STRESSED OXIDATION LIFE PREDICTION FOR C/SIC COMPOSITES

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ABSTRACT

The residual strength and life of C/SiC is dominated by carbon interface and fiber oxidation if seal coat and matrix cracks are open to allow oxygen ingress. Crack opening is determined by the combination of thermal, mechanical and thermal expansion mismatch induced stresses. When cracks are open, life can be predicted by simple oxidation based models with reaction controlled kinetics at low temperature, and by gas phase diffusion controlled kinetics at high temperature. Key life governing variables in these models include temperature, stress, initial strength, oxygen partial pressure, and total pressure. These models are described in this paper.

INTRODUCTION

The application of ceramic matrix composites (CMC) to advanced airframe and propulsion systems for future space transportation vehicles can provide benefits in life, performance, temperature margin, and weight savings. One CMC system of interest to the aerospace community is carbon fiber reinforced silicon carbide. This system offers weight savings and higher temperature capability compared to oxide based or SiC fiber based systems. But it does suffer from very serious oxidation problems. Life is dominated by oxidation in non-inert environments. Oxidation of the carbon fibers and the pyrolytic carbon interface can occur because of the matrix cracks that are generated upon cooling from the processing temperature. These matrix cracks form due to thermal expansion mismatch between the silicon carbide matrix and the lower axial expansion carbon fibers.[1] Coatings and sealants are often used to close these cracks. But tensile stresses can force cracks open at any temperature below or above the processing temperature and allow oxygen access to carbon.

For implementation of ceramics to occur, reliable performance and accurate life prediction are essential. Some state-of-the art CMC life prediction methodologies are based on empirical formulations.[2,3] In general, these models have to be calibrated using experimental data. Elegant, physics-based life prediction tools based on oxidation have also been developed.[4,5] They incorporate the appropriate oxidation models and Weibull weakest link theory to predict life. But since the fibers are changing as a result of thermal and oxidation exposure, the value added by this approach is questionable. In addition the reaction can follow one of three paths: (1) CO formation, (2) CO_2 formation, or (3) CO formation close to the carbon source and subsequent reaction to CO_2 along the diffusion path. Each reaction path yields a different relation between the reaction rate constant and oxygen concentration.[6] However, the three mechanisms yield less than a factor of 2 variation between them over an oxygen mole fraction range from 0.001 to 1. As a result, these reaction details are deemed non-critical for the approach taken here. An alternative approach is to derive simplified oxidation models that incorporate the effects of as-produced strength, applied stress, and the proper functionality for the effects of pressure, oxygen partial pressure, and temperature.[6] The necessary constants can be empirically determined by a limited amount of testing.

In this paper the basic simplified oxidation models are derived for the principle cases, combined into a stressed oxidation life prediction tool, and calibrated empirically. Standard C/SiC (1K T-300 fibers, plain weave, pyrolytic carbon interface, SiC matrix and seal coat) from GE Power Systems Composites LLC is the material for this study.

LIFE PREDICTION MODELS

The oxidation behavior of carbon can be described by two kinetic regimes. A simplified conceptual picture of the attack mechanisms is shown in Figure 1a.[7] At higher temperatures kinetics are controlled by the rate at which oxygen is transported to the reactive carbon surface. In the high temperature transport controlled regime, the carbon fiber core shrinks as carbon is consumed. At lower temperatures the reaction of carbon with oxygen is rate controlling and the kinetics follow an Arrhenius rate equation for temperature dependence. At low temperature carbon reacts slowly so that the entire cross-section is exposed to oxygen and damage occurs throughout. Here the much slower oxidation rate of the pyrolytic carbon interface compared to the fibers becomes significant. However, we can simplify for modeling purposes by assuming that either the area of the tows or of the fibers is reduced uniformly throughout the composite, or that the tows or fibers have notch type defects introduced uniformly.[5]

