研究解説

# Evaluation of Creep Behavior in SiC/SiC Ceramic Matrix Composites

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## 1. Introduction

In recent decade, mechanical properties of continuous fiber reinforced ceramic matrix composites (CMCs) have been investigated for the application of CMCs industry [1–15]. One way to achieve high fracture toughness and thermal shock resistance is through the design of weak interfaces between fibers and matrix, e.g., the use of carbon-coated fibers in SiC/SiC composites produced by CVI from as-received SiC-based fibers. The weak interface can cause crack to deflect along the interfaces, permitting intact fibers to bridge crack faces [1]. However, although the use of weak interfaces can increase fracture toughness and thermal shock resistance [2], it is not compatible with creep resistance, which demands strong interfaces resisting the nucleation and growth of cavities [3]. Moreover, carbon coating layer in SiC/SiC leads to low oxidation resistance at high temperatures in air. A glass-forming, boron-based particulate can be added to the matrix that reacts with oxygen to produce a sealant glass that inhibits oxidation [9]. This technology is applied to SiC/SiC composites. The modified SiC/SiC was called Enhanced SiC/SiC composite [9].

Since matrix microcracking occurs during initial application of a creep load, fiber bridging of matrix cracks operates in creep of Standard SiC/SiC[1] at high stresses. Therefore, increasing creep resistance of fibers can improve creep behavior of the composite. The presence of $SiC_xO_y$ amorphous phase in Nicalon™ fibers is responsible for the low creep resistance owing to a viscous flow at temperatures as low as 1000–1200°C [16]. The silicon oxycarbide phase decomposes, forming SiC and gaseous species such as CO and SiO, whose diffusion through the fiber and reaction with the free carbon are believed to create pores and other defects in the fiber structure [17]. Such a decomposition causes strength and Young's modulus degradations and affects the fiber creep behavior even in inert atmospheres [18–20]. The elimination of $SiC_xO_y$ from the fibers by electron irradiation in vacuum instead of curing in air can improve creep resistance [21]. The Young's modulus is also increased [21]. The modified Nicalon™ fibers are called Hi-Nicalon™ fibers. Using Hi-Nicalon™ fibers to reinforce the enhanced SiC matrix is expected to create a composite having a high creep resistance in air.

This paper will present creep behavior of Standard SiC/SiC, Enhanced SiC/SiC[2] and Hi-Nicalon™/SiC[3] composites in argon and air at the temperature of 1300 °C.

## 2. Materials and Experimental Procedures

The composites used in this investigation were processed by chemical vapor infiltration (CVI) of SiC into woven fiber preforms (made by Du Pont Lanxide Composites Inc., DE, U.S.A.). Before the infiltration, the preforms were coated with carbon by CVD in order to decrease interface bonding between fibers and the matrix, thereby increasing toughness. The composites, processed as 200 mm x 200 mm panels with a thickness of 3.2 mm, contained 40 vol% SiC fibers and 9.7% porosity. The diameter of a fiber was about 12 $\mu$m and each bundle consisted of 500 fibers. The specimens for creep tests were machined from the panels using diamond cutting tools. The shape and dimensions of the specimens were described in references [6–11]. The surfaces of the specimens were machined by an 800 grit grinding wheel before testing. The specimens were not protected by a final CVI run after machining.

Creep tests were carried out with a servo-hydraulic MTS 810 testing system (MTS System Corporation, Minnesota, USA) at 1300 °C in argon. The creep tests were conducted under a constant

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[1] Standard SiC/SiC indicates Nicalon™ fibers reinforced SiC composite, in which SiC matrix is pure SiC.

[2] Enhanced SiC/SiC indicates Nicalon™ fibers reinforced SiC composite, in which the SiC matrix contains glass-forming, boron-based particulates.

