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Modeling the Oxidation Kinetics of Continuous Carbon Fibers in a Ceramic Matrix

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MODELING THE OXIDATION KINETICS OF CONTINUOUS CARBON FIBERS IN A CERAMIC MATRIX

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ABSTRACT

A finite difference model has been developed and was used to study the oxidation kinetics of carbon fibers exposed by the presence of a through-thickness matrix crack in a ceramic matrix composite. Air was the environment of interest so that the model could be compared to experimental testing. The limiting steps of diffusion controlled and reaction controlled kinetics were investigated by changing the value of the simulated temperature which, in turn corresponds to a change in the diffusion coefficient and reaction rate constant. The reaction rates for the oxidation of carbon fibers were compared to theoretical values and oxidation trends predicted by the model were compared to experimental trends.

INTRODUCTION

Carbon fiber reinforced ceramic matrix composites are materials with potential for high temperature structural applications such as nozzles, nozzle ramps, thrusters, and turbines. The oxidation of exposed carbon fiber reinforcement is often the limiting life factor in these applications, which involve oxidizing environments and high temperatures. In order to better predict how a material will perform under certain conditions, it is useful to develop a testable, quantitative model for oxidation kinetics.

This paper builds upon previous experimental and modeling work. In the experimental work, stressed oxidation tests were conducted on carbon/silicon carbide (C/SiC) composites. Test coupons were brought to a constant temperature ranging from 350 °C to 1500 °C and a tensile stress of either 69 MPa (10 ksi) or 172 MPa (25 ksi) was applied. The test conditions were maintained until the coupon failed or 25 hr had elapsed. The samples that survived 25 hr were fast-fractured at room temperature to determine the residual strength. Different results were obtained from experiments conducted above and below 750 °C. Below 750 °C, samples had much longer lives, greater than 25 hr versus less than 2 hr for the high temperature tests. A sample tested at 550 °C and 172 MPa failed at 25 hr, similarly a sample tested at 69 MPa survived 25 hr and had a residual strength about half that of the as-received materials. All samples tested at 750 °C and above had much shorter lives, ranging from 17–36 min. for tests at 172 MPa and from 91 to 142 min. for tests at 69 MPa. Qualitative changes in the microstructure were also found to differ when tests were conducted above and below 750 °C. Above 750 °C, oxidation patterns suggested diffusion controlled kinetics. At 750 °C and below, oxidation patterns suggested reaction controlled kinetics [1].

In an earlier oxidation paper, a finite difference model was presented which modeled the diffusion of oxygen from the edge of a cracked matrix into the interior where an array of fiber tows bridges a crack [2], typical of C/SiC composites in their as-received condition. The cracks form due to thermal expansion mismatches between the fiber and matrix when the composites are cooled from their processing temperature. During application conditions, these cracks, without sufficient external seal coatings or fiber interfaces, represent serious flaws, which can allow oxygen to diffuse into the matrix and consume the carbon fibers.

This early model, however, was only capable of calculating a quasi-steady state oxygen concentration profile, for a given carbon phase configuration. The output from this model allowed calculations of the instantaneous oxidation rates for an arbitrary arrangement of a fiber tow array. Gradients in oxygen

concentration showed conditions where the kinetics were either diffusion controlled, reaction controlled or mixed control.

In this current paper, the model is extended to include consumption of the carbon fiber array and, thus, the evolution of patterns in the fiber array are calculable. Considerations in developing the model will be discussed and calculated trends are compared to experimental results.

THEORY AND MODEL DEVELOPMENT

In the previous oxidation work, oxygen concentrations were determined as oxygen diffused into a 2-dimensional surface of a 250 x 250 grid matrix containing a 12 x 12 array of fiber tows. The fiber tows were 10 grids in diameter and spaced 10 grids apart. With a continuous supply of oxygen from the edge and a continuous supply of carbon from the array, the oxygen concentrations were determined by iterating until a quasi-steady-state was reached. The oxygen concentrations across the midline of the surface were determined for several Sherwood (Sh) numbers. The Sherwood number is an important variable in the finite difference model used to relate the reaction rate constant, K (m/s), and diffusion coefficient, D (m^2/s), as a unitless ratio. It is defined by the following equation, where Δx is a characteristic length (m):

