MODELING THE THERMOSTRUCTURAL STABILITY OF MELT-INFILTRATED SiC/SiC COMPOSITES

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ABSTRACT

SiC/SiC composites developed by NASA with Sylramic-iBN fibers and melt-infiltrated (MI) SiC-Si matrices have demonstrated 1000-hour rupture life in air at 100 MPa and 1315°C. Recently it has been determined that a major factor controlling the long-term rupture life of these composites is not environment or stress, but an intrinsic microstructural and strength instability caused by a thermally-induced silicon attack of the SiC fibers. The objective of this paper is to present a simple diffusion-based analytical model which predicts well the observed effects of stress-free thermal exposure on the residual tensile strength of Sylramic-iBN/SiC-Si composites. The practical implications of the model for SiC/SiC composites with MI matrices are discussed.

INTRODUCTION

NASA has recently developed SiC/SiC composites with Sylramic-iBN SiC fibers, BN-based interphases, and SiC-Si matrices as candidate materials for next generation gas-turbine hot-section components [1]. The Sylramic-iBN fiber is produced at NASA Glenn from the commercial Sylramic fiber by a high-temperature treatment that removes boron-sintering aids from the fiber bulk and forms a thin in-situ grown BN layer on the fiber surface. This results in a SiC fiber with the high strength (>3 GPa) and high thermal conductivity of the precursor Sylramic fiber, but with a dense BN surface layer and better creep-rupture strength in air than any other fiber SiC fiber type [2]. For interphase and matrix processing, NASA has developed a component fabrication approach [3] in which BN-based interphases and SiC interphase over-coatings are chemically vapor infiltrated (CVI) into the component fiber architecture. The CVI SiC over-coating not only protects the interphase, but is also the initial constituent of the final matrix, providing its primary load-carrying capability. The remaining matrix open

porosity is filled by slurry infiltration of SiC particulate, followed by melt-infiltration (MI) of molten silicon near 1400°C. The BN-based interphases are much more oxidatively stable than carbon-based interphases, and the final low-porosity MI matrix displays high thermal conductivity and low permeability. Under tensile creep-rupture testing at 1315°C and 100 MPa stress, these composites have demonstrated 1000-hour rupture life in air [4]. The creep results show primary and secondary stages, but no tertiary stage, suggesting composite rupture occurs at matrix rupture with no subsequent load-carrying capability from the crack-bridging fibers.

As a possible explanation for this last observation, it has recently been determined that SiC fibers can lose strength within MI SiC/BN/SiC-Si composites even under *stress-free* high-temperature conditions [5]. This intrinsically controlled property loss is manifested by a reduction in the ultimate tensile strength (UTS) of composites after thermal exposure between 1300 and 1400°C for up to 500 hours in air. UTS loss is observed to be time-dependent and thermally activated. SEM microscopy clearly indicates that the fiber strength loss is caused by diffusion of elemental silicon from the matrix through grain boundaries in the CVI SiC interphase over-coating. Because the fibers are clumped as part of multi-fiber tows, silicon attack of the fibers initiates near the tow surface and gradually works its way by diffusion into the tow center. In support of this physical model, it has been observed that when the thickness or volume fraction of the CVI SiC over-coating is increased, the strength loss is less for a given time/temperature exposure condition. The objective of this paper is to employ these residual strength results and thermally activated diffusion theory to develop a simple analytical model that could be used to predict the intrinsic UTS retention of the NASA SiC/BN/SiC-Si composite system for any time, temperature, and CVI SiC condition of practical interest. The implications of this model for composite structural behavior and long-term service are discussed.

EXPERIMENTAL OBSERVATIONS

Fabrication methods, test procedures, and UTS test results for the thermally exposed Sylramic-iBN fiber-reinforced MI SiC/BN/SiC-Si composites are presented in a companion paper [5]. In the as-fabricated condition, these 2D 0/90 composites displayed an average UTS value of ~400 MPa with ~ 37 total volume % fibers. To understand the effects of the CVI SiC interphase over-coating, its volume fraction was varied from ~20 to 35 %. For each individual fiber tow, SEM micrographs show that the thickness of the BN coating on top of each fiber was nearly uniform, and that above ~20 vol. % of CVI SiC, all BN-coated fibers within the tows were fully coated with the CVI SiC over-coating.

