

TIME-DEPENDENT BRIDGING AND LIFE PREDICTION OF SiC/SiC IN A HYPOTHETICAL FUSION ENVIRONMENT -- C. H. Henager, Jr., C. A. Lewinsohn, C. F. Windisch, Jr., and R. H. Jones (Pacific Northwest National Laboratories)

OBJECTIVE

The objective of this work is to discuss a methodology for component life prediction based on subcritical crack growth in typical fusion environments. Data are supplied for effects of C-interphase oxidation rates on crack growth rates in SiC/SiC composites. A simple crack growth model is presented based on time-dependent bridging concepts and used to predict the time for an initially bridged crack to grow 5×10^{-4} m as an estimate of component useable life. These calculations are useful in determining the relative merits of pursuing material modifications for the fusion environment, which can be a very expensive proposition. A useful outcome of this effort is to define the performance limitations for these materials as a function of temperature and oxygen.

SUMMARY

Growth of subcritical cracks in SiC/SiC composites of CG-Nicalon fibers with a ~ 1 μm C-interphase has been measured on a related Basic Energy Sciences program using environments of purified argon and mixtures of argon and oxygen at 1073K to 1373K. Companion thermo-gravimetric (TGA) testing measured mass loss in identical environments. The TGA mass loss was from C-interphase oxidation to CO and CO₂, which was undetectable in argon and linear with oxygen concentration in argon-oxygen mixtures, and was converted into an interphase linear recession rate. Crack growth in pure argon indicated that fiber creep was causing time-dependent crack bridging to occur, while crack growth in argon-oxygen mixtures indicated that time-dependent C-interphase recession was also causing time-dependent bridging with different kinetics. A model of time-dependent bridging was used to compute crack growth rates in argon and in argon-oxygen mixtures and gave an estimate of useable life of about 230 days at 1073K in a He + 1.01 Pa O₂ (10 ppm) environment.

PROGRESS AND STATUS

Introduction

Continuous fiber ceramic matrix composites (CFCCs) with a chemically-vapor infiltrated (CVI) SiC matrix and polymer-derived SiC fibers, so-called SiC/SiC materials, are being developed and evaluated for utilization in a wide variety of high-temperature applications. These applications can be divided into two categories: 1) high-temperature ($>1273\text{K}$) in oxidizing environments and 2) moderate temperatures (1073-1273K), relatively inert chemical environments, and neutron environments. The second category includes advanced fusion energy systems and fission reactors. The primary environmental concern for category 1 is the high-temperature, oxidizing environment, while for category 2 the primary challenge is the radiation environment. High-temperature, oxidizing environments present a challenge to SiC/SiC CFCCs because of the chemical reaction between the fiber/matrix interphase material and oxygen. The fusion environment poses different problems in contrast to rapid oxidation of the interphase material; however, the results are similar. The response of SiC/SiC CFCCs to neutron irradiation was reported [1] and a loss of strength from fiber shrinkage and the accompanying loss of fiber/matrix bonding was observed. A summary of the issues associated with the application of SiC/SiC CFCCs for fusion energy systems has been presented by Jones et al. [2-4]. Since newer, more stable fibers are being developed and will eventually be incorporated into these SiC/SiC composites the effects of neutrons on fiber dimensional stability are expected to be mitigated. However, current and future interphase technology suggests that even "high-purity" inert

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chemical environments need to be evaluated because of the high reactivity of C-interphases with oxygen.

A model for crack growth in oxygen-containing environments has been formulated [5, 6] and is used to make an estimate of useable life for a fusion first wall made of C-interphase SiC/SiC. Temperature and oxygen effects are incorporated into a single model for lifetime prediction calculations. For this model, the rate of C-interphase removal was determined from experiments and related to a time-dependent bridging-fiber relaxation process as indicated. Calculations using this approach can be used to estimate composite lifetimes in environments and at temperatures where thermal creep of fibers is insignificant, such as the fusion energy environment. Of course, other effects, as yet to be determined, such as irradiation-induced creep, may play a role in this severe environment. These calculations are useful in determining the relative merits of pursuing material modifications for the fusion environment, which can be a very expensive proposition. A useful outcome of this effort is to define the performance limitations for these materials as a function of temperature and oxygen.