$$Sh = \frac{K \ \Delta x}{D} \tag{1}$$

The characteristic length is based on the geometry of experimental test coupons and is equal to one-half the distance between rows or columns of fiber tows in the array. Over a temperature range of 550 °C–1500 °C, the value of the diffusion coefficient will change by about 3 times, while the reaction rate constant changes by three orders of magnitude. That is, the temperature sensitivity of Sh is essentially dictated by that of K. It was determined that at low Sherwood numbers (low reaction rate constant relative to the diffusion coefficient), the interior becomes saturated in oxygen and the reaction process (though slow) is expected to be nearly uniform, i.e., reaction control. At high Sherwood numbers (high relative reaction rate constant relative to diffusion), there is a very sharp gradient in oxygen concentration at the perimeter of the sample, as the oxygen is consumed as soon as it comes in contact with the carbon. In this case, the carbon in the interior is starved for oxygen and the reaction will only take place near the free surface. This situation is characteristic of diffusion control.

Prior to generalizing the model, calculations were carried out to see how well the model was predicting the different regimes. Specifically, comparison was made to the Sherwood number extracted from the value of the linear reaction rate, k_l determined from an experiment.

First, the reaction rate constant was determined from the following equation:

$$k_r = (k_l \ N) / \chi \ C_t \tag{2}$$

where N is the molar density of the carbon, C_t is the total gas concentration, and χ is the oxygen partial pressure in air. In determining the values in the above equation, the temperature of interest was 800 °C because carbon, in general, has a transition temperature starting around 800 °C and as temperature is increased, diffusion control is quickly approached [3,4]. The density of carbon was taken as 1.65 g/cc and the linear reaction rate was an experimentally determined value of 2.5 x 10^{-4} cm/s for the oxidation of SCS–6 carbon at 800 °C in air [3]. This gave a reaction rate of 0.153 m/sec. Assuming a diffusion coefficient of about 1.8 x 10^{-4} m^2/sec (determined from Chapman-Enskog theory using Lennard-Jones potential energy function) and a Δx of 2 x 10^{-5} m (one-half the distance between fiber tow arrays and based on real composite geometries), the calculated Sherwood value was 4.25 x 10^{-2}. The oxygen concentrations for this calculated Sherwood are plotted in Figure 1. This plot of oxygen concentration at Sh=4.25 x 10^{-2} shows mixed control. Oxygen supply is partially depleted as it reacts with the carbon near the edge and is present beyond several fiber tows into the interior. The model therefore appears to be consistent with experimentally observed transitions from diffusion control and reaction control. That is, 800 °C is calculated to be close to the transition temperature from reaction-to-diffusion control.

Trends for two other Sherwood numbers near the transition region were also calculated, assuming an activation energy of 100kJ/mol for K: Sh=9.66 x 10^{-2} relating to a temperature of 900 °C and Sh=1.57 x 10^{-2} relating to a temperature of 700 °C. From these addition plots, trends toward diffusion control and reaction

control can be interpreted. When the Sherwood number increases, relating to increased reactivity and higher temperature, the gradient in oxygen concentration will become much steeper as oxygen is more quickly consumed near the edge. In this case, diffusion control is approached. When the Sherwood number decreases, more oxygen will reach the interior so that it becomes saturated and the trough in the plots becomes shallower. In this case, reaction control is approached as the oxygen saturates the interior and is there to supply the slower reaction process.

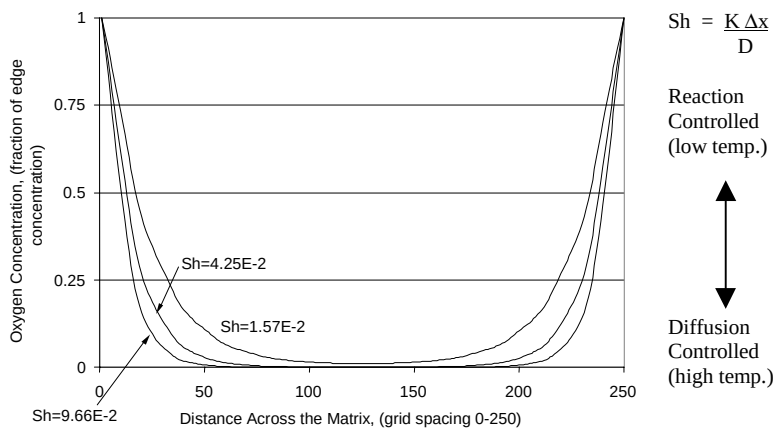

Figure 1. Oxygen concentration across the matrix for different Sherwood Numbers relating to temperatures at and around the transition temperature.

