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Analysis of oxidation-assisted stress-rupture of continuous fiber-reinforced ceramic matrix composites at intermediate temperatures

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Abstract

A model is presented to estimate the reliability and time-to-failure of an unidirectional continuous fiber-reinforced ceramic composite when subjected to stresses beyond the matrix cracking stress. The particular case of oxidation-assisted stress-rupture at intermediate temperatures is considered. The effects of stress and temperature on the reliability of the model composite are examined. Model predictions are presented for the specific case of CG-Nicalon™/SiC CFCCs with carbonaceous fiber coatings. © 1999 Published by Elsevier Science Ltd.

Keywords: A. Ceramic-matrix composites (CMCs); Carbonaceous fiber coatings; Oxidation; Stress rupture

1. Introduction

The driving force behind the development of continuous fiber-reinforced ceramic composites (CFCCs) is the promise of substantial economic and environmental benefits if these materials are used to fabricate components for the energy and related industrial technologies [1]. In contrast to monolithic ceramics, CFCCs are attractive because of their potential to exhibit high strength and non-catastrophic mode of failure.

Many applications of interest for CFCCs (e.g. combustor liners for gas turbine engines and filters for the energy and chemical industries) involve mostly steady state operating conditions. Typically components would be subjected to relatively constant stresses at intermediate and elevated temperatures over periods of time that are measured in thousands of hours. However, it is also expected that over their service life such components will experience transients, either planned or accidental. Thus, the successful implementation of CFCC components in the envisioned applications will depend on knowing the thermomechanical behavior of the CFCC over periods of time comparable to their expected service life and on the availability of design methodologies to predict their life under the expected (planned and unplanned) service conditions.

Although it was argued that in the absence of environmentally stable fibers and fiber coatings the design stress for CFCC components will not exceed the so-called matrix cracking stress, it will still be necessary to determine and predict the behavior of these materials during transients when they could be subjected accidentally to stresses beyond the matrix cracking stress. In this paper a model is presented to estimate the reliability of a CFCC when subjected to a constant tensile stress larger than the matrix cracking stress (i.e. stress-rupture conditions). The specific case of CG-Nicalon™/SiC CFCCs with a fiber coating that becomes fugitive upon oxidation is considered.

2. Model

2.1. Micromechanics

Consider a unidirectional model composite of length h, that is reinforced with fibers of equal diameter $2r$ that occupy a fraction v_f of the composite volume (see Fig. 1). It is assumed that the fibers are coated with a different material layer of finite thickness to impart composite behavior to the CFCC and that the distribution of tensile strengths for the fibers and the fiber interfacial shear stress, τ, are known. By assuming that the fibers are uniformly distributed in the matrix, the conceptualization of the model composite can be simplified to a system of three concentric cylinders representing the fiber, the fiber coating and the matrix [see Fig. 2(a)].

Consider the case when such a composite is subjected to a tensile stress, σ_c, larger than the matrix cracking stress, σ_{mc}, so that a series of parallel and equally spaced cracks are formed in the matrix. It is assumed that for stresses larger than the matrix cracking stress, but, lower than the stress at which the matrix saturates with cracks, σ_{sat}, the density of

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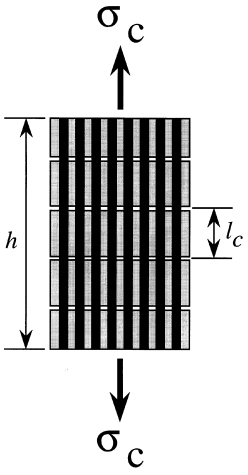

Fig. 1. Schematic representation of model unidirectional composite of length h subjected to a constant tensile stress σ_c.

matrix cracks ρ_c, or the matrix crack spacing, l_c, are a known function of the applied tensile stress,[1] i.e.

$$\rho_c = \frac{1}{l_c} = f(\sigma_c) \quad \sigma_{mc} \le \sigma_c \le \sigma_{sat} \tag{1}$$

At the plane of the matrix cracks the axial stress in the bridging fibers will increase to support the entire load applied to the composite. Away from the crack surfaces, the average fiber axial stress will decay linearly at a rate of $2\tau/r$ as the matrix picks up the complementary portion of the load. The axial stress distribution along the fiber will then be given by

$$\sigma_z^f(z) = T - \frac{2\tau z}{r} \quad 0 \le z \le l_c/2 \tag{2}$$

where T is the axial stress in the fibers at the crack plane. Fig. 2(b) is a diagram of the idealized fiber's axial stress profile.