Figure 1 shows the effects of a 500-hr thermal exposure in air at 1300, 1350, and 1400°C on the residual room-temperature stress-strain curves for MI SiC/BN/SiC-Si composites with ~34 vol. % CVI SiC. It can be seen that as exposure temperature increased, the primary modulus, secondary modulus, and

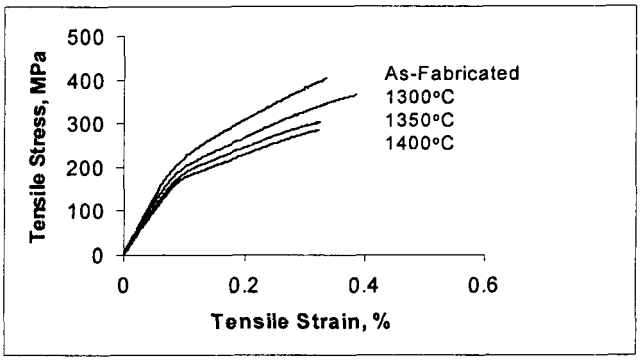

Figure 1. Effects of a 500-hr thermal exposure in air at 1300, 1350, and 1400°C on the room-temperature stress-strain curves of SiC/BN/SiC-Si composites with ~34 vol. % CVI SiC interphase over-coating.

UTS decreased, suggesting a decrease in the interphase shear strength and number of fibers that can carry load.

Figure 2 shows the effects of CVI SiC content on the normalized UTS ratio for Sylramic-iBN-reinforced SiC/BN/SiC-Si composites that were exposed in air for 100 and 500 hours at 1350°C. These results clearly show that the observed strength degradation was time dependent and that as CVI SiC content increased, UTS degradation decreased. It also shows that under the worse condition, the residual UTS was close to reaching the matrix cracking stress of ~160 MPa (ratio ≈ 0.4), where the composite stress-strain curves suggest monolithic behavior.

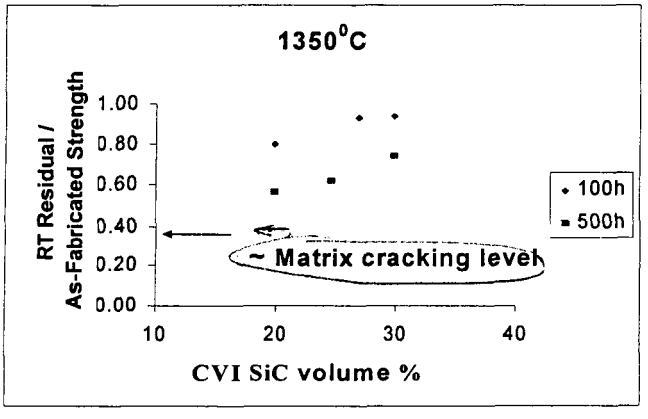

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Figure 2. Effects of CVI SiC vol. % on the UTS ratio for Sylramic-iBN/BN/SiC-Si composites that were exposed in air for 100 and 500 hours at 1350°C.

STRENGTH DEGRADATION MODEL

To develop an analytical model that predicts the results of Figs. 1 and 2 and other UTS degradation results under different conditions [5], three simplifying assumptions were made. First, the migration of elemental silicon into the tows occurs by thermally activated diffusion through the CVI SiC interphase over-

coating. As such, the diffusion distance **X** depends on exposure time **t** by the simple relation: $\mathbf{X} = \alpha\ \mathbf{t}^{1/2}$ where α is a constant. Also, exposure time **t** and exposure temperature **T** (Kelvin) are inter-related by the thermal activation equation: $\mathbf{t} = \Theta\ \mathbf{exp\ (-Q/RT)}$, where Θ is a constant, **Q** is the activation energy for silicon diffusion through CVI SiC, and **R** (= 8.314 kJ/mole•K) is the gas constant. A second assumption is that each tow is equally coated with the same CVI SiC content. The final assumption is that each Sylramic-iBN fiber in each multi-fiber tow loses all of its load-carry capability when elemental silicon reaches its BN interphase coating. Thus for each tow, the fraction of load-bearing fibers ϕ decreases with time in the same manner as silicon diffuses from the coated tow surface to the tow center. Since composite strength is directly proportional to the number of load-bearing fibers in each tow, it follows that the retained UTS (= **U**) should then be predictable from the simple relation:

$$\mathbf{U / U_0\ (as\text{-}fabricated)} = \phi\ \mathbf{(t, T, m)} \qquad \mathbf{(1).}$$

Here **m** ≡ CVI SiC volume %, which determines maximum diffusion distance.

