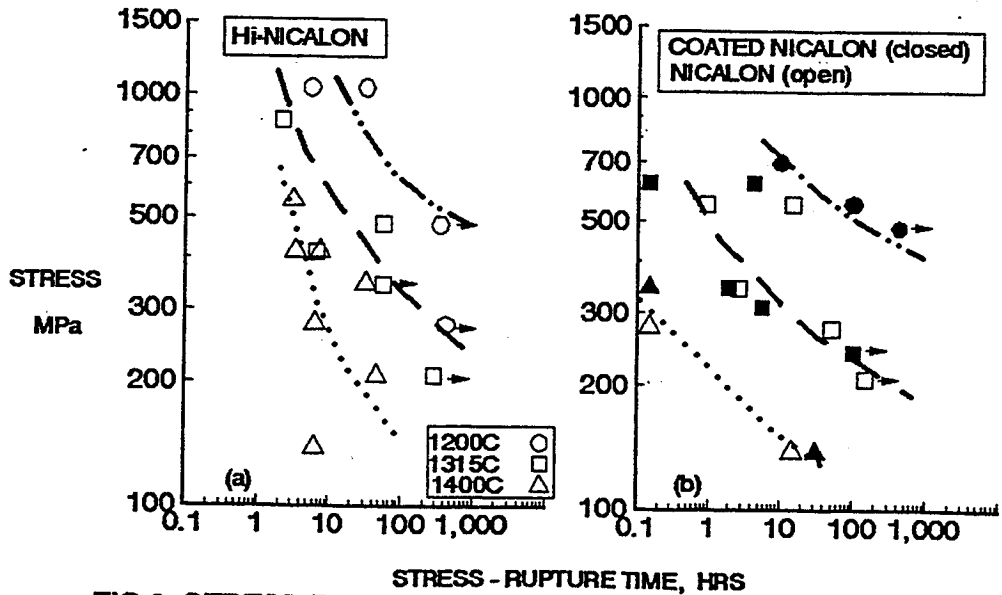


FIG.3. STRESS-RUPTURE STRENGTH OF Hi-NICALON, NICALON, AND SiC/BN-COATED NICALON IN AIR

At the moment, the initial drop with time is assumed to follow a $t^{-1/N}$ dependence with N of about 5 to 6. This is believed to be related with slow crack growth. At 1400 °C, the strength drop was more severe for all polymer derived SiC fibers, even at low stresses and long times, suggesting that fiber decomposition might also be occurring.

