Thermodynamic calculations were performed to analyze the simultaneous oxidation of BN and SiC. The results show that, with limited amounts of oxygen present, the formation of SiO$_2$ should occur prior to the formation of B$_2$O$_3$. This agrees with experimental observations of oxidation in glass-ceramic matrix composites with BN-coated SiC fibers, where a solid SiO$_2$ reaction product containing little or no boron has been observed. The thermodynamic calculations suggest that this will occur when the amount of oxygen available is restricted. One possible explanation for this behavior is that SiO$_2$ formation near the external surfaces of the composite closes off cracks or pores, such that vapor phase O$_2$ diffusion into the composite occurs only for a limited time. This indicates that BN-coated SiC fibers will not always oxidize to form significant amounts of a low-melting, borosilicate glass.

I. Introduction

Oxidation of fiber coatings is a key limitation of ceramic matrix composites that are currently being developed for high-temperature structural applications. The thin carbon layers that are commonly used to promote interface debonding typically degrade under oxidizing conditions, where the carbon reacts to form volatile byproducts (i.e., CO and CO$_2$). Boron nitride coatings can also be used to obtain crack deflection and fiber pullout and have thus been considered as an alternative to carbon coatings. This communication presents experimental evidence which indicates that the oxidation of an SiC-containing composite with BN interlayers will not necessarily produce a low-melting borosilicate glassy phase during oxidation. A relatively simple thermodynamic analysis is then used to explain this behavior.

In previous experimental work, Baskaran and Halloran exposed BN/SiC fibrous monoliths to air at 1200°-1500°C. The internal regions of these materials, SEM showed evidence of a silica scale produced by SiC oxidation, while a distinct oxidation product associated with BN was not observed. However, these measurements could not determine whether boron was present in the silica scale. Previous thermodynamic analyses have treated systems with SiC, SiO$_2$, and C and focused on carbon-coated SiC fibers and Nicalon (i.e., Si-O-C) fibers. Lee and Jacobson analyzed thermochemistry in the BN–SiC system, but did not consider oxidation. Baskaran and Halloran presented a brief calculation of oxygen partial pressures associated with SiC and BN oxidation, but did not assess the effects of limited oxygen availability.

II. Procedures

The interface stability of SiC/BN-coated Nicalon fibers in a glass-ceramic matrix was recently investigated using transmission electron microscopy (TEM) and concurrent electron energy loss spectroscopy (EELS). The coatings were deposited by chemical vapor deposition at ~1000°C. The boron magnesium aluminosilicate (BMAS) matrix was crystallized at 1200°C, after a brief 5 min exposure at 1450°C. Figure 1 shows a TEM image of a typical interface region in this type of composite, taken from the inside of a sample that was tensile fatigued in air at 1100°C (10$^7$ cycles at 2–3 Hz and a maximum stress of 103 MPa). More detailed descriptions of the procedures used for composite fabrication, mechanical testing, and TEM are described elsewhere. The region between the fiber and the BN coating exhibits a mottled appearance caused by oxidation. The EELS results show that the oxidized region consists almost entirely of SiO$_2$. Given the proximity of the adjacent BN phase, the absence of boron in this oxide was unexpected. This effect is potentially beneficial, because boron will decrease the viscosity of the silicate and may thus degrade mechanical properties.

Nicalon fibers consist of nanocrystalline SiC grains mixed with an oxy carbide amorphous phase and a smaller amount of free carbon. When Nicalon is exposed to O$_2$ at elevated temperatures, an oxide forms at the external surface of the fiber. This resembles the silica in Fig. 1, which was apparently produced by oxidation of the SiC and oxy carbide phases. This conclusion is reinforced by the observation that these oxide regions occur inside of composites after they are subjected to a mechanical load (i.e., where microcracking permits rapid diffusion of oxygen into the interior of the composite). When these cracks are not present, the interfacial layer between the fiber and the BN coating is considerably different from that in Fig. 1 (it is more than an order of magnitude thinner, with a carbon-rich region near the fiber and a silica-rich region near the matrix).

Thermodynamic calculations were performed to assess the oxidation process in more detail, based on the premise that only a limited amount of oxygen can reach the fiber/coating interface. This corresponds to the oxidation of internal regions...
in a fiber-reinforced composite, where gas enters the material through small cracks. This is shown in Fig. 2, where it was assumed that only the SiC undergoes oxidation (based on the experimental results in Fig. 1). The volume expansion associated with SiO$_2$ formation eventually closes off the crack, such that further internal oxidation does not occur (except for minimal amounts of oxygen that diffuse through the solid). Thus, crack closure or pore closure limits the amount of oxygen that reaches internal interfaces.

