

OXYGEN EFFECTS ON SiC/SiC COMPOSITES FOR FUSION STRUCTURAL APPLICATIONS -
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OBJECTIVE

The purpose of this study was to quantitatively assess the stability of SiC/SiC composites in high-temperature, low-oxygen (<2500 ppm) environments by thermal gravimetric analysis (TGA) in regards to their potential use as structural materials in fusion reactors.

SUMMARY

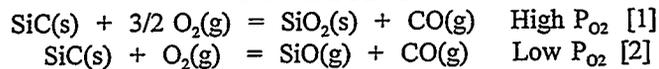
Linear-parabolic kinetics governed the oxidation reaction with 100 to 1500 ppm oxygen at 1100°C. This behavior concurs with the previous research of Windisch et al.⁽¹⁾ which observed a deviation from linearity beginning below 2500 ppm. By focusing on the linear region, a simple model estimated the linear rate dependency on oxygen partial pressure to be on the order of 0.911. Future tests will be performed with 100 and 1000 ppm in the temperature range of 800 to 1000°C in order to refine the understanding of temperature and partial pressure effects. The relationship between interfacial oxidation and experimental parameters, such as temperature, pressure, and interfacial thickness, will be described in an upcoming comprehensive model.

Introduction

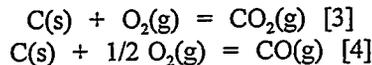
Ceramic matrix composites (CMCs) are being considered for advanced first-wall and blanket structural applications in fusion reactors. This consideration is based on a host of favorable properties, including low density, low neutron activation, low coefficient of thermal expansion, good thermal conductivity, and good corrosion resistance. An area of concern, however, is the interfacial depletion in oxygen environments leading to a decline in mechanical properties by increased fiber/matrix debonding.

This study will focus on the exposure of SiC/SiC composites with C interfaces to oxygen concentrations between 100 and 1500 ppm. The composite can be expected to evolve gas by the following reactions^(2,3):

Fiber and Matrix:



Interface:



Below 1200°C there should be no reaction with the fiber or matrix. If silica did form between the fiber and matrix by reaction 1, the pore could seal under the proper conditions and effectively stop the reaction by cutting off gaseous diffusion. This sealing effect has been observed to be dependent on several factors, primarily interface thickness, test duration, and oxygen concentration^(4,5). The SiC/SiC samples used in this study had a relatively large interface thickness of 1.0 micron and it is unlikely that the pore could be completely sealed even if reaction 1 did take place.

The purpose of this study was to measure the loss of C-interface due to reaction 3 and/or reaction 4 under low-oxygen concentrations and high temperatures, typical of the environment in a gas cooled fusion blanket.

Experimental

The samples used in this study were acquired from Refractory Composites, Inc. of Whittier, California. Fabrication was accomplished by the chemical vapor infiltration (CVI) of Beta-SiC matrix into 8-ply Nicalon fiber cloth, pre-coated with C-interface. This formed a 0°/90° weave pattern with fiber diameters of 15 microns and interface thicknesses of 1 micron. Final sample shape was rectangular with average dimensions of 0.3 x 0.3 x 0.4 cm. In order to better isolate the reaction fronts, three faces were uncoated, while three sides were completely coated with SiC in order to prevent any reaction.

A TA Instruments SDT 2960 TGA/DTA was used for all experiments. This unit provided high sensitivity and good accuracy. Experimental conditions were programmed into the computer, specially designed for the SDT 2960, with capabilities of data acquisition, storage, and real-time monitoring. Next, TGA preparation was necessary that included sample taring, reference material placement, and furnace closure. Purging, the final step before testing, achieved good gas mixing by maintaining a flow rate of 100 mL/min for about an hour. Actual testing was done at 100 mL/min, with real-time temperature and weight measurements being continually observed.

PROGRESS AND STATUS

TGA Data

Figure 1 displays the raw data from TGA testing at 1100°C with 0, 100, 500, 1000, and 1500 ppm oxygen. The sample weight losses, taken directly from the TGA, were divided by the total exposed surface area to produce the normalized units of mg/cm². This normalization assumes that interfacial oxidation along one fiber axis does not affect interfacial removal down the perpendicular fiber axis.