Experimental Technique

SiC/SiC CFCC materials fabricated by Refractory Composites Inc. with Nicalon-CG and C-interphase (CG-C) and by DuPont with Hi-Nicalon fibers and a C-interphase (Hi-C) were evaluated by thermal gravimetric analysis (TGA) and high-temperature mechanical testing. A summary of the material characteristics is given in Table 1 where the fracture toughness values are for 1373 K for the CG-C and CG-BN material and 1473 K for the Hi-C material. All material was made with eight plies of 0/90 fiber cloth and the composite plates were 4 mm thick.

Table 1. Summary of SiC/SiC CFCC material characteristics.

Composite Type:	CG-C	Hi-C
Fiber Type	"Ceramic grade"	"Hi-Nicalon"
Fiber Coating	1.0 ± 0.1 μm carbon	1.0 ± 0.5 μm carbon
Fibers/Tow	420	321
Fiber Diameter	14.0 ± 0.5 μm	14 ± 2.3 μm
Fiber Vol. Fraction	30	30
Composite Coating	CVD Silicon Carbide	CVD Silicon Carbide
Porosity	20 ± 5%	6 ± 1.4%
Modulus*	98 ± 6.6 GPa	150 ± 4 GPa
Fracture Toughness	17.5 MPa·m ^{1/2}	23 ± 1.5 MPa·m ^{1/2}

*The modulus is calculated from the specimen compliance measured from the linear portion of loading during flexural testing of SENB specimens at elevated temperature.

Samples with dimensions of about 4 mm x 4 mm x 8 mm were tested at 1373K using thermal gravimetric analysis (TGA). One face of the 4 mm x 8 mm of the samples was cut so that it was free of the SiC coating applied to the surface of the material during the last phase of fabrication. All other faces of the samples had a thin, approximately 5 μm-thick, SiC coating. All rates were normalized with respect to the cut, uncoated surface. Mixtures of O₂ with Ar were used in these experiments and the gas flow was maintained at about 1 SCFH through the instrument furnace and composition was controlled using a multi-gas controller and an oxygen meter. In each test, a sample was placed in an alumina cup in the analyzer furnace, the furnace was sealed, gas flow was adjusted, and the balance was allowed to equilibrate for about 2 h before heat up.

The SCG studies were performed using constant load tests for times up to 1 x 10⁵ s, giving long-term crack velocity data, and using stepped load tests with load holding times of 1000 s carried out at

1100°C in Ar and Ar plus varying O₂ levels. Single-edge-notched bend bar (SENB) specimens with dimensions of 4 mm x 5.5 mm x 50 mm were tested. The SENB specimens were tested in 4-point bending using a fully articulated SiC bend fixture [5]. The specimens were typically loaded at an applied stress intensity of 7 to 8 MPa√m to begin the test. The test continued until a load drop was observed. Specimens that were tested in Ar plus O₂ were brought up to temperature in pure Ar. The displacement-time curves were fit to polynomial functions and differentiated to give $\partial\delta/\partial t$. This quantity was then converted into a crack velocity [5].

Results and Discussion

Mass losses from C-interface oxidation measured by TGA were generally linear as a function of time for the composite materials between 3.1×10^2 Pa to 2.5×10^3 Pa O₂ and between 1073K and 1373K [6]. Microscopic examination of the C-interfaces in cross-sectioned SiC/SiC samples that had been exposed to oxidizing conditions revealed a remarkable uniformity in the recession distance from the unsealed surfaces exposed to O₂ [7, 8]. Recession rates calculated from these measured recession depths were compared to those calculated from TGA data assuming all the mass losses were due to C oxidation. The recession rates calculated from the two approaches were in acceptable agreement considering the experimental uncertainties. The measured optical recession rates are shown in Figure 1 as a function of pO₂ for the CG-C materials.