The next step in the advancement of the model was to include the process of carbon recession within the carbon fiber array. This involved allowing incremental carbon recession, in a method used by Glime and Cawley to study profiles of oxidized fiber tips [5]. In this method, the entire array is examined to determine the time necessary for each exposed carbon grid to be completely reacted at the instantaneous local oxygen concentration. The smallest time increment is determined from this set, and then, oxidation is allowed to occur throughout the array for that amount of time. The oxygen concentrations are then recalculated until the quasi-steady state is reached. The process of carbon removal and recalculations of oxygen concentrations is repeated until the desired amount of carbon has been removed.

When analyzing the results from initial calculations using this model, it was observed that the grids along the diagonal of the 'circular' fiber tows were reacting at a faster rate so that the circle assumed a diamond shape. This effect, due to representing a circular region with square grids, can be understood by the two dimensional illustration in Figure 2 of a circle showing the smooth surfaces (edges) and a rough surfaces (diagonals) that make up the circle. Grid 1 located on the diagonal has two sides exposed while grid 2 located on the smooth edge only has one side exposed. This difference is important since the oxygen concentration for a grid is determined by the net flux of oxygen into the grid from its neighboring grids and out of the grid to its neighboring grids. By determining the net flux, setting it equal to zero and solving for the oxygen concentration in grid 1, the oxygen concentration was found to be equal to

$$C(i,j) = \frac{C(i-1, j) + C(i, j+1)}{(2 + 2\,Sh)} \tag{3}$$

At quasi-steady state the open oxygen containing grids, C(i-1, j) and C(i, j+1), will have nearly the same oxygen concentration. Therefor equation (3) becomes

$$C(i,j) = \frac{2C(i-1, j)}{(2 + 2\,Sh)} \tag{4}$$

The oxygen concentration for a partially oxidized carbon containing grid on the smooth edge, grid 2, was calculated to be

$$C(i,j) = \frac{C(i, j-1)}{(1 + 1\ Sh)} \tag{5}$$

which will have the same concentration at quasi-steady state as grid 1. The time to oxidize grid 2 is

$$t = \frac{d\ \Delta x}{K\ C} \tag{6}$$

where d is the density of carbon. For grid 1 the time is

$$t = \frac{d\ \Delta x}{K\ C\ \sqrt{2})} \tag{7}$$

Thus a geometry correction is needed so that the grid is considered as a triangle to more closely represent the arc of the circle so that the exposed surface area has a length of the square root of 2 grid lengths and a width of 1 grid length.

With the geometry correction, the carbon oxidized uniformly independent of orientation and initially circular single fiber tow arrays maintained a circular shape during oxidation. Using this correction in the model, a circle of bulk carbon with a radius of 59 grids was oxidized away. The recession of the 'smooth' edge and the 'rough' edge were monitored. Both radii receded at an even rate, the shape remained circular and the linear reaction rates were very nearly the same. This is opposed to results without the geometry correction, where the circular bulk carbon assumed a diamond shape as recession occurred faster along the rough surface and had a higher linear reaction rate than the smooth surface.

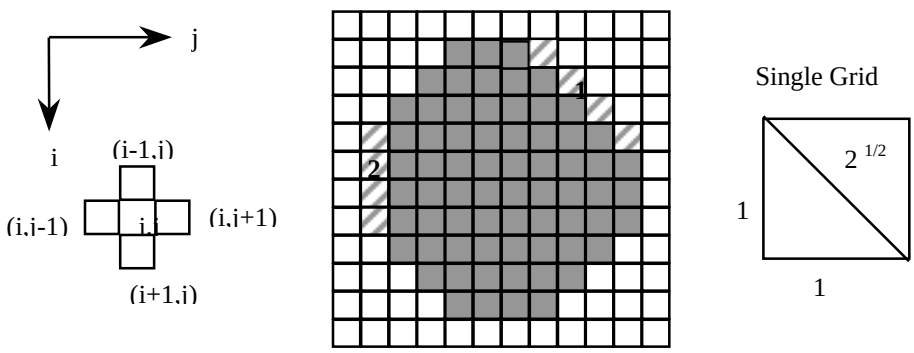

Figure 2. Grid orientation is shown at the left. Center figure shows 10 grid diameter pattern used to represent a fiber tow showing smooth and rough edges. Side and diagonal lengths are shown in the single grid to the right.