For modeling the dependence of ϕ on **t**, **T**, and **m**, one can examine the Fig. 3 schematic, which depicts a typical coated tow in the SiC/BN/SiC-Si composites. As indicated, the tow is generally elliptical in shape, and after the tow is filled with CVI SiC, further SiC deposition leads to a cladding of thickness **H** on the tow surface. Thus the fiber distribution ϕ should be different as silicon diffuses along the **x** or **y** direction toward the tow center (see equations in Fig.3). For simplicity, this study assumes that (1) **H << A, B**, (2) **A =B** (circular tows or one-dimensional diffusion), and (3) the tow radius (**A** or **B**) is directly proportional to **m.** It then follows that **F = x/B**, so that

$$\mathbf{1 - \phi\ (t, T, m)} = \mathbf{[x/B]} = (\beta)^{1/2}\ [(t)^{1/2}/\mathbf{m}] \qquad \mathbf{(2).}$$

Here $\beta = \beta_0\ \mathbf{exp\ (-Q/RT)}$, and β_0 and **Q** are empirical constants to be determined.

Equations 1 and 2 indicate that if the model assumptions are close to characterizing the underlying strength degradation mechanism, plots of **[1-U/Uo]**

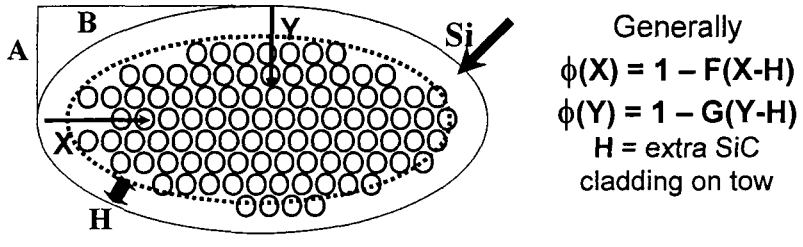

Figure 3. Schematic of a typical coated tow in the SiC/BN/SiC-Si composites. Fibers are distributed by the F and G functions from the tow center outward.

versus $[(t)^{1/2}/m]$ at the three exposure temperatures should be straight lines with zero intercepts and with slopes of $(\beta)^{1/2}$. Fig. 4a shows that this indeed is the case at 1350 and 1400°C, but scatter exists at 1300°C where strength degradation is small. Furthermore, if one examines the best-fit slopes, one should obtain a straight line for **ln** β versus **(1/T)**. Fig. 4b clearly shows that this again is the case for the three exposure temperatures. From this last plot, one obtains an activation energy **Q** = 540 kJ/mole, which in turn is in very good agreement with the 480 kJ/mole value for creep of silicon-containing CVI SiC fibers [6]. Thus, although the model is based on simple assumptions, Equations 1 and 2 with the **βo** and **Q** constants given in Fig. 4b can closely predict the intrinsically controlled strength degradation data for the Sylramic-iBN SiC/BN/SiC-Si composites.

