

THERMOGRAVIMETRIC AND MICROSCOPIC ANALYSIS OF SiC/SiC MATERIALS WITH ADVANCED INTERFACES - C. F. Windisch Jr., R. H. Jones (Pacific Northwest National Laboratory)* and L. L. Snead (Oak Ridge National Laboratory)

OBJECTIVE

The objective of this effort is to determine the chemical stability of SiC/SiC composites with advanced fiber/matrix interfaces in Ar+O₂ environments.

SUMMARY

The chemical stability of SiC/SiC composites with fiber/matrix interfaces consisting of multilayers of SiC/C/SiC and porous SiC have been evaluated using a thermal gravimetric analyzer (TGA). Previous evaluations of SiC/SiC composites with carbon interfacial layers demonstrated the layers are not chemically stable at goal use temperatures of 800-1100°C and O₂ concentrations greater than about 1 ppm. No measurable mass change was observed for multilayer and porous SiC interfaces at 800-1100°C and O₂ concentrations of 100 ppm to air; however, the total amount of oxidizable carbon is on the order of the sensitivity of the TGA. Further studies are in progress to evaluate the stability of these materials.

INTRODUCTION

A previous analysis (1) of the chemical stability of SiC/SiC in inert gas containing impurity levels of O₂ suggested that composite material with C as the fiber/matrix interfacial debond layer may not be suitably stable in fusion relevant environments. This study, which was only based on chemical stability and did not include radiation effects, predicted that O₂ concentration in an inert gas must be kept to less than 1 ppm to obtain a 10 year lifetime. While it may be possible to achieve less than 1 ppm O₂ in small laboratory equipment, the concentration would be difficult to achieve in a large engineering device. Therefore, materials with advanced fiber/matrix interfacial debond layers are being developed which minimize the amount of carbon in the interface. Two such composites are the multilayer approach where the interface debond layer is several layers of SiC/C/SiC where the C layer is very thin. This material has been made by Hypertherm. A second approach utilizes defective or porous SiC as the interfacial debond layer. Samples with this interface were made at ORNL by the forced CVI method.

Thermogravimetric analysis (TGA) was previously used to quantify carbon oxidation in the interface during exposure to oxygen gas at varying conditions of temperature and partial pressure of oxygen (2). This approach was found to be very useful in studies on SiC/SiC with 1- μ m thick interfaces. Linear TGA mass losses as a function of time, with slopes dependent on both temperature and oxygen partial pressure, were measured in these previous experiments and used to conclude that the mass losses were limited primarily by the carbon oxidation reactions at the gas/carbon interface. It was hoped that TGA studies on the ORNL SiC/SiC materials, with their compositionally more complex interfaces, would be similarly informative.

EXPERIMENTAL

TGA studies were performed using a TA Instruments SDT 2960 analyzer. SiC/SiC samples, about 0.30 cm x 0.50 cm x 0.25 cm in size, were ramped from room temperature to the temperature of interest at 65°C/minute and then held at this temperature for 24 h, during which time the mass of the sample was monitored. Gas flow through the instrument was maintained at 0.1 L/min. Other than the tests in air, all

* Pacific Northwest National Laboratory (PNNL) is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO-1830.

gases tested were premixed concentrations of oxygen in argon. Optical microscopy and scanning electron microscopy (SEM) were performed on selected samples before and after TGA analysis.

RESULTS

Multilayer Interface SiC/SiC

TGA data for all the experiments in this study, illustrated for two sets of conditions in Figures 1a and 1b, contained a region at less than 200 minutes dominated by an instrumental artifact. In this region, the mass appears to decrease rapidly by about 0.1 to 0.3 mg and then increase by about the same amount. (The system achieves the set temperature at about 12-17 minutes into the run, or at the approximate position of the "peak" in the data.) Several runs on control samples (no SiC/SiC) exhibited the same response, so all data below 200 minutes were considered to be subject to too much error to be useful. Data above 200 minutes showed some trends that appeared to depend on temperature and oxygen partial pressure. However, caution must be taken not to misinterpret the >200-minute data as well since the experimental uncertainty from several control runs was estimated to be ± 0.05 mg compared to the observed mass change, which was 0.1 mg at the most between 200 and 1440 minutes.

As shown in Figures 1a and 1b, the TGA data between 200 and 1440 minutes was different for Ar at 800°C and air at 1100°C. In Ar, the data exhibit a slow mass loss (Figure 1a). In air, they show a mass gain (Figure 1b). A transition from one form of behavior to the other appeared to occur at about 100 ppm oxygen. The TGA data in Ar may indicate a slow mass loss in the absence of oxygen. However, since the total mass loss in these tests was only about 0.05 mg, or about the same magnitude as the uncertainty, this conclusion is questionable. An approximate calculation was performed to determine the maximum amount of carbon in the sample that could burn out and cause this mass loss, even though it is uncertain what the burnout mechanism could be in the absence of oxygen. Using geometric measurements on previously tested SiC/SiC composite samples and assuming similar geometries for the ORNL materials, it can be shown that about 0.2 mm³ of the samples is interface material. However, only a fraction of the interface material is carbon (about 30% for the multilayer interface and 15-20% for the porous interface). For the multilayer interface material, it is estimated that only 0.12 mg of carbon was present in an entire sample. This amount is larger than the mass losses observed in the present study suggesting that loss of interfacial carbon could explain the results. However, the data are still too close to the experimental uncertainty to produce reliable conclusions.