A balance of forces at the plane of the matrix cracks yields a relationship between the maximum stress in the fiber, T, and the constant applied stress to the composite, σ_c, according to Ref. [2]:

$$\sigma_c = v_f T(1 - \Phi) + \frac{2\tau}{r}\lambda\Phi \tag{3}$$

where Φ is the fraction of failed fibers and λ is the average fiber pullout length. By assuming global load sharing conditions, the maximum stress in the surviving fibers, T, will increase with progressive fiber failure as dictated by Eq. (3), even though the value of the applied composite stress, σ_c, remains constant. Note that the second term in the right hand side of Eq. (3) accounts for the contribution of fibers that failed away from the matrix crack plane, to the load-bearing capacity of the CFCC.

Assuming that the distribution of fiber strengths is described by a two-parameter Weibull distribution, then

[1] Such a functionality can be determined experimentally.

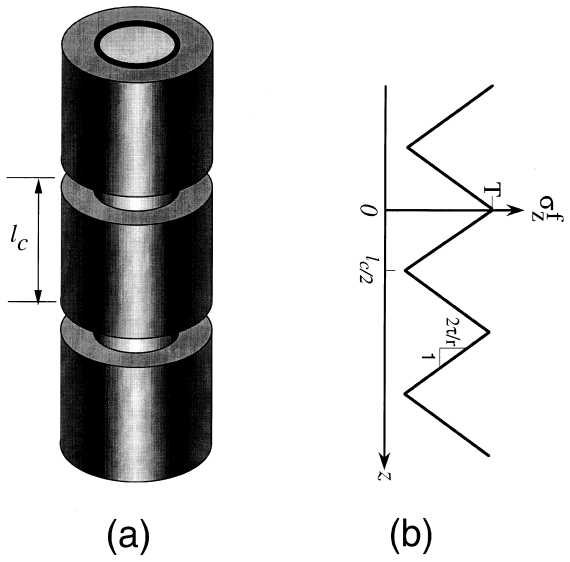

Fig. 2. (a) Corresponding unit cell comprised by three concentric cylinders (fiber, fiber coating and matrix) and uniform matrix crack spacing l_c; and (b) Axial stress profile for the reinforcing fibers.

the fraction of broken fibers will be given by

$$\Phi = 1 - \exp\left\{ - \int_{\text{gauge length}} \frac{1}{l_o}\left(\frac{\sigma_z^f(z)}{\sigma_o}\right)^m dz \right\} \tag{4}$$

where m is the Weibull modulus, and σ_o is the characteristic strength at the reference length l_o.

2.2. Environmental effects

Matrix cracks will serve as avenues for the ingress of the environment into the composite. In this analysis we are concerned with the effects of oxidizing environments on the reliability of a CFCC at intermediate temperatures. Neglecting the oxidation of the matrix,[2] the following scenarios are considered for the interaction of the environment with the fiber coating:

1. it does not oxidize, but allows the diffusion of oxygen to the interior of the composite (e.g. an oxide fiber coating);
2. it oxidizes and forms solid oxide products (e.g. Si);
3. it oxidizes and becomes fugitive (e.g. carbon).

Similarly, the following scenarios are considered for the interaction between the fibers and the environment:

1. the fibers do not oxidize (e.g. oxide fibers);
2. the fibers oxidize (e.g. non-oxide fibers).

To address the behavior of CG-Nicalon™/SiC with carbonaceous fiber coatings we will focus the analysis to

[2] Note that matrix oxidation may, under certain circumstances, result in the healing of matrix cracks, delaying thus, the oxidation of the fibers and the fiber coating. An analysis considering the oxidation of the matrix is currently under development.