[3] Hi-Nicalon™/SiC indicates Hi-Nicalon™ fibers reinforced SiC composite, in which the SiC matrix contains glass-forming, boron-based particulates.

load in MTS 659 controlled atmosphere furnace. Creep strain was measured directly from the gage length of the specimen by a contact extensometer (MTS Model 632.53-F71, MTS System Corporation, Minnesota, USA), which has measuring range of ± 2.5 mm over its gage length of 25 mm. Repeated unloading-reloading with a rate of 50 MPa/s was applied to measure the modulus change during the creep tests. The specimens were allowed to soak over 30 min. at the testing temperature before starting creep tests.

## 3. Results and Discussion

### 3.1 Creep behavior

A constant tensile load produces an instantaneous strain response followed by a time dependent strain. The instantaneous strain consists of recoverable (elastic) strain at low stresses and non recoverable strain at high stresses. The time dependent (creep) strain is transient, and continuously decreasing strain rate (primary stage) appears at first. Then it goes to a steady state (constant strain rate, secondary) stage, at last accelerating (tertiary stage) to rupture. The existence of one or two or three stages depends on stress and temperature conditions, also on materials. Three stages creep can be found at low stresses at in Standard SiC/SiC composites, but there is no tertiary stage or even no secondary stage at high stresses [7]. For Enhanced SiC/SiC and Hi-Nicalon$^{TM}$/SiC, tertiary stage does not exist normally [9–11]. Therefore, the minimum creep strain rate is used to characterize creep deformation resistance in this paper.

In argon, the minimum creep strain rate of the Hi-Nicalon$^{TM}$/SiC at 1300°C is lower than that of the Enhanced SiC/SiC (Fig. 1 (a)), and the time to rupture of the Hi-Nicalon/SiC is longer than that of the Enhanced SiC/SiC (Fig. 1(b)). However, although the creep rate of both the Hi-Nicalon/SiC and Enhanced SiC/SiC at 1300°C is higher than that of Standard SiC/SiC (Fig. 1 (a)), the time to rupture of both the Hi-Nicalon/SiC and Enhanced SiC/SiC is longer than that of Standard SiC/SiC (Fig. 1 (b)). Since the fiber and interphase in Enhanced SiC/SiC are the same as in the Standard SiC/SiC, the higher creep strain rate in Enhanced SiC/SiC is attributed to the addition of glassy phases. The glassy phases soften the matrix and may also promote the sliding of the interfaces between fiber and matrix as a lubricant at high temperature. Both the effects can increase creep deformation. However, creep crack growth path in the matrix of Enhanced SiC/SiC is zigzag and discontinuous [9]. This is beneficial to resist crack growth compared to the straight crack path in the pure SiC matrix in Standard SiC/SiC. Moreover, the high creep deformation reduces stress concentration at pores which are crack initiation sites. As a result, time to rupture in Enhanced SiC/SiC is longer than that in Standard SiC/SiC. The higher creep resistance in Hi-Nicalon$^{TM}$/SiC than in the Enhanced SiC/SiC is because the Hi-Nicalon$^{TM}$ fibers in Hi-Nicalon$^{TM}$/SiC is more creep-resistant than normal Nicalon$^{TM}$ fibers in the Enhanced SiC/SiC considering their same matrix and interphases.