At 100 ppm oxygen and above at 1100°C, a gradual mass gain was observed as illustrated in Figure 1b. The rate of mass gain also appeared to increase with increasing oxygen partial pressure. The magnitude of the mass gain was small, but was larger than the experimental uncertainty at the higher oxygen partial pressures (air, Figure 1b). A thin interference-type coating was also observed over the whole surface of samples that showed a mass gain. For this reason, we believe the mass gains are real and reflect the growth of a film, probably SiO₂, that results from the reaction of the SiC and oxygen. Attempts to use the TGA data to quantify the kinetics of the film formation were not successful. The "slopes" of the mass gain region (200 to 1440 minutes) do, indeed, increase with increasing oxygen (i.e. more reaction with more oxygen) but it was difficult to model this increase, probably because the film growth kinetics was linear-parabolic. Linear-parabolic kinetics would be expected to show the most dramatic effects of temperature and oxygen partial pressure near the transition zone (when the curve changes from linear to parabolic control), and this behavior is probably observed at times shorter than 200 minutes where the large instrumental artifact also occurs.

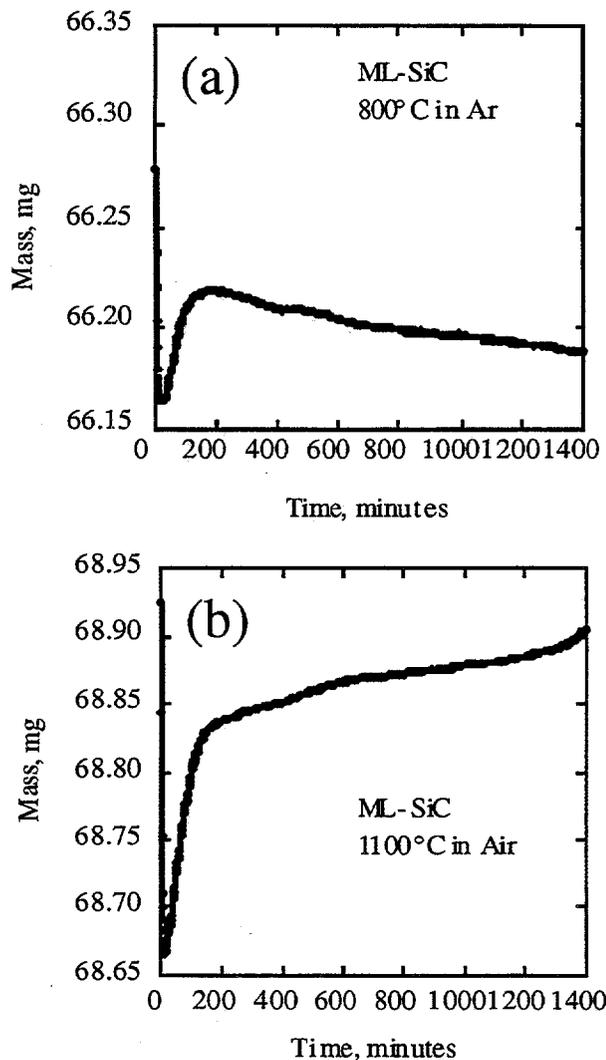


Figure 1. TGA Data for Multilayer Interface SiC/SiC (a) at 800°C in Ar and (b) at 1100°C in Air.

Porous Interface SiC/SiC

As shown in Figures 2a and 2b, the porous and multilayer interface SiC/SiC show essentially the same behavior as a function of temperature and oxygen partial pressure. This is consistent with the behavior arising largely from either instrumental factors or reactions of the entire sample surface (which is similar for both samples) rather than from the interface (which is different). Both of these possibilities were discussed in detail above, for the multilayer interface SiC/SiC material.

If the mass gains observed for the samples at higher temperatures and oxygen partial pressures are due to the growth of an SiO₂ film over the whole sample, the data are not useful for quantifying effects on the interface material. Attempts to use optical microscopy and SEM to observe changes in the interface have not been successful to date. As shown in Figure 3, the interface is less than 100 nm thick, close to the resolution limit of the techniques. Samples tested in air have not yet been evaluated and these may show some effects

around the ends of the interfaces that could relate to "pinching" from SiO_2 previously observed in thin-interface materials and associated with mitigating interface reactions. Future work will study this possibility. At this point, however, it does not appear that either microscopy or our TGA instrument can be used to say much about reactions of the interface material.