In a composite the picture is complex with the type of carbon fiber and its heat treatment condition, matrix cracking, coatings, and sealants coming into play. The importance or effectiveness of these factors can be dominated by applied stress. The kinetic regimes overlap as illustrated in Figure 1b.[7] For the high temperature case the shrinking core picture fits quite well. For the lower temperature case features of both types of attack are apparent. Using models for oxidation attack and the above simplified conceptual pictures of the resulting degradation, equations that incorporate the correct physics will be derived in the next section. These derivations use constants that can be measured by testing rather than calculating them from first principles as in the more elegant methods available in the literature.[4,5]

Reaction Controlled Life Model

The basic equation for reaction controlled oxidation of carbon is given by[6]

$$x = k_l t = k_l^* t\,(\Phi P/T)\,exp\,(-Q/RT) \qquad [1]$$

where the nomenclature for this and all subsequent equations is given in Table 1 in the order introduced. Two modes of fiber or tow attack are considered. For uniform attack the failure criterion is obtained by equating initial load and final load. The former is proportional to σ_{appl} times initial dimension squared and the latter to initial strength times dimension at failure squared.

$$\sigma_{appl}\,d_o^2 = \sigma_o(d_o-k_l t)^2 \qquad [2]$$

Substituting for k_l in eq. [2], combining constants d_o/k_l* into the constant U and solving for t gives

$$t = U\,Texp(Q/RT)\,\{1 - (\sigma_{appl} / \sigma_o)^{1/2}\} / \Phi P \qquad [3]$$

For notch defect generation the failure criterion is given by

$$\sigma_{appl} = \sigma_o K/c^{1/2} = \sigma_o K / (k_l t)^{1/2} \qquad for\ x = c > c_o \qquad [4]$$

Substituting for k_l in eq. [4], combining constants K^2/k_l* into the constant L, and solving for t gives

$$t = L\,T\,exp(Q/RT)\,\{\sigma_o / \sigma_{appl}\}^2 / \Phi P \qquad [5]$$

Equations [3] and [5] are similar except for constants and the stress dependence term. The validity of the models will be examined in a later section.

Diffusion Controlled Life Model

Assume that Knudsen diffusion does not occur or is insignificant relative to molecular diffusion.[6] Oxidation of carbon with CO diffusion out is given by[6]

$$x^2 = k_p t = k_p^* \, t \, T^{1/2} \ln(1 + \Phi) \qquad [6]$$

The initial area of the composite is given by $A_o = w_o h_o$. The residual area is given by

$$A_r = w_o h_o - (2w_o + 2nh_o)x \qquad [7]$$

for an empirically observed edge attack rate = n times the surface attack rate. For an applied load $P_{appl} = \sigma_{appl} \, w_o h_o$ failure occurs when the stress increases to σ_o.

$$\sigma_o = \sigma_{appl} \, w_o h_o / (w_o h_o - (2w_o + 2nh_o)x) \qquad [8]$$

Rearranging and substituting for x from Eq. [6] gives

$$w_o h_o / (w_o + nh_o) = 2x / (1 - \sigma_{appl} / \sigma_o) = 2\,(k_p^* t T^{1/2})^{1/2} (\ln(1+\Phi))^{1/2} / (1 - \sigma_{appl} / \sigma_o) \qquad [9]$$

Solving for t gives the expression

$$t = \{(1 - \sigma_{appl} / \sigma_o) \, w_o h_o / (w_o + nh_o)\}^2 / \; 4\,(k_p^* T^{1/2}) \ln(1+\Phi) \qquad [10]$$

This relationship contains the constant $4\,k_p^*$ and, if geometry is fixed, $w_o h_o / (w_o + nh_o)$ can also be considered a constant. The model validity will be examined in a later section.

Stressed Oxidation Life Model

The oxidation of carbon involves two processes that occur in series: delivery of oxygen to the carbon surface and reaction at the surface. The rate of damage is controlled by the slowest process except at intermediate temperatures where different processes can be going on at different depths within the composite. Dealing with this issue is beyond the scope of this paper. As a first approximation stressed oxidation life is given by the life predicted for the rate limiting or slowest process.