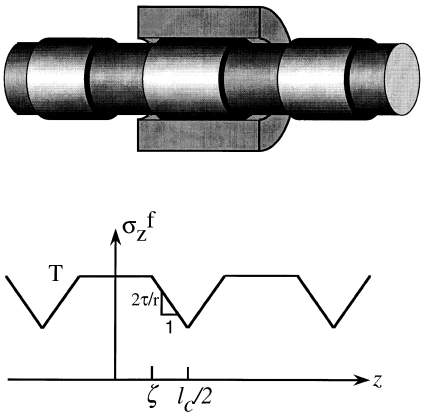

Fig. 3. Axial stress distribution in the fibers after partial removal of the carbonaceous fiber coating. Note that longer portions of the fiber are subjected to the peak fiber stress, *T*, in contrast to the stress distribution in Fig. 2(b).

interactions of the type III and II for the fiber coating and the fibers, respectively.

When the oxidizing environment ingresses into the composite a sequence of events is triggered starting first with the oxidation of the fiber coating. As a result of this, both the axial stress distribution in the fibers and their probability of failure will change, because longer portions of the fibers are subjected to the peak stress, *T*. (Fig. 3). The fiber axial stress will change with the rate of oxidation of the fiber coating and will be given by

$$\sigma_z^f(z,t) = T(t)[U(z)] - \frac{2\tau}{r}(z-\zeta(t))[U(z-\zeta(t))]$$

$$0 \le z \le l_c/2 \tag{5}$$

where ζ is the recession length of the fiber coating measured from the plane of the matrix crack, and $[U(z - z_o)]$ is Heaviside's unit function defined as

$$[U(z-z_o)] = \begin{Bmatrix} 1 & z > z_o \\ 0 & z < z_o \end{Bmatrix}$$

The removal of the fiber coating will expose the fibers to the environment leading to the oxidation of the fibers and eventually to their loss of strength [3,4]. In the case of CG-Nicalon™, as with other SiC-based fibers, its oxidation is controlled by diffusion of oxygen through the oxide layer. Therefore, the oxide layer will grow on the fiber's surface according to:[3]

$$\alpha = \sqrt{k_2 t} \tag{7}$$

where k_2 is the parabolic rate constant [5,6]. Because the oxidation of the fiber is contingent upon the removal of the carbonaceous fiber coating, the thickness of the oxide film on the fiber surface will not be uniform, but, will vary along the exposed length of the fiber as follows:

$$\delta^2(z) = k_2 t - \frac{k_2}{k_1} z \quad 0 \le z \le l_c/2 \tag{8}$$

where k_1 is the rate of carbon oxidation. Obviously the thickness of the oxide on the fiber surface will be greatest at the plane of the matrix cracks.

It was found that when the presence of a coating on the surface of a fiber results in loss of fiber strength, the reduction of fiber strength is inversely proportional to the square root of the coating thickness [4,7]. This observation suggests that the fiber strength can be related to the thickness of the oxide layer according to linear elastic fracture mechanics as follows

$$K_{IC} = Y\sigma_o\sqrt{a} \tag{9}$$

where K_{IC} is the fracture toughness, Y is a geometric parameter, σ_o is the strength and a is the critical flaw size.

By assuming that the fracture toughness of the fibers remains constant and that the characteristic fiber strength, σ_o, is related to the mean oxide layer thickness, $\alpha(t)$, then the time-dependence of the fiber characteristic strength will be given by [8]

$$\sigma_o(t) = \bar{\sigma}_o, \quad t \le \frac{1}{k_2}\left(\frac{K_{IC}}{Y\bar{\sigma}_o}\right)^4$$

$$\sigma_o(t) = \frac{K_{IC}}{Y\sqrt{\alpha(t)}}, \quad t > \frac{1}{k_2}\left(\frac{K_{IC}}{Y\bar{\sigma}_o}\right)^4 \tag{10}$$

Note that Eq. (10) indicates the existence of an incubation period equal to the time required to grow an oxide layer as thick as the size of the average critical flaw in the virgin fibers.[4] Also note that afterwards, the characteristic fiber strength changes with time as $\approx t^{-1/4}$.

In the interest of simplicity but without losing generality, the contribution of the broken fibers to the load carrying capacity of the model composite will be neglected. Although this assumption will lead to underestimating the ultimate strength of the composite, the contribution of broken fibers to the load bearing capability of the composite will decrease with time as the fiber coating becomes fugitive reducing the contact area between the fibers and the matrix.