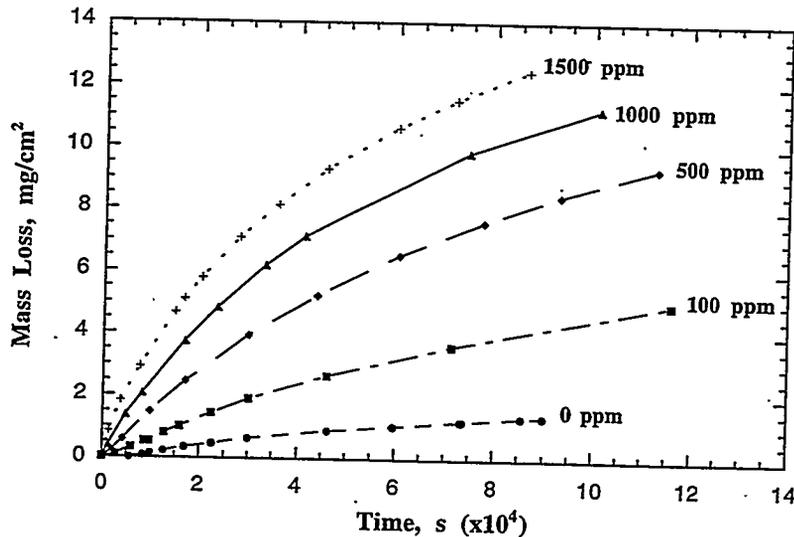


Figure 1: TGA Data for C-Interface SiC/SiC Composites in O₂ (balance Ar) at 1100°C

Clearly, all of the curves deviate from linear behavior and exhibit parabolic characteristics. Although there are no distinct transition points, the curves likely shift from linear to parabolic regions over a wide range of time. This transition typically indicates that the oxidation has changed from *reaction control* to *diffusion control* and is expected to depend on carbon type, system pressure, partial pressure, and temperature⁽⁶⁾.

The baseline curve, tested in ultrahigh-purity argon, revealed a slight amount of weight loss. This loss is best explained by either the imperfect sealing of the SDT 2960, possibly from the backflow of outside air through the exhaust nozzle, or the evolution of a volatile species, such as SiO, from the Nicalon fibers. Adsorbed oxygen may have been trapped in the sample, but its contribution to oxidation would have appeared early on as a quick burst of weight loss, which was not the case. Data were corrected for the background weight loss by simply subtracting the baseline curve from the other curves at equivalent times.

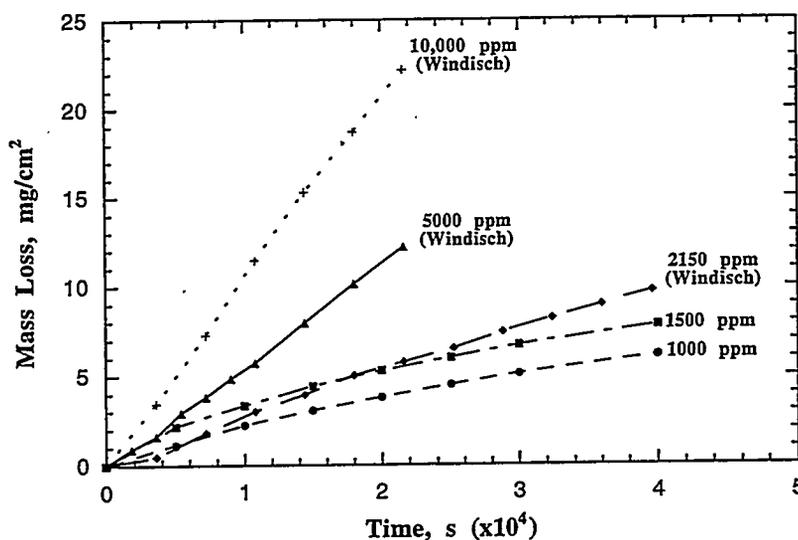


Figure 2: TGA Comparison Data for C-Interface SiC/SiC Composites in O₂ at 1100°C

Figure 2 offers a comparison with the results of Windisch et al. It can be seen that the 5000 and 10,000 ppm curves are linear, while the 2150 ppm curve departs from linear behavior around 15,000 seconds. Overlapping the lower two curves from Windisch are the upper two curves from the present study, which exhibit parabolic behavior much sooner than the 2150 ppm curve. Surprisingly, the 1000 and 1500 ppm runs initially exceed the 2150 ppm experiment in normalized weight loss. Future work will attempt to explain this result.