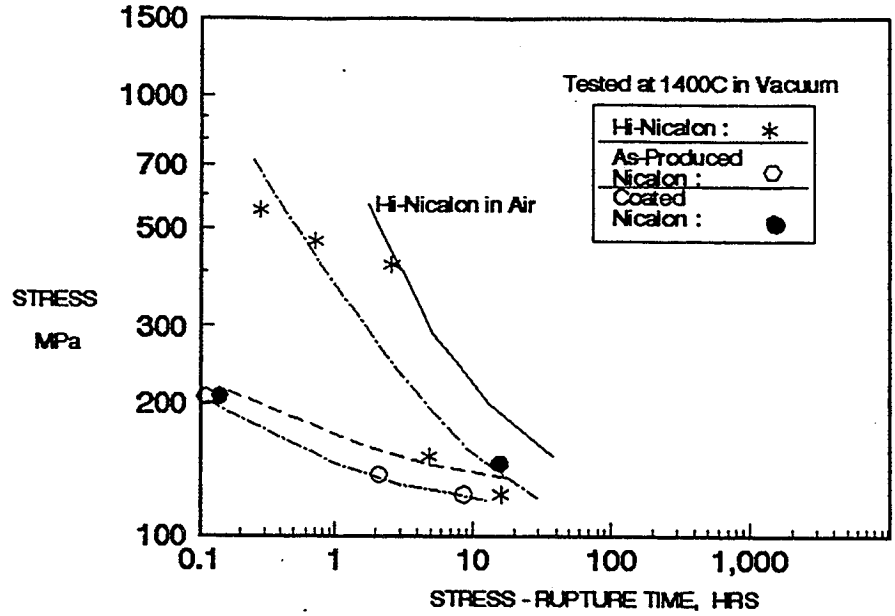


FIG.4. 1400C STRESS-RUPTURE STRENGTH OF POLYMER DERIVED SiC FIBERS IN VACUUM

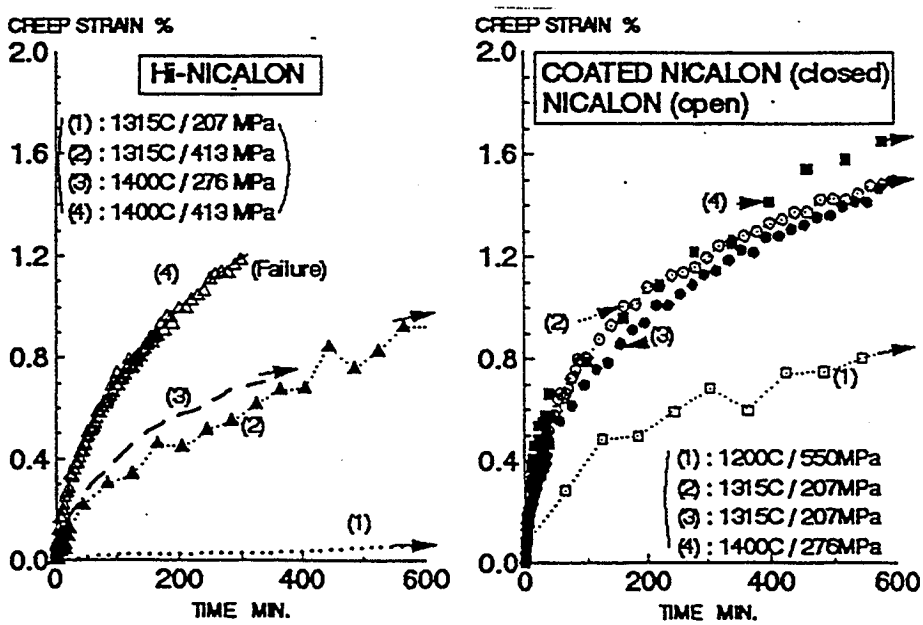


FIG.5. REPRESENTATIVE CREEP CURVES OF Hi-NICALON, NICALON, AND SiC/BN-COATED NICALON IN AIR

The stress versus rupture time data at 1400 °C in vacuum are shown in Fig. 4. In general, the rupture strengths of the fibers in vacuum were lower than those in air, especially for the Hi-Nicalon fibers. The coated Nicalon fibers indicated a slight advantage for rupture strength in vacuum in comparison to the as-received fibers.

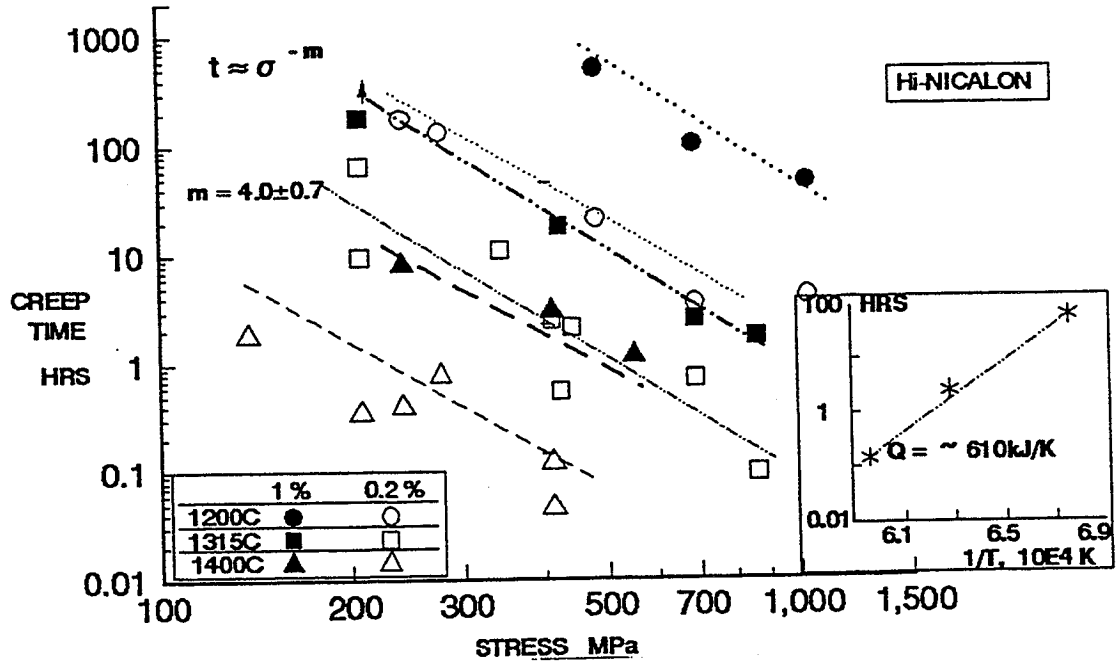
Typical results for creep deformation versus time for the Hi-Nicalon and Nicalon are shown in Fig. 5. In this figure, creep data were taken from 1200 to 1400 °C in air. For all fibers, primary creep occurred; while for Hi-Nicalon steady-state creep may also evident. In general, the Nicalon fiber required lower stress than Hi-Nicalon to obtain the same creep strain. At 1200 and 1315 °C, the creep deformation of Hi-Nicalon was relatively small; most cases below 1 % in 100 hours. At 1400 °C, creep deformation increased to about 2 % for the same time conditions.