2.3. Reliability

To determine the reliability of the composite it is necessary to make use of a basic concept of the theory of probability. In a system comprised of sub-elements arranged in series, the reliability of the system will be given by the

[3] Although in a cylindrical geometry the surface through which molecules diffuse is not constant, experimental results have demonstrated that the classical parabolic law derived for planar geometries fits the oxidation data for fibers very well [6].

[4] It is found that at short oxidation times the strength of SiC increases because the oxide layer heals surface defects. However, oxidation results in strength reduction at longer times. Here it is assumed that the characteristic strength of the fibers remains constant until the mean oxide layer thickness becomes larger than the critical defect size associated with the characteristic strength of the original virgin fiber strength distribution.

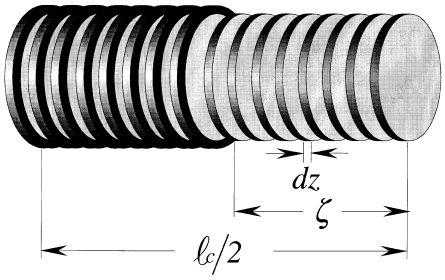

Fig. 4. Discretization of unit cell into differential elements. The reliability of the unit cell will be given by the product of the reliabilities of the differential elements.

product of the reliability of the individual sub-elements [9]. To apply this concept to our model CFCC it is necessary to discretize the unit cell [Fig. 2(a)] into differential elements of length dz as illustrated in Fig. 4. Then, considering that the reliability is obtained by subtracting the probability of failure from unity, i.e.

$$\Re = 1 - \Phi \tag{11}$$

the combination of Eqs. (4) and (5) and the product of the reliability of the differential elements yields [10,11]

$$\Re(t) = \exp\left\{-\frac{2h}{l_c l_o}\left\{T^m \int_0^{\zeta} \frac{\mathrm{d}z}{(\sigma_o(z,t))^m} + \frac{1}{\bar{\sigma}_o^m}\int_{\zeta}^{l_c/2} (\sigma(z))^m \mathrm{d}z\right\}\right\} \tag{12}$$

The strain of the composite is calculated by integrating the stress along the fiber length, i.e.

$$\varepsilon(t) = \frac{2}{E_f l_c}\left\{T(t)\zeta + \int_{\zeta}^{lc/2} \sigma_z^f(z,t)\mathrm{d}z\right\} \quad 0 \le t \le \frac{l_c}{2k_1} \tag{13}$$

Once the carbonaceous fiber coating is removed, i.e. when $\zeta = l_c/2$, then the reliability of the model composite and its axial strain become

$$\Re(t) = \exp\left\{-\frac{2h}{l_c l_o}\left\{T^m \int_0^{l_c/2} \frac{\mathrm{d}z}{(\sigma_o(z,t))^m}\right\}\right\} \tag{14}$$

Table 1
Numerical values used in the calculations

r	8 μm
τ	4 MPa
v_f	0.2
h	0.05 m
m	3.5[15]
σ_o	1.8 GPa[15]
E_f	200 GPa[15]
K_{IC}/Y	0.5 MPa $m^{-0.5}$
s_{mc}	50 MPa
s_{sat}	150 MPa
k_1	[1070 exp(− 123000/RT)]/2200 m s^{-1}[14]
k_2	{exp[11.383 − (8716/T)]}(10^{-18})/60 m^2 s^{-1}[6]
Crack density/σ	25 μ$m^{-1}$$MPa^{-1}$

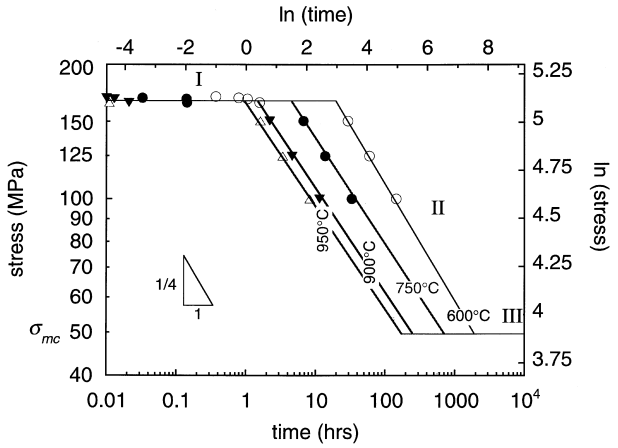

Fig. 5. Predicted stress-rupture curves for model composite. Note that rupture curves have three well defined regimes.

and

$$\varepsilon(t) = \frac{T(t)}{E_f} \quad t > \frac{l_c}{2k_1} \tag{15}$$

Note that at the end of the first stage, the analysis is reduced to that of a bundle of fibers in the Daniels sense [12] subjected to a non-uniform stress distribution that changes with time.