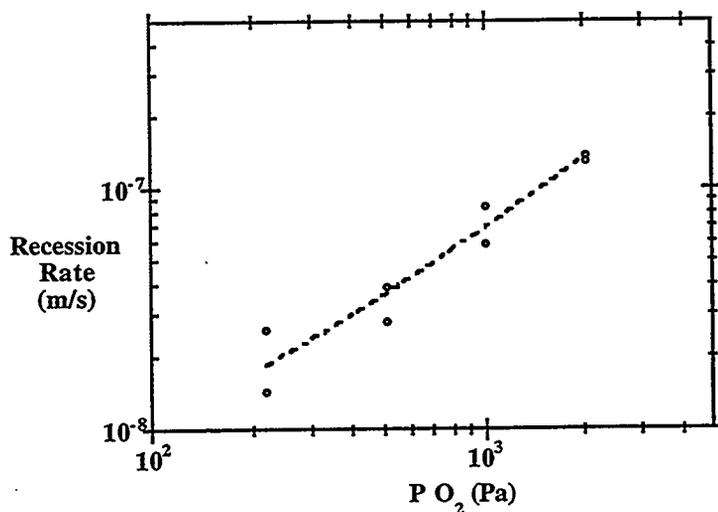


Figure 1. Measured (optical microscopy) C-interphase recession rates at 1373K as function of indicated pO₂. This recession data was used in the time-dependent bridging model.

Slow crack growth data were also obtained for these same SiC/SiC composites in mixtures of Ar and oxygen (O₂) [6-8]. Slow crack growth rates were measured as a function of pO₂ (Figure 2) and temperature in Ar + O₂ using a unique environmentally-controlled, high-temperature test apparatus at PNNL. Representative data plots are shown below in Figure 2 for C-interphase composites with Nicalon CG fibers for three different oxygen partial pressures. The addition of oxygen to the 1373K Ar environment increases the crack velocity in stage-II and shifts the stage-II-to-III transition to lower *K*-values, Figure 2. This leftward shift is consistent with a reduction in the closure forces imparted on the crack faces by the bridging fibers. Scanning electron micrographs of polished cross-sections of cracked specimens exposed to O₂ plus Ar revealed that oxidation at 1373K partially removed the

C-interphase where the crack intersects the bridging fibers [7, 8]. The removal of this interphase material reduces the extent to which the matrix can transfer load to the fibers, and, in turn, reduces the bridging-zone effectiveness. Therefore, in addition to relaxation of bridging zone stresses caused by fiber thermal creep, the strength of the fiber-matrix mechanical coupling will fall in time-dependent fashion as the interphase is removed.

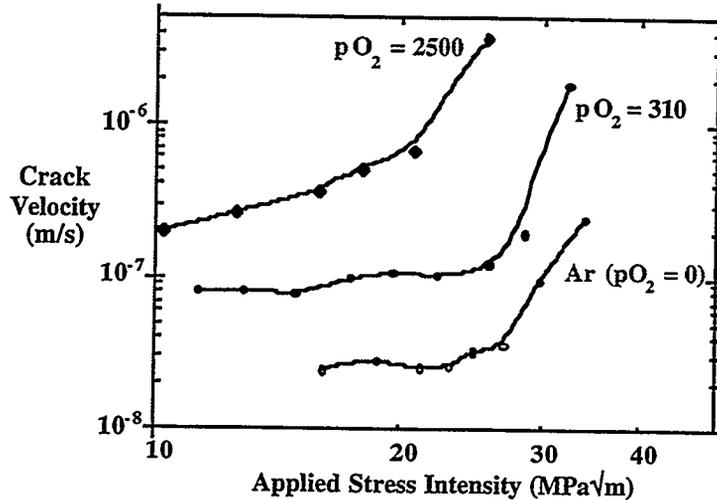
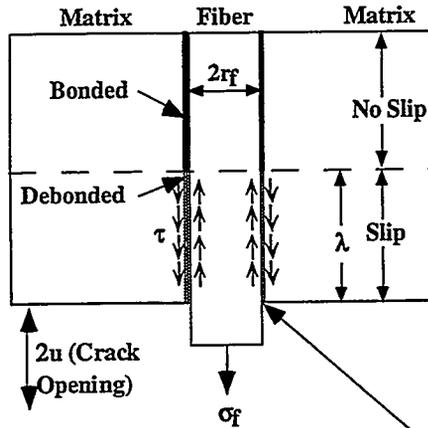


Figure 2. Crack velocity as function of oxygen partial pressure in pascals (Pa) at 1373K. Total system pressure was 1.01×10^5 Pa (1 atm.) with the balance Ar. Materials with easily oxidizable interphases, such as C, are vulnerable to oxidation and lifetimes are greatly decreased.