RESULTS AND DISCUSSION

Now that the finite difference model had been advanced to consider carbon/oxygen reactions, the kinetics of oxidation in a fiber array were investigated and compared to experimental observations.

In the analysis of polished cross sections that had been tested in stressed oxidation at high temperatures, oxidation patterns relating to diffusion controlled kinetics were observed. Figure 3 shows the polished cross section of a sample that had been stress oxidation tested at 1400 °C and 69 MPa. It is seen that a significant amount of oxidation, which appears as darkened, "burned out" areas, has occurred along the outer perimeter of the sample. As soon as oxygen comes in contact with the highly reactive carbon, the oxygen supply is quickly depleted as carbon is consumed so that no oxygen reaches the interior of the sample. In the close-up micrograph of the edge of the sample, a reaction front is observed which moves inward as carbon recession continues. The detailed view of the interior shows how the center of the sample remains pristine since there is no oxygen presence. Only cracks in the fiber bundles and closed porosity are observed.

Corresponding to these conditions, the model was run for the case of a relatively high Sherwood number that would relate to diffusion controlled kinetics, Sh=1.07, which was determined from calculations for the diffusion coefficient and reaction rate constant at 1400 °C. Figure 4 shows the different stages of oxidation on a 2-dimensional surface of an 8 x 8 array of fiber tows in a matrix. This arrangement represents fibers that

bridge a cracked matrix where oxygen is able to diffuse from the edge into the interior and begin to oxidize the fiber tows. A shrinking core effect is seen as oxidation progresses from 25% to 75% to 95% of the carbon reacted. This moving reaction front and shielding of the interior compares well with the optical microscopy relating to diffusion control. The oxygen concentrations for one quarter of the matrix are also shown in Figure 4 under the relative 2-D carbon consumption plots. It is seen that as oxygen at atmospheric conditions diffuses into the matrix, it is very quickly consumed in the carbon/oxygen reactions so that the

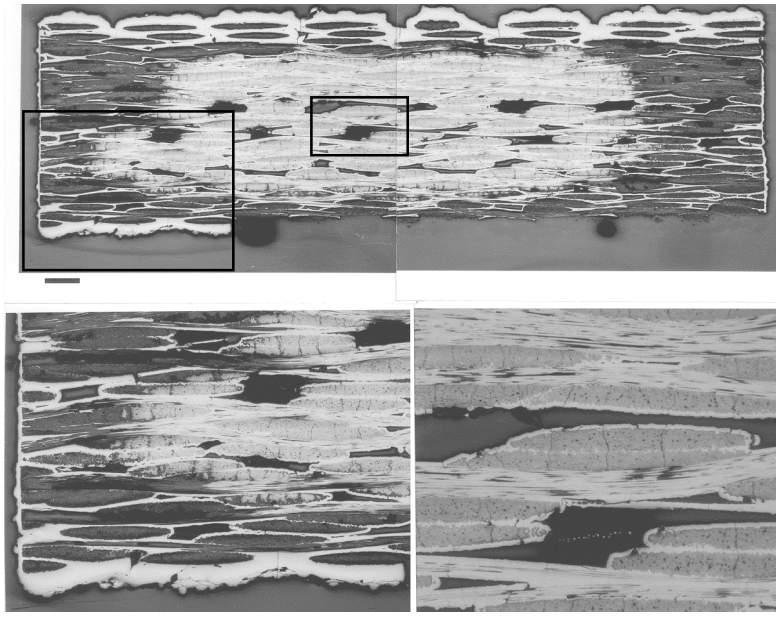

Figure 3. Diffusion controlled kinetics. Optical micrograph of a polished cross-section of a C/SiC sample stressed oxidation tested at 1400 °C/69 MPa. Time to failure was 86 minutes. Scale bar in top micrograph equals 0.5 mm.