Modeling and Fitting

A comparison of results other than normalized weight loss was also desired. Equation 4, which focuses on the linear region, was chosen for modeling and comparative purposes.

$$k_1 = k_1' \times p(\text{O}_2)^n \quad [5]$$

By this equation, the oxygen-dependent linear rate constant, k_1 , is related to the partial pressure of oxygen, $p(\text{O}_2)$, where k_1' is the oxygen-independent linear rate constant, in units of cm/s/atm, and n is the order of the reaction with respect to oxygen.

Cawley et al. have proposed the linear-parabolic model for the oxidation of carbon.

$$x^2/k_p + x/k_1 = t \quad [6]$$

At some oxidation time, t , and recession distance, x , the reaction shifts from being dominated by the linear term, x/k_1 , to being governed by the parabolic term, x^2/k_p . As mentioned earlier, this shift most likely corresponds to a transition from reaction control to diffusion control.

In order to obtain k_1 and the order of the oxygen dependency, n , the following steps were applied to the normalized weight loss per unit time data:

- 1) The baseline curve from the 0 ppm run was subtracted from the other curves.
- 2) Time was plotted versus normalized weight loss and the curves were fit to a parabolic function.
- 3) From these parabolic fits, the linear coefficients for the first-order terms were reciprocated, divided by the density of carbon, and divided by the fraction of surface area that is interface.

These manipulations yield the oxygen-independent linear rate constant, k_1' . For valid comparisons with other sources, the log of k_1' was plotted against the log of $p(\text{O}_2)$. Figure 3 depicts this plot along with a simple linear fit. According to equation 7, the logarithm of both sides of equation 5, this linear fit provides k_1 at 1 atm partial pressure, by its intercept and n by its slope.

$$\log k_1 = \log k_1' + n \log p(\text{O}_2) \quad [7]$$

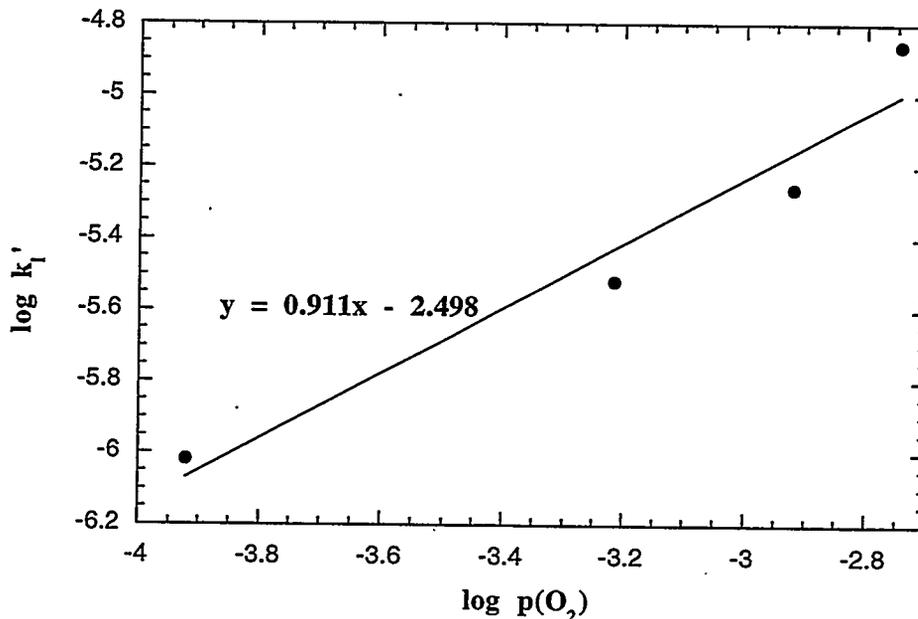


Figure 3: Log of Linear Rate Constant vs. Log of Partial Pressure of O₂

The parabolic coefficients from step 2 can also be translated into oxygen-independent parabolic rate constants. Step 3 is the same except the coefficients are divided by the square of the density of carbon. Figure 4 shows the log of k_p' versus the log of $p(\text{O}_2)$ along with a linear fit. Similar to the linear region, this fit produces k_p at 1 atm partial pressure, by its intercept.