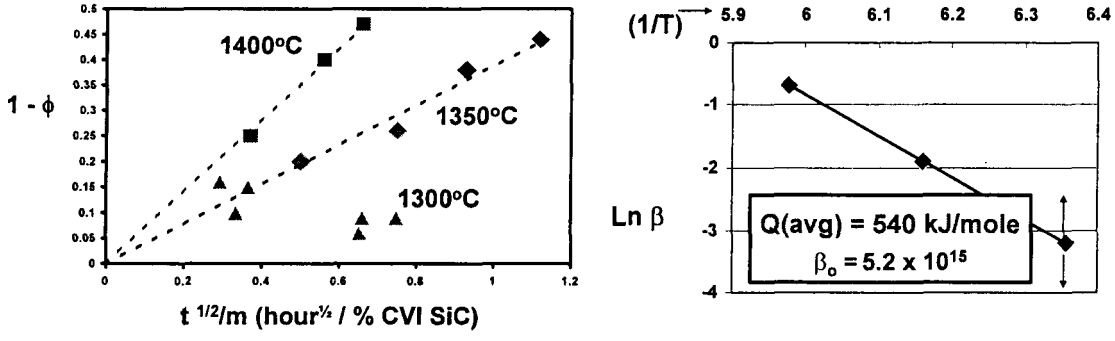

Figure 4. Fit of strength degradation data to Equations 1 and 2.

MODEL IMPLICATIONS

Using the silicon diffusion model, one can now predict the UTS strength retention of SiC/SiC composites with Sylramic-iBN fibers and MI silicon-containing SiC matrices for stress-free conditions both within and outside the available data set. Figure 5 shows such predictions for continuous values of exposure time and temperature; for CVI SiC contents (**m**) of 22 and 35 vol. %, and for strength retention ratios (ϕ) of 0.7 and 0.4. The CVI SiC **m** values represent the approximate range available for MI panels made from 2D fabric; while the ϕ values relate to two important conditions for composite application. For example, at ϕ = 0.7 the composite retains much of its as-fabricated strength, thus some degree of damage tolerant performance. However, at ϕ = 0.4, the tows have lost sufficient strength to fracture at or below matrix cracking, thereby providing no extra strain capability and allowing the composite to behave as a monolithic ceramic. Thus conditions with ϕ values above ~0.7 are desirable.

Based on these arguments, Fig. 5 contains many important implications. First, higher CVI SiC content is desirable under all conditions; but for a given exposure condition and ϕ value, the allowable exposure time is only increased by a factor of ~ five. Second, during low-stress rupture testing of the composites for 1000 hours at 1315°C, the composite UTS should degrade almost to the matrix cracking

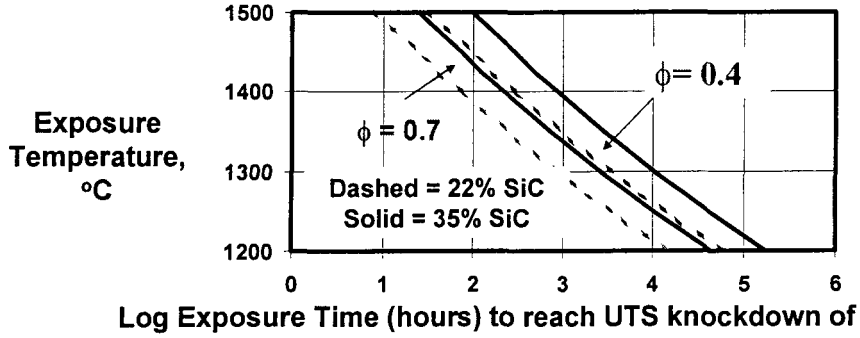

Figure 5. Model predictions of UTS retention (ϕ) for some realistic conditions

strength, even without creep-induced damage. Thus tow life after matrix rupture should not be expected, as has been observed [4]. Third, for applications of 10,000 hours or more (such as in land-based gas turbines), maintaining damage tolerance behavior would exclude maximum use temperatures above 1250°C. Finally, although the silicon MI approach contributes high thermal conductivity and low permeability, the composite upper use temperature is matrix limited. Thus higher temperature applications will require approaches to inhibit silicon diffusion into the CVI SiC or to completely eliminate silicon from the matrix.

SUMMARY

In a companion paper [5], stress-free thermal exposure studies were performed to evaluate the UTS retention of SiC/BN/SiC composites with Sylramic-iBN SiC fibers and silicon-containing MI SiC matrices. In this paper, a simple UTS degradation analytical model was developed based on fiber attack by silicon diffusion through CVI SiC coated tows. It was shown that this model predicts well the effects of exposure time, temperature, and CVI SiC content. Practical implications of the model for MI SiC/BN/SiC applications were discussed.

ACKNOWLEDGEMENT

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