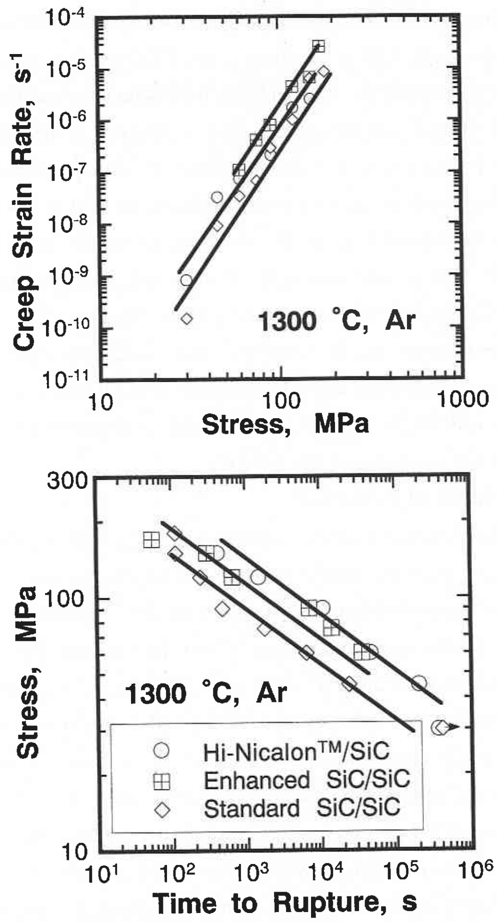


Fig. 1 Creep properties in Hi-Nicalon$^{TM}$/SiC, Enhanced SiC/SiC and Standard SiC/SiC at 1300°C in argon. (a) minimum creep strain rate as a function of stress; (b) time to rupture versus stress.

### 3.2 Modulus Change

The change of the modulus with creep time in argon is shown in Fig. 2. The modulus in Standard SiC/SiC is almost constant, but the modulus in Enhanced SiC/SiC and Hi-Nicalon$^{TM}$/SiC decreases with creep time. The reduction of the modulus indicates creep damage evolution. If the fibers have a lower creep resistance than the matrix, the gradual decrease in modulus during creep is because creep of the bridged fibers transfers stress to the matrix and causes matrix cracking and crack growth. However, it is not known whether Nicalon$^{TM}$ or Hi-Nicalon$^{TM}$ fibers have a higher or lower creep resistance than the SiC matrix with the additives. Fig. 2 only gives the data at the stress of 60 MPa which is lower than the matrix cracking stress. Therefore, the first loading and the early stage of creep do not exhibit reduction of modulus. If the reduction of modulus is thought to reflect multiplication and propagation of the matrix cracks in the specimens, no extensive matrix cracks can be expected according to the constant modulus for Standard SiC/SiC. This is consistent with the observation results of cracks [7]. Comparing Enhanced SiC/SiC with Hi-Nicalon™/SiC, it can be understood that the Hi-Nicalon™ fibers cause less creep damage. The reason for the degradation of modulus after an early creep in Enhanced SiC/SiC and Hi-Nicalon™/SiC is considered to be the lower creep resistance in the matrix.

### 3.3 Effects of Oxidation

For the Standard SiC/SiC, strength and stress rupture life in air are always lower than those in argon or vacuum due to oxidation [22–24]. The oxidation of the Standard SiC/SiC includes two concurrent phenomena: oxidation of the pyrocarbon interphase which creates an annular porosity around the fibers; and silica formation on the free surfaces of the fiber and/or the matrix, which progressively closes the porosity and the access for oxygen towards the interphase, and consequently stops the oxidation processes [25–28]. The annular porosity around the fibers decreases fiber strength, which decreases with an increase in gage length. The silica formation on the free surfaces of the fiber and/or the matrix produces a strong interface which is harmful for both strength and ductility. Therefore, both the annular porosity around the fibers and the silica formation on the free surfaces of the fiber and/or the matrix decrease the strength of the composite. This is the primary reason for the lower creep resistance of the Standard SiC/SiC in air than in argon (Fig. 3). However, the thermodynamic stability of Nicalon™ fiber at high temperature should be also considered. The fibers heat-treated in argon at high temperatures showed severe degradation caused by the decomposition of the silicon oxycarbide phase, which resulted in CO and silicon monoxide gas evolution. While, fibers treated in an oxidizing environment ($O_2$, air) showed slightly less degradation. Only 25% of the initial strength of the fibers was retained after the treatment at 1300°C in argon. The instability of Nicalon™ fiber at high temperature in argon may be the reason for the close creep resistance at low stresses in air and argon.

Creep strain rates of Hi-Nicalon™/SiC in air are compared with those in argon (Fig. 4). It can be seen that the creep rates in argon are evidently higher than in air. The stress exponent for creep in argon is 5, which is lower than in air (n = 9.4). The effect of environment on creep resistance in the Hi-Nicalon/SiC is the same as in the Enhanced SiC/SiC [9], since they have the same matrix.