3. Results and discussion

Using the data listed in Table 1, stress-rupture predictions were generated for a hypothetical CG-Nicalon™/SiC composite with a carbonaceous fiber coating. Fig. 5 shows a plot of stress versus time to failure for temperatures between 600°C and 950°C. The stress-rupture curves in Fig. 5 exhibit three regimes. In regime I, the composite fails at stresses close to its tensile strength, but, in a period of time that is less than the time required to consume all of the carbonaceous fiber coating. In this case, failure of the composite results from the inability of the fibers to bear the stress originally carried by the matrix and that is transferred to the fibers when the fiber coating becomes fugitive [10]. In regime II, composite failure occurs after all the carbonaceous fiber coating was completely consumed and the rate of loss of strength for the composite is determined solely by the oxidation of the fibers. Note that the slope of the stress-rupture curves in regime II is equal to −1/4, which is consistent with the time-dependence of the decrease in the characteristic strength of the distribution of fiber strengths (10) and experimental results at 950°C for CG-Nicalon™/Enhanced SiC [13]. Obviously no composite failure is expected at stresses below the matrix cracking stress (regime III).

As indicated by the curves in Fig. 5, the effect of temperature is to shift the stress-rupture curves towards shorter times, i.e. it accelerates the loss of strength of the composite. This is a direct consequence of the Arrhenius-like

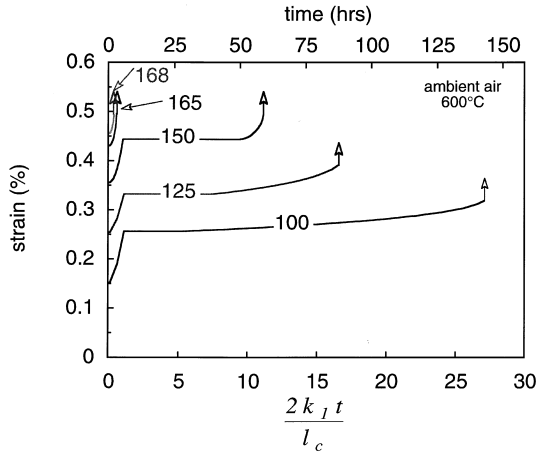

Fig. 6. Predicted strain histories at 600°C and different stresses (in MPa).

temperature-dependence for both the rates of oxidation of the carbonaceous fiber coating and the CG-Nicalon™ fibers.

Fig. 6 shows the predicted strain histories for tests conducted at 600°C and different composite stresses. The time was normalized by the time required to consume all the carbonaceous fiber coating, so that when

$$\frac{2k_1 t}{l_c} = 1$$

the analysis is reduced to that of a fiber bundle subjected to constant loading [8]. Note that these curves also show three well-defined regimes. During the first regime the burnout of the carbonaceous fiber coating is responsible for the increase in compliance and at high stresses, for composite failure. As it was indicated in Section 2, the removal of the carbonaceous fiber coating results in subjecting longer segments of the fibers to the peak stress, T, increasing at the same time the probability of failure of the fibers. This process can be best described using the 'snow ball effect' analogy. When the fibers are subjected to a larger tensile stress, their probability of failure increases. Therefore, some fibers will fail and because of global load sharing