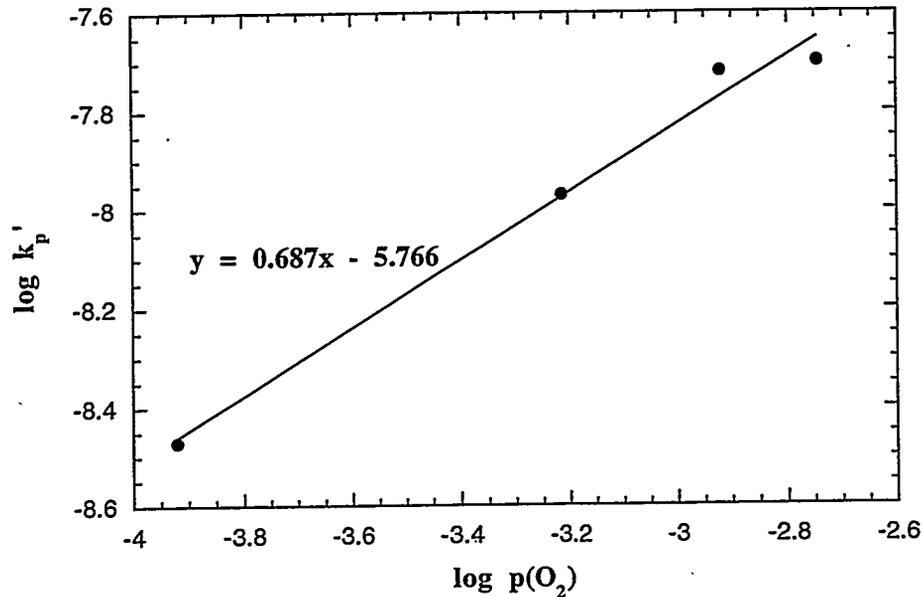


Figure 4: Log of Parabolic Rate Constant vs. Log of Partial Pressure of O₂

Literature Comparison

A comparison with the work of Windisch and Cawley is given by Table 1. As can be seen, the n terms compare closely while the values of k_l and k_p differ to a greater degree.

All of the n terms given are reasonably close to one, indicating that the partial pressure of oxygen has a nearly linear effect on oxidation. The geometric n term reported by Windisch was done by optical examination of interfacial recession distances. Currently, a similar examination is being done with the samples from this study.

| Source | Temp(°C) | n | $k_l(\text{cm/s})$ | $k_p(\text{cm}^2/\text{s})$ |
|----------|----------|-----------|--------------------|-----------------------------|
| Springer | 1100 | 0.911 | 3.2E-3 | 1.7E-6 |
| Windisch | 1100 | 0.9(geom) | 6.4E-4 | ----- |
| | 1100 | 0.8(TGA) | 4.0E-4 | ----- |
| Cawley | 1000 | ----- | 1.7E-4 | 6.4E-4 |
| | 1200 | ----- | 3.2E-4 | 6.8E-4 |

Table 1: Literature Comparison of the Partial Pressure Exponent Term, Linear Rate Constant, and Parabolic Rate Constant

Reasons for the discrepancy in k_p and k_i values are uncertain at this point. Differences in sample geometry and carbon type may help explain the variation with Cawley, while differences in $p(O_2)$ range and the number of exposed faces may account for the lower results of Windisch. Also worth considering is the unknown nature of the oxidants, CO and CO_2 , which may change at lower partial pressures.

CONCLUSIONS

In the oxygen range of 100 to 1500 ppm, linear-parabolic kinetics governed the oxidation of carbon interface at 1100°C. Further experimentation at lower temperatures should refine the understanding of the interfacial oxidation. An upcoming comprehensive model will incorporate the results of this work with several other sources to predict interfacial loss given various experimental parameters, such as temperature, partial pressure, system pressure, and interfacial thickness.

FUTURE WORK

Testing will be done with 100 and 1000 ppm oxygen in the temperature range of 800 to 1000°C. Recession distances will be measured along two fiber axes through microscopic analysis. All of this work is aimed at the development of a comprehensive model including temperature dependence.

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