For estimation of the creep strength of the polymer derived SiC fibers, the times for 0.2 and 1 % total creep strain were determined from the creep curves. Fig. 6 illustrates the stress dependence of the 0.2 and 1% creep time of Hi-Nicalon and Nicalon in air. For the same stress, Hi-Nicalon had a longer creep time than Nicalon fiber at the higher temperatures, but a comparable creep time at 1200 °C. Least squares fit lines through the data in Fig. 6 suggest a power law creep time relation of $t \approx \sigma^{-m}$. From the best fit lines, the stress exponents m were determined to be about 4 for the Hi-Nicalon and about 5.1 for both coated and uncoated Nicalon at 1200 °C, and about 2.5 from 1315 to 1400 °C. It can also be seen that the data for Nicalon exhibit an increase in scatter with increasing temperature.

The inserts in Fig. 6 illustrate the effect of temperature on the 0.2 % creep time at 400 MPa and at temperatures in the range of 1200 to 1400 °C. The apparent activation energy for creep, Q_{creep}, can be obtained from the slope of the best fit line using the following equation:

$$Q_{creep} = R\ (\Delta \ln(t)/(\Delta(1/T)) \qquad (1)$$

where R is the universal gas constant, t is the creep time (hr), and T is theabsolute temperature (K). The Q_{creep} was determined to be about 610 kJ/molfor Hi-Nicalon and 430 to 660 kJ/mol for Nicalon (coated & as-produced). The 660 kJ/mol energy for the Nicalon was determined at the two lower temperatures, and the 430 kJ/mol at the two higher temperatures. The Hi-Nicalon value is somewhat higher than that of Bodet et al. [6] who reported Q_{creep} to be 340 to 420 kJ/mol. On the other hand, the 610 kJ/mol value from