Role of Thermal Expansion Mismatch and Stress

At the processing temperature matrix cracks are closed. As the composite cools from the processing temperature, a temperature range is reached in which matrix cracks develop. On subsequent thermal cycles these cracks are open below the processing temperature and closed at or above the processing temperature in the absence of an applied stress. The amount of tensile stress necessary to open transverse cracks sufficiently to allow oxygen ingress to the fibers above the processing temperature is temperature dependent. It is also a function of time because of stiffness reductions due to fiber oxidation and due to crack sealing as a result of silica formation. One possible definition of the magnitude of this sufficient crack size can be derived by considering the crack size at which cracks close rapidly by SiC oxidation above 1100 °C. Filipuzzi et al[8] observed that the interface region in SiC/C/SiC composites seals rapidly by oxidation at 1100 °C if interface thickness is limited to 0.1 μm thickness or less. A crack opening of 0.1 μm is selected on this basis. For a composite with about 25 volume per cent fibers in the loading direction, a fiber stiffness of about 230 GPa (e.g. T-300) and a crack spacing of 0.005 ± 0.002 cracks/micrometer, a threshold stress level of about 58 ± 12 MPa at the processing temperature is required to open transverse cracks. For each 100 °C above the processing temperature the threshold stress would increase by about 35 MPa.

Model Calibration

Two series of stress rupture experiments will be used for model calibrations. In the first series of experiments stress rupture life was measured at 800 °C in air and pure oxygen at ambient pressure, and stresses of 34.5, 69, and 138 MPa. The uniform area reduction model did not fit the data as well as the notch model. Results for the notch model are shown in Figure 2 where life is plotted versus $\{1 - (\sigma_{appl} / \sigma_o)^2\} / \Phi P$. A straight line through all of the data points represents a perfect fit for the model. The fit is reasonable for short lives.

In the second series of experiments life was measured as a function of specimen gage width at 800 and 1200 °C in a relatively benign 1000 ppm O_2 in argon environment to force specimen failures to occur in the reduced specimen gage section located in the hot zone of the furnace. In addition to the standard gage width of 10.8 mm, specimens with gage widths of 17.8 and 25.4 mm were tested. $(\text{Life})^{1/2}$ is plotted versus a normalized dimension parameter, $w_o h_o/(w_o + n h_o) * (1 - \sigma_{appl} / \sigma_o) / T^{1/4}$ in Figure 3. A straight line through the origin and all data points represents a perfect fit to the model. The fit is close to the model, but not perfect in that the data line slopes are greater and the y intercepts are negative.

Life Prediction

Using equations [5] and [10] life curves were calculated as a function of temperature for specimens with a 10.8 mm gage width tested in ambient air. A Q/R value of 18030 K was used.[9] These curves for stresses of 34.5, 69, and 138 MPa are shown in Figure 4. In addition, curves for face crack closure above the deposition temperature are included. Life is dominated by the rate limiting mechanism. At low temperatures reaction kinetics are rate limiting and strongly temperature dependent. At high temperatures delivery of oxygen via diffusion is rate limiting and is weakly temperature dependent. Above the deposition temperature crack closure can play a role, but would tend to diminish well above the deposition temperature. Crack closure sets an upper bound on life and the diffusion controlled life model sets a lower bound. The wide band drawn through the 69 MPa predictions schematically indicates how life is expected to vary with temperature.

Model Confirmation

Limited confirmation of the model can be obtained by carrying out stress rupture tests in air at various stress levels and carefully observing the temperature at which failure occurs. Such tests with multiple thermocouple instrumented specimens are underway. Failure at a temperature corresponding with the intersection of the reaction controlled and diffusion controlled life curves is the expected result. In tests of normally instrumented specimens in air at center gage section temperatures above the CVI temperature, failure almost always occurs at intermediate temperature (estimated to be in the range ~ 600 to ~800 °C). This behavior interferes with data base generation over a wide temperature range.