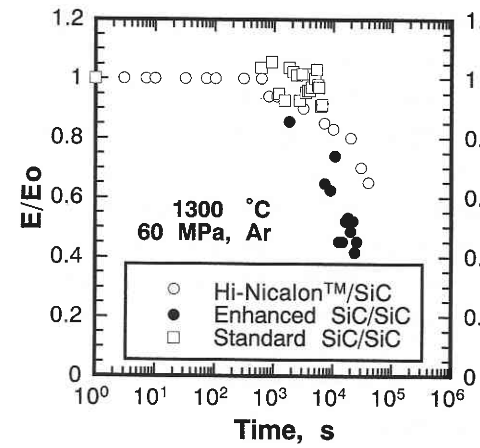


Fig. 2 The elastic modulus normalized by the value of the modulus under the first loading ($E/E_0$) versus time for creep in Hi-Nicalon™/SiC, Enhanced SiC/SiC and Standard SiC/SiC at 1300°C at 60 MPa in argon.

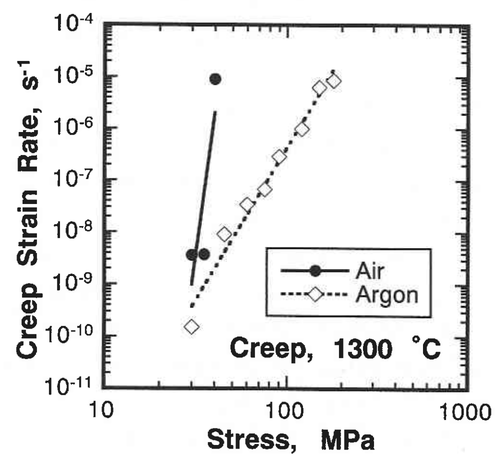


Fig. 3 The minimum creep strain rate as a function of stress in Standard SiC/SiC at 1300°C in air and argon.

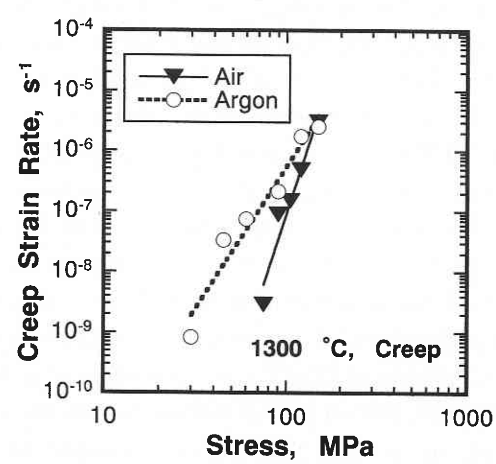


Fig. 4 The minimum creep strain rate as a function of stress in Hi-Nicalon™/SiC at 1300 °C in air and argon.

When the matrix is enhanced by adding glass-forming particulates (borosilicate) that is capable of sealing the outer surface and the cracked surface of the specimen at elevated temperatures, the oxidation of the interphase becomes little. Thus, instability of Hi-Nicalon™ (or Nicalon™) fiber at high temperature in argon is the key factor to cause the lower creep resistance in argon than in air. Moreover, the sealing of cracks by glass may more effective in air than in argon, since there are more oxygens in air to react with the glass-forming particulates than in argon.

## 4. Conclusion

(1) Creep strain rate of the Standard SiC/SiC is the lowest, then Hi-Nicalon™/SiC, and the Enhanced SiC/SiC has the highest creep rate in argon at 1300°C. But, the time to rupture of the Standard SiC/SiC is the shortest, and Hi-Nicalon™/SiC has the longest life. This means that the addition of glassy phases in the matrix decreases creep rate but increase the resistance to creep fracture.

(2) For the Standard SiC/SiC composite, creep resistance in air was much lower than that in argon. However, creep resistance of Enhanced SiC/SiC and Hi-Nicalon™/SiC in air was higher than those in argon.

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