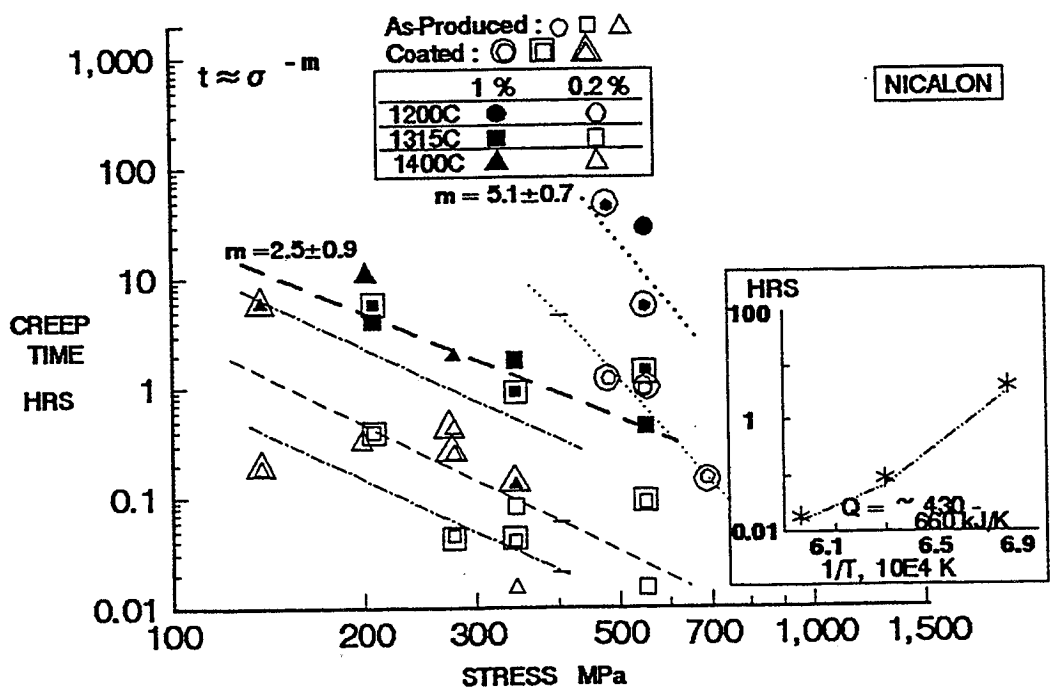


FIG.6. STRESS-EFFECTS ON 0.2 AND 1 % CREEP TIME OF POLYMER -DERIVED SiC FIBERS

this study appears to agree with the sintered bulk SiC data and is similar to that of the activation energy (560kJ/mol) for grain boundary diffusion of carbon [7].

DISCUSSION

The single filament creep and stress-rupture results of this study indicate that radiation-cured low-oxygen Hi-Nicalon fiber appears to have higher strength capabilities than as-produced Nicalon fibers. The SiC/BN coating on Nicalon improves only the short-term rupture strength, not the long-term stress-rupture strength. The creep curves of the coated Nicalon in air were similar to the uncoated fibers, suggesting the double layer SiC/BN coating did not delay decomposition of the Si-C-O phase, at least in fibers fully exposed to the oxygen environment. The abrupt change in Nicalon creep above 1200°C may be related to the fact that during fabrication these fibers did not experience temperatures greater than about 1200°C.

The influence of free carbon in Hi-Nicalon appears to be significant for creep behavior. The initial free carbon of the as-produced Hi-Nicalon may cause the measurable initial creep strain in the primary stage similar to the creep behavior of Nicalon. Nevertheless, the amount of creep was much smaller than that of Nicalon. This suggests that the radiation-curing which significantly reduces the amount of the Si-C-O phase can also minimize the creep contribution of this phase. Also the Hi-Nicalon have probably been produced at higher temperatures than Nicalon which may help to stabilize the free carbon phase and reduce its creep contribution. In terms of carbon phase stabilization at high temperatures, creep deformation should be further studied after the Hi-Nicalon fibers are pre-annealed at temperatures of 1400°C and above. In comparison to as-produced fibers, Bodet et.al. [6] reported creep deformation at 1400°C decreases after a pre-anneal at 1600°C for 1 hr.

The influence of the air environment appears to exist for the creep and rupture of the SiC fibers. Creep in vacuum of Hi-Nicalon and Nicalon at 1400°C was observed higher than that in air, and resulted in a shorter rupture life in vacuum. This higher creep in vacuum is not fully understood. However, the improved rupture strength in air could be explained by the protective SiO_2 layer which forms on the fiber during testing in air and could then inhibit release of the decomposition gases, SiO and CO.

In other studies [8], it was found that the primary creep behavior of the polymer derived SiC fibers in air can be expressed in terms of the tensile

stress, σ, absolute temperature, T, and time, t, by the relation:

$$\epsilon = A\ \sigma^n\ t^p\ (-pQ_{creep}/RT) \qquad (2)$$

Here n is the stress exponent, p the time exponent, Q_{creep} the effective activation energy for creep, and A a creep constant. This equation can be manipulated to predict creep stress versus time for a given strain, that is:

$$\sigma = \sigma_0\ (t \exp\ (Q_{creep}/RT))^{-1/m} \qquad (3)$$

where σ_0 depends on creep strain and m is a time exponent (m = n/p). Creep parameters determined here for the Hi-Nicalon and Nicalon are summarized in Table II. For Nicalon, the previously reported value of n/p = 3 [8] is in agreement with the m value measured here for 1300 - 1400°C, but lower than the m value at 1200°C.