CONCLUSIONS

Stressed oxidation life prediction models for reaction controlled and diffusion controlled oxidative degradation of C/SiC models were developed, and calibrated with limited experimental data. From these models a typical set of life curves were generated. Mission cycle life fraction consumed in a given increment of time is based on the life limiting oxidation mechanism for the temperature, environment and stress of that increment. Instrumented tensile stress rupture tests are proposed as a simple model confirmation method.

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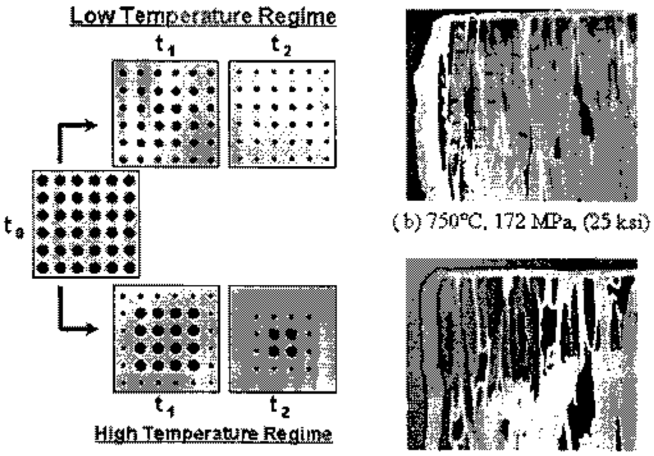
Table 1. Nomenclature

x = *measure of damage or depth of attack, cm*	σ_o = *initial strength, MPa*
k_l, k_l^* = *linear rate constants*	d_o = *initial fiber or tow diameter, cm*
t = *time, s*	σ_{appl} = *applied stress, MPa*
Φ = *oxygen mole fraction*	U, K, L = *constants*
P = *total pressure, atm*	c, c_o = *flaw and initial flaw diameter, cm*
T = *temperature, K*	k_p, k^*_p = *parabolic rate constants*
Q = *activation energy, kcal/mole*	w_o = *initial specimen width, cm*
R = *constant, kcal/mole-K*	h_o = *initial specimen thickness, cm*



(a) Schematic of oxidation attack

(b) 750°C, 172 MPa, (25 ksi)

(c) 1250°C, 172 MPa, (25 ksi)

Figure 1. (a) Schematic of low temperature reaction controlled and high temperature diffusion controlled kinetic regimes that need to be considered to model C/SiC behavior. Microstructures (b) of an intermediate and (c) high temperature stressed oxidation specimen cross-section.

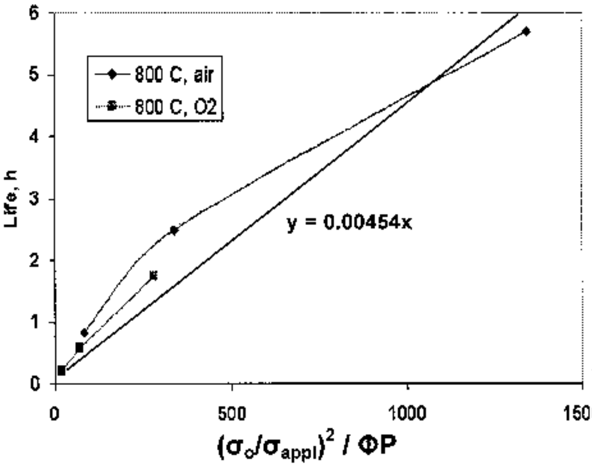


Figure 2. Life prediction calibration for reaction controlled kinetics.

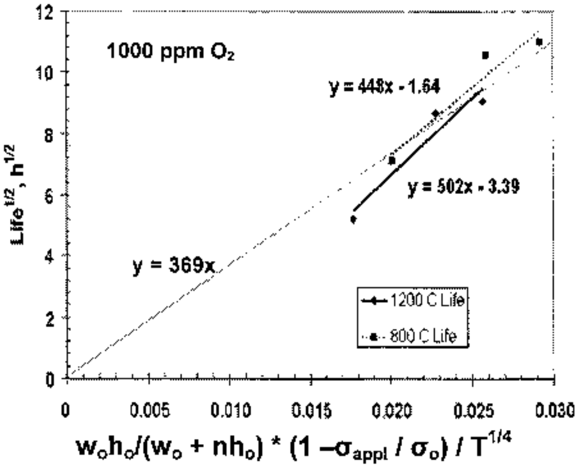


Figure 3. Life prediction calibration for diffusion controlled kinetics.