The temperature data was used to calculate activation energies for cracking in both pure Ar and in Ar + O₂ [8]. Data from the TGA experiments and crack growth experiments of C-interphase materials at 1373 K indicate that the activation energies for both weight loss as a function of time and crack growth rate are about 50 kJ/mol [9-11]. Based on these results, the rate controlling step for crack growth in oxygen-containing environments is carbon oxidation which results in mechanical de-coupling of the fiber from the matrix due to fiber/matrix interphase removal. The process envisioned for de-coupling the bridging-fibers from the matrix is shown schematically in Figure 3. The time-dependence of the fiber-bridging stress can be related to the rate of interphase removal by oxidation [6] through the implied time-dependence of the debonded region, λ , and fiber-matrix shear strength, τ .

A model for the effects of oxygen was developed by considering the time-dependent debonding of fibers from the matrix as suggested by Figure 3. For this model, the rate of C-interphase removal was determined from experiments (Figure 1) and related to a time-dependent bridging-fiber relaxation process [6]. Calculations using this approach can be used to estimate composite lifetimes in environments other than Ar and at temperatures where thermal creep of fibers is insignificant, such as the fusion energy environment. Sample calculations for this are shown in Figure 4 using Ar + 1.01 Pa O₂ at 1073K. Fiber thermal creep is considered to be negligible at this temperature [12] and only C-interphase oxidation is considered. Note that the time for an initially bridged crack to grow 0.5 mm is only about 200 days in this environment, suggesting that the C-interphase is not suitable for this environment. Of course, other effects, as yet to be determined, such as irradiation-induced creep, may play a role in this severe environment.



Oxygen-containing environment reacts with C-interphase and increases fiber slip length, λ , as a function of time. Thus, λ and shear strength, τ , are time-dependent.

Figure 3. A schematic drawing of the time-dependent debonding mechanism envisioned for mechanically decoupling the Nicalon fiber from the SiC-matrix due to fiber-matrix interphase removal. A time-dependent debonded region implies that λ and τ are time-dependent, which suggests an approach for modeling such behavior.

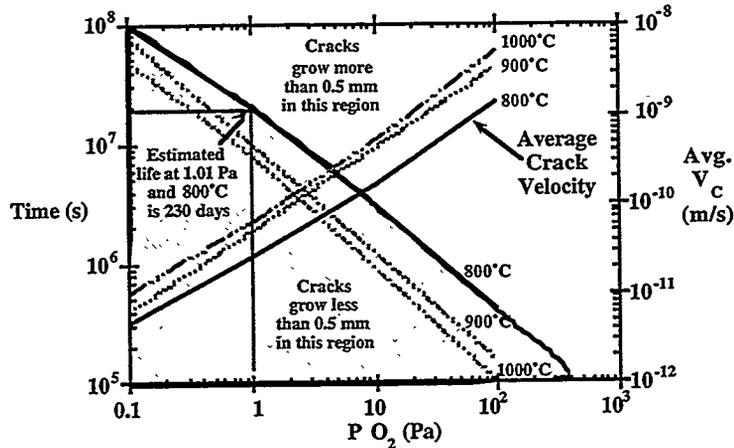


Figure 4. Calculated lifetime based on the time for a bridged crack to grow 5×10^{-4} m (0.5 mm) for a C-interface SiC/SiC composite as a function of pO_2 at three different temperatures, such as would be encountered in proposed helium-coolant, fusion energy environment. The lifetime for He + 1.01 Pa O_2 (10 ppm) at 800°C would be an estimate for a typical fusion energy environment if other mechanisms were negligible. This calculation is independent of fiber type.

Summary

It was shown that C-interphase removal accelerates the crack growth rates through time-dependent debonding and that a simple time-dependent bridging model can be used to estimate useful component life based on measured activation energies and recession rates. The results

suggest that improved environmental resistance is required for even a high-purity fusion energy environment. This improvement could result from more stable fiber/matrix interphase materials such as porous SiC, use of glass formers in the matrix to seal the matrix microcracks and use of coatings. The use of porous SiC interphase material is the most appealing because additions of glass formers to the matrix affects composite properties while high-temperature, oxidation resistant coatings will crack as a result of thermal cycling and creep of the composite.

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