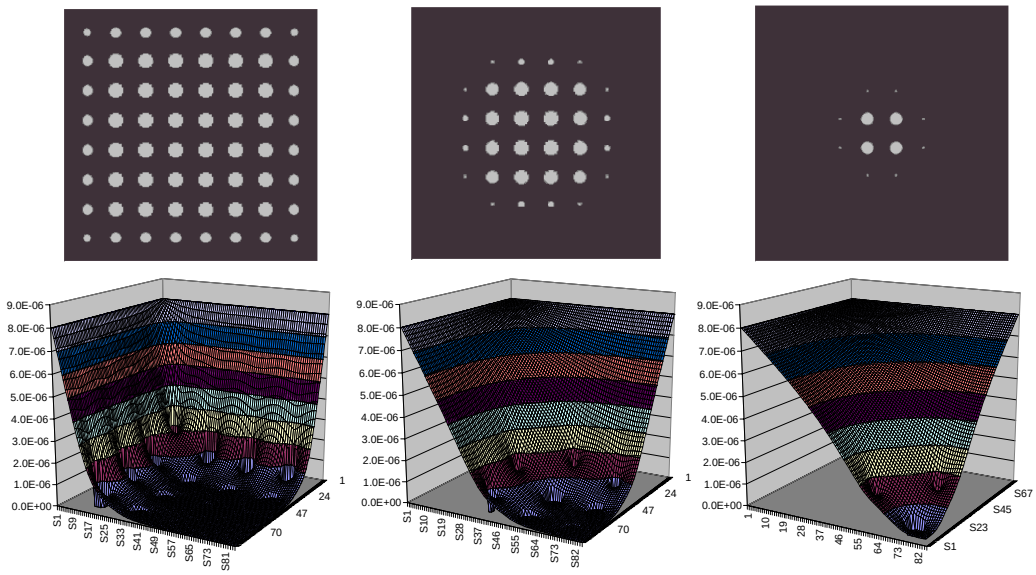

Figure 4. Diffusion controlled kinetics for Sh= 1.07 (relating to 1400°C) at 25%, 75%, and 95% carbon consumption of the 8 x 8 fiber array. The top illustrations are of the remaining area of carbon on the 2-dimensional surface. The bottom plots are of the related oxygen concentrations (mol//cm3) for one quarter of the surface.

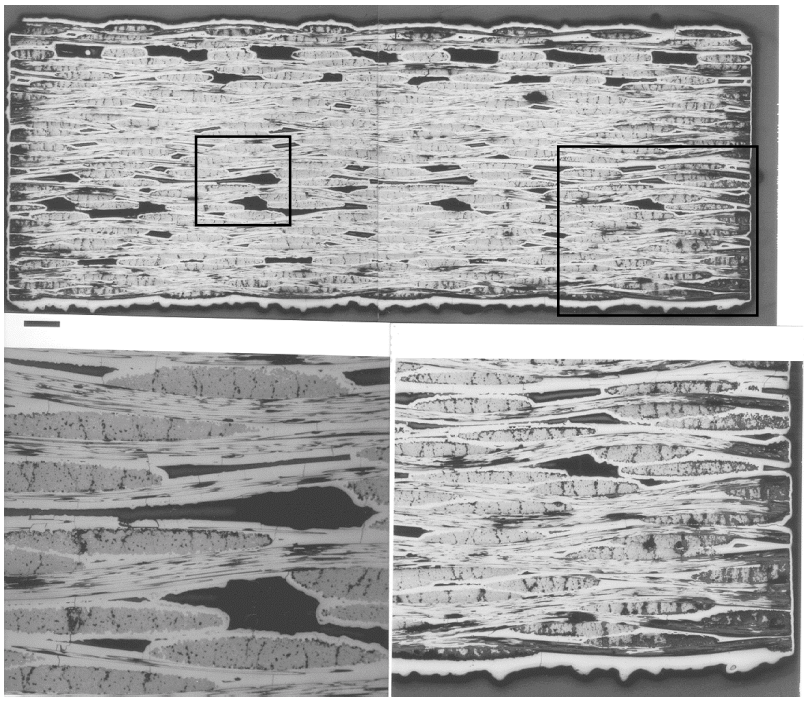

Figure 5. Reaction controlled kinetics. Optical micrograph of a polished cross-section of a C/SiC sample stressed oxidation tested at 700°C/69 MPa. Time to failure was 91 minutes. Scale bar in top micrograph equals 0.5 mm.