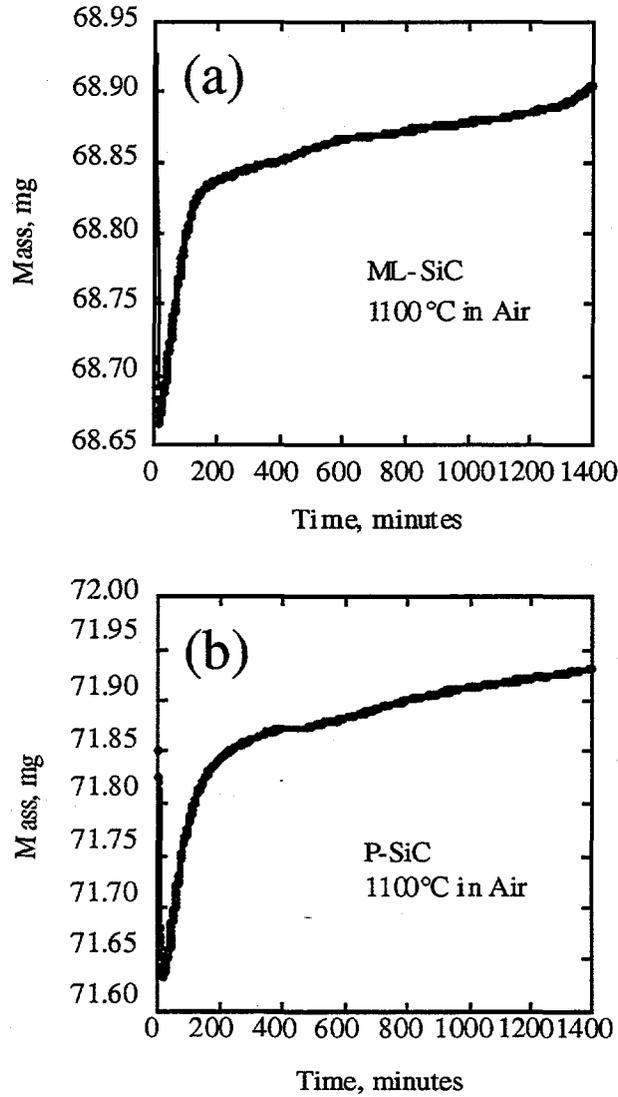


Figure 2. Comparison of TGA Data for (a) Multilayer and (b) Porous Interface SiC/SiC at 1100°C in Air.

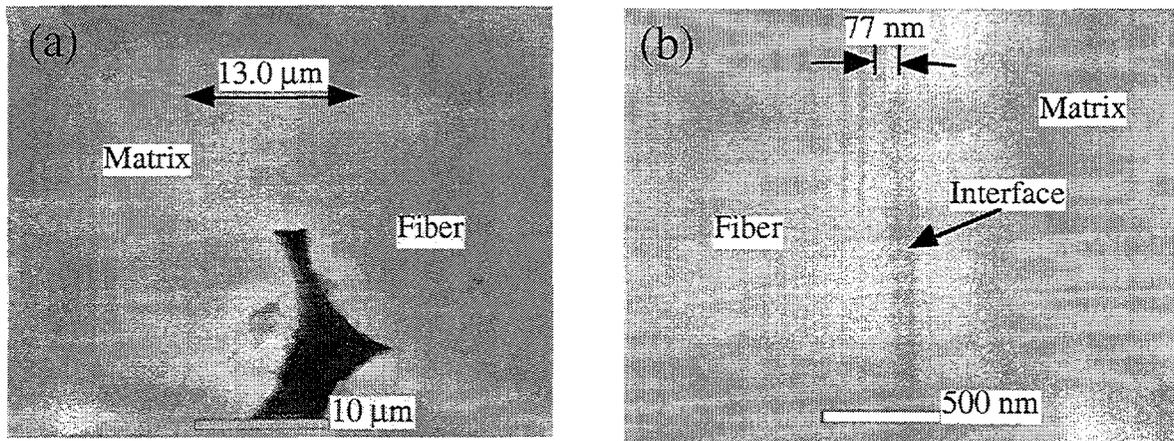


Figure 3. SEM Images of Porous Interface SiC/SiC Illustrating the Difficulty in Resolving the Interface.

FUTURE WORK

Additional microscopy work will be performed in cases where reaction of the SiC/SiC and oxygen was observed to determine whether any "pinching" of the interfaces occurs that could, possibly, slow the interface reaction kinetics, similar to mechanisms proposed for other SiC/SiC materials. Crack growth rate studies are being considered since the crack velocity for these materials has been shown to be sensitive to the interface oxidation.

REFERENCES

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