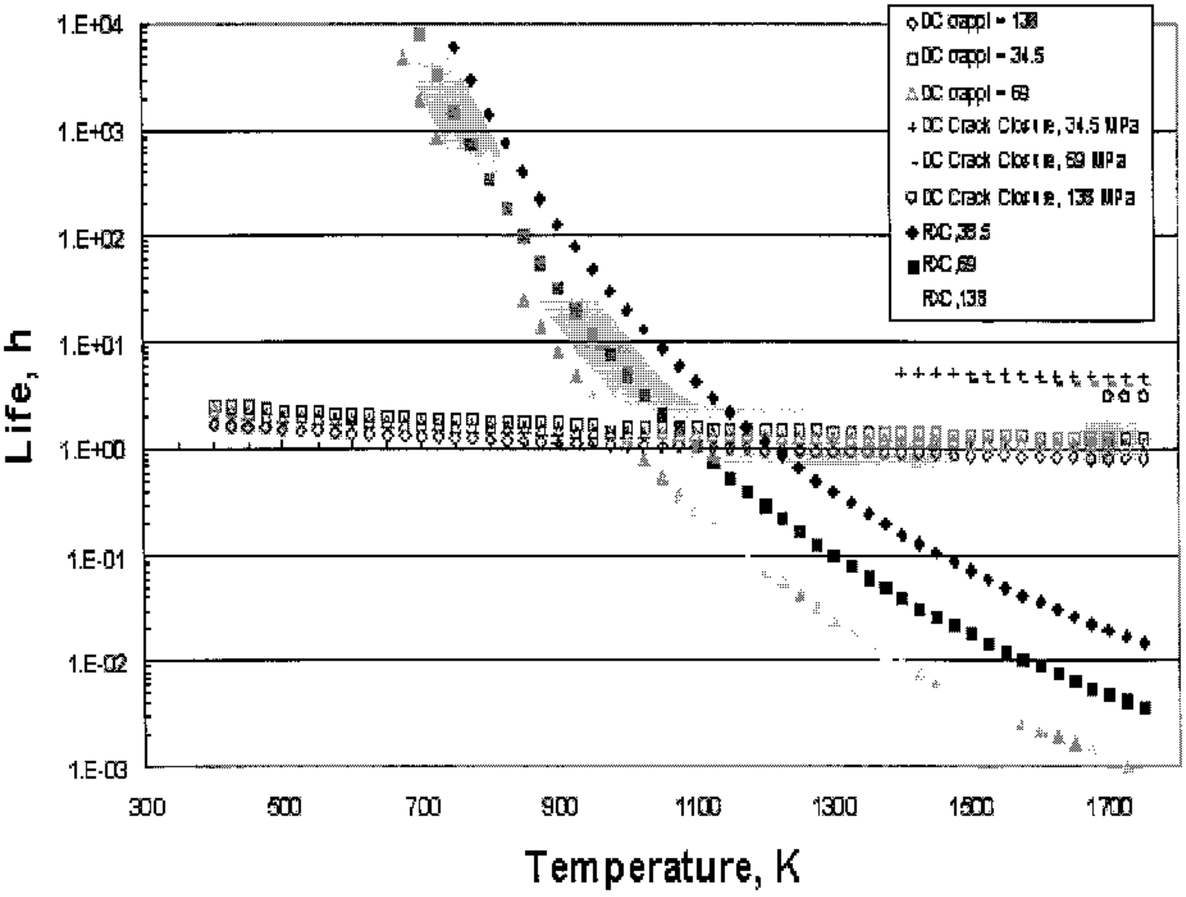


Figure 4. Life prediction curves for C/SiC stress rupture in air