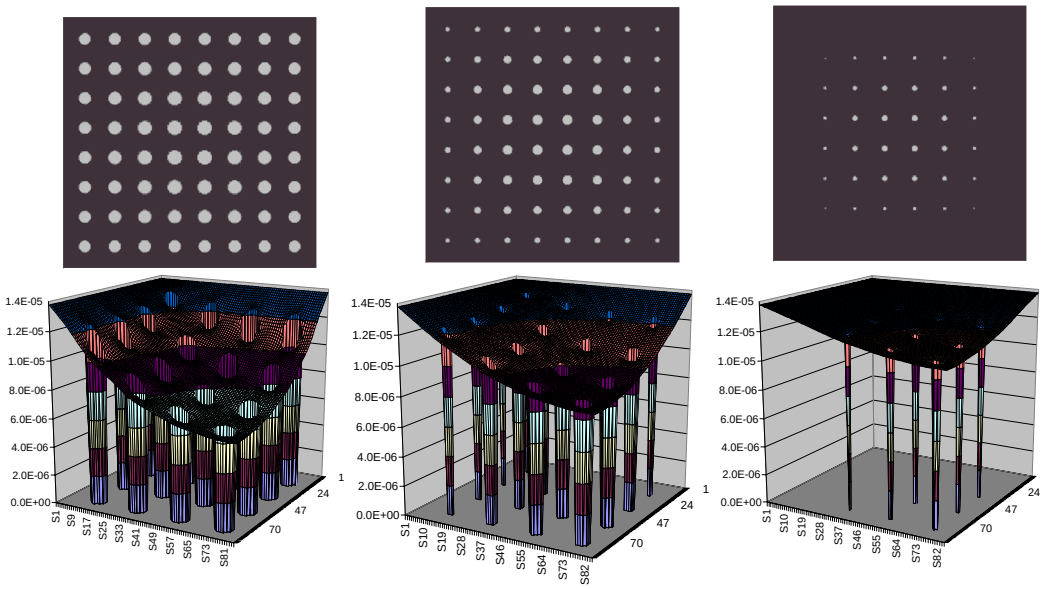

Figure 6. Reaction controlled kinetics for Sh=1.57E-2 (relating to 700°C) at 25%, 75%, and 95% carbon consumption of the 6 x 6 fiber array. The top illustrations are of the remaining area of carbon on the 2-dimensional surface. The bottom plots are of the related oxygen concentrations (mol/cm^3) for one quarter of the surface.

interior is deprived of oxygen. Also note that at 95% of the carbon reacted, the oxygen concentration is still pinned at low values and sharp gradients in oxygen concentration are still observed.

Optical microscopy also showed evidence of the other type of oxidation kinetics, reaction control. Figure 5 shows micrographs of the polished cross-section for a sample that had been stressed oxidation tested at 750°C and 69 MPa. In this case, it is seen that oxidation had occurred along the edge of the sample as well as throughout the sample. The close-up micrograph of the edge shows a modest degree of oxidation occurred without a well-defined reaction front. The close-up view shows that oxidation also occurred deep in the interior of the sample as proven by the evidence of oxidized fibers around the edge of individual fiber tows and along the matrix cracks within the fiber tows. This suggest reaction controlled kinetics since oxygen reactions with carbon were slow enough that oxygen was able to diffuse past the edge into the interior. The interior became saturated in oxygen and was there to supply the slower reaction process.

To simulate this case, the model was used with a relatively low Sherwood number, $Sh=1.57 \times 10^{-2}$, which was determined from calculations for the diffusion coefficient and reaction rate constant at 700°C. Figure 6 shows the trend relating to kinetics as the 8 x 8 fiber array is consumed. As oxidation progresses from 25% to 75% to 95% of the carbon reacted, minimal gradients occur throughout the array. Even at 95% of the carbon reacted, small amounts of carbon are still present along the outer edge and the array diameters in the interior show almost as much recession as those near the edge. In the related one-quarter plots of the oxygen concentration, it is seen that there are no steep gradients in oxygen concentrations and the interior is saturated in high local oxygen concentrations.

CONCLUSIONS

A finite difference oxidation model was extended to include the consumption of carbon from an array of fiber tows. The model compared well with experimental results for test values of the determined Sherwood number. There was good agreement between the oxidation trends predicted in the model and those identified in the microstructural analysis of experimentally tested samples. The model proved to be useful in studying the role certain variables (temperature, diffusion coefficient, and reaction rate) play in the oxidation of a fiber array.

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