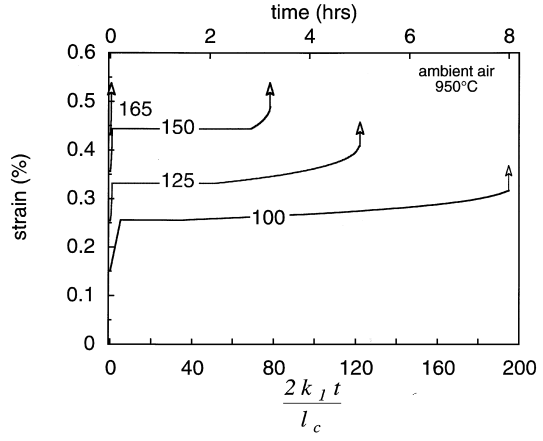

Fig. 7. Predicted strain histories at 950°C and different stresses (in MPa).

assumptions, the load originally carried by the now broken fibers will be transferred to the surviving fibers. Consequently, the surviving fibers are now subjected to a larger tensile stress, increasing hence, their probability of failure. This process continues to occur until either an equilibrium point is reached, at which point the composite is able to withstand the applied load without further fiber failure, or alternatively, the composite fails when the surviving fibers are unable to withstand the applied load [11].

The second regime exhibited by the strain history curves in Fig. 6 coincides with the incubation period referred to in relation to Eq. (10). During this period the composite doesn't experience further changes in compliance and its duration is as long as the time required to grow defects on the surface of the fiber larger than the critical defects associated with the virgin distribution of fiber strengths.

The third regime is associated with a continuous increase in composite compliance as a result of oxidation-assisted fiber failure. Failure of the composite occurs when a critical number of fibers ($\approx$ 20%) fail in the critical matrix crack plane [13]. Note that this regime of accelerated deformation is also exhibited by ductile metal when undergoing 'necking' during creep. However, in contrast to the time-dependent creep (i.e. flow) mechanisms responsible for the deformation of metallic specimens, the regime of accelerated deformation exhibited by the composite modeled here, arises from the progressive failure of the reinforcing fibers.

Fig. 7 shows the predicted strain histories for stress-rupture tests at stresses of 100, 125, 150 and 165 MPa at 950°C, which are qualitatively similar to those obtained experimentally for CG-Nicalon™/enhanced SiC in ambient air at 950°C [13].

One of the major concerns expressed by designers of components that would incorporate CFCCs is knowing the response of these materials when subjected to accidental stress excursions beyond the matrix cracking stress. Accidental stress excursions can occur during fabrication, shipping, installation or later on during service. In addition to the need for non-destructive evaluation techniques to qualify and quantify damage in these materials, models such as the one presented in this paper will be needed to predict the behavior and reliability of these materials after accidental stress excursions that would result in matrix cracking. Further, this type of model could easily be implemented to define the behavior of a representative volume element in stress analyses of components using finite element techniques. Note that the model presented in this paper was reduced to the analysis of a unit cell that was normalized by the matrix crack spacing, which will further facilitate its implementation.

In its current form the model addresses only thermochemical processes at intermediate temperatures, or conditions where the oxidation of the matrix does not occur or can be neglected. However, to address the behavior of CFCCs at temperatures higher than those considered in this paper, it

will be necessary to account for matrix oxidation since it can lead to matrix crack healing, which will in turn modify the kinetics of oxidation of the fibers and fiber coating.

4. Summary

A model was presented to predict the reliability and life of a CFCC subjected to oxidation-assisted stress-rupture conditions. The model is based on the micromechanical analysis of a unidirectional composite and on a sequence of events that lead ultimately to the rupture of the composite. These events include: cracking of the matrix, ingress of the environment to the interior of the composite, oxidation of the fiber coating and oxidation of the fibers. The case of a composite containing fiber coatings that become fugitive after oxidation and fibers that lose strength because of oxidation was analysed. It was shown that the oxidation of the fiber coating leads to changes in the stress distribution of fibers and exposure of the fibers to the environment. In turn oxidation of the fibers leads to fiber loss of strength and ultimately composite failure. The strain histories predicted by the model indicate the continuously increasing compliance of the composite, which is consistent with experimentally recorded strain histories under similar conditions. It is also found that the model predicts a rate of composite loss of strength proportional to $t^{-1/4}$ which is also consistent with experimental results. It will be necessary to improve the model to account for the oxidation of the matrix in order to predict the behavior of composites at temperatures above 950°C, when it is expected that the oxidation of the matrix may lead to crack healing, altering in turn the kinetics of oxidation of the fiber coatings and fibers.

Acknowledgements

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