TABLE II. APPROXIMATE CREEP STRENGTH MODEL FOR POLYMER DERIVED COMMERCIAL SiC FIBERS AT 0.2 % CREEP

	Hi-NICALON	NICALON / COATED NICALON	
σ_0	$(3.48\pm0.25) \times 10^{-2}$	$(7.3\pm0.7)\times10^{-2}$*	$(9.9\pm0.5)\times10^{-3}$+
m	4.0±0.7	5.1±0.7*	2.5±0.9+
Q	610 kJ/mol.	660kJ/mol.*	430kJ/mol.+

* at 1200C
\+ 1300 - 1400C

Using the stress-rupture curves in Fig. 3, one can estimate the 1000-hour stress-rupture strength at three temperatures for each of these fibers. By using Eq. 3 and extrapolation from 0.2 and 1 % creep strength curves in Fig. 6, one can project the 1000-hour creep strength for the fibers. Fig. 7 illustrates the projected 1000-hr creep and stress-rupture strengths in air. In ceramic composite application, the polymer derived SiC fibers should not be expected to deform beyond 1%. Therefore the 0.2 and 1 % creep strengths will probably limit the use temperature of these fibers, rather than the fiber stress-rupture behavior. The 1000 hr creep strength of Nicalon appears to change abruptly between 1200 and 1300 °C, and the Fig. 7 shows discontinuous line. Thus, even though Hi-Nicalon has higher creep strength than the uncoated or SiC/BN coated Nicalon, the Hi-Nicalon is creep limited to a use temperature

of about 1250°C at 200 MPa and 0.2 % creep strain. This can be compared to the 1350 °C stress-rupture use temperature limit for this fiber at the same 200 MPa stress level.

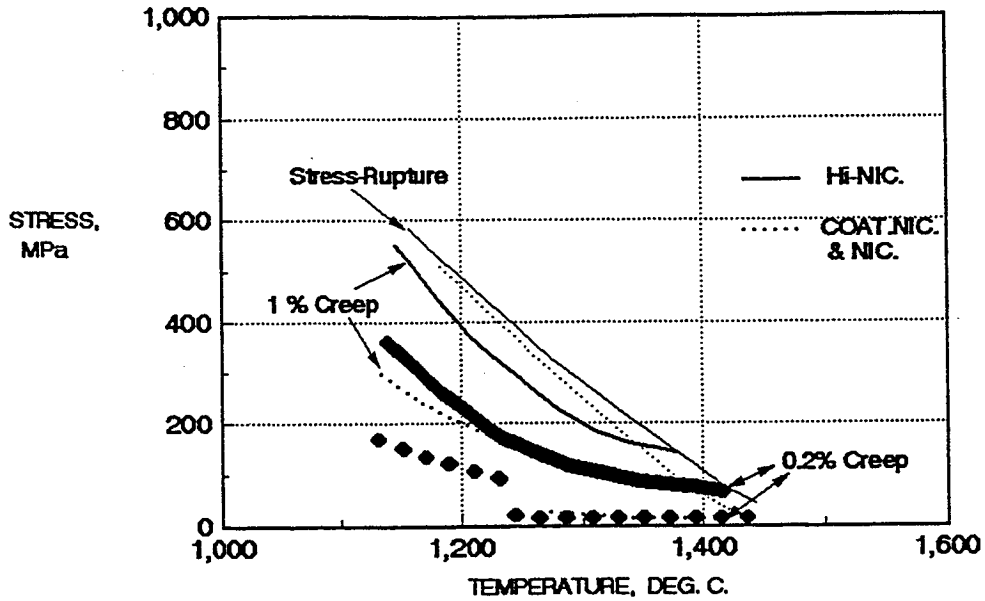


FIG.7. PROJECTED 1000 - HR CREEP AND RUPTURE STRENGTHS OF POLYMER DERIVED SiC FIBERS

CONCLUSIONS

For times up to 1000 hours at 1200 to 1400 °C, Hi-Nicalon is projected to have a greater 0.2 % creep strength and stress-rupture strength than the SiC/BN coated and as-produced Nicalon. The greater creep strength of Hi-Nicalon appears to be related to its low oxygen content. Excess free carbon beyond the stoichiometric Si/C ratio in Hi-Nicalon may reduce its creep strength, but apparently does not seriously influence its oxidation resistance as suggested by its high stress-rupture strength in air.

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