To consider the simultaneous oxidation of SiC and BN, equilibrium compositions were obtained at a temperature of 1100°C and a pressure of 1 atm, using SOLGASMIX. The calculations consider 40 gas-phase species, although only results for the dominant species are presented in Figs. 3 and 4. The Nicalon fiber is treated as a mixture of distinct phases (i.e., SiC, SiO$_2$, and C). Although this is an oversimplification, several recent analyses have used the same approach to consider the oxidation and thermal degradation of Nicalon. Setting the activities of SiC and SiO$_2$ equal to one is reasonable, because the fiber contains a pure SiC phase and the oxidation reaction produces a relatively pure SiO$_2$ phase. This effectively treats the Si-O-C phase as a nonequilibrium solution of C, SiC, and SiO$_2$ whose thermodynamic properties are not assessed.

The calculations were initiated with fixed amounts of SiC and BN (usually a 1:1 ratio). Oxidation was then investigated in the presence of a limited amount of oxygen. Based on experimental observations, all calculations assumed that Si$_3$N$_4$ did not form. Recent results show that some Si$_3$N$_4$ can form after long exposure times; however, this possibility was not considered.

III. Results

(1) SiC Oxidation

Equilibrium results are plotted in Fig. 3 as a function of available oxygen. Three different stages are apparent, corresponding to the sequential oxidation of SiC, C, and BN. Although the calculations incorporate a large number of species, the results can be interpreted with a small number of reactions. During stage I, Fig. 3 shows that SiC oxidizes to form solid carbon and SiO$_2$:

\[
\text{SiC}(s) + \frac{1}{2}\text{O}_2(g) \leftrightarrow \text{SiO}_2(s) + \text{C}(s)
\]

\[
K_i = \frac{P_{\text{O}_2}^{1/2}}{P_{\text{CO}}}
\]

(1)

The solid components are assumed to have an activity of one (an oxide solid solution is considered in a later section). Based on Eq. (1), the oxygen partial pressure is equal to $K_i^{-1}$.

The equilibrium partial pressures for the other gas-phase species can be obtained by writing appropriate equilibrium reactions in terms of O$_2$, such as:

\[
\text{C}(s) + \frac{1}{2}\text{O}_2(g) \leftrightarrow \text{CO}(g)
\]

\[
K_2 = \frac{P_{\text{CO}}}{P_{\text{O}_2}^{1/2}}
\]

(2)

and

\[
2\text{BN}(s) + \frac{3}{2}\text{O}_2(g) \leftrightarrow \text{B}_2\text{O}_3(g) + \text{N}_2(g)
\]

\[
K_3 = \frac{P_{\text{B}_2\text{O}_3}P_{\text{N}_2}}{P_{\text{O}_2}^{3/2}}
\]

(3)

Similar expressions describe the formation of SiO$_2$(g), BO(g), and the other species in the system. For the two examples given above, $P_{\text{CO}}$ can be evaluated directly with Eqs. (1) and (2) while $P_{\text{B}_2\text{O}_3}$ depends on $P_{\text{N}_2}$, which depends on the concentrations of all of the other gas-phase species (since all of the pressures must sum to a total of 1 atm). During stage I, Fig. 3 shows that most of the available oxygen is consumed by SiO$_2$ formation; therefore, the partial pressures that depend on $P_{\text{N}_2}$ (e.g., BO and B$_2$O$_3$) can be obtained by using $P_{\text{N}_2} = 1.0$. With this approximation, the values obtained for B$_2$O$_3$ using Eq. (3) are in good agreement with the detailed numerical results in Fig. 3.

After all of the available SiC has undergone oxidation, the equilibrium condition given in Eq. (1) is no longer relevant. This leads to the second stage of the process, which corresponds to the oxidation of solid carbon according to Eq. (2). The production of CO alters the gas-phase composition continuously, as the amount of available oxygen increases. Thus, the partial pressures vary as stage II proceeds (as opposed to stage I, where they are relatively constant).

(2) BN Oxidation

Stage III corresponds to the oxidation of BN according to

\[
2\text{BN}(s) + \frac{3}{2}\text{O}_2(g) \leftrightarrow \text{B}_2\text{O}_3(l) + \text{N}_2(g)
\]

\[
K_4 = \frac{P_{\text{N}_2}}{P_{\text{O}_2}^{3/2}}
\]

(4)
During stage III, $P_{N_2}$ can be estimated by assuming that all of the carbon in the system oxidizes to form CO (via Eq. (2)), and that 1 mol of additional $N_2$ forms for every 2 mol of BN that are oxidized (via Eq. (4)). For oxidation in air, this gives:

$$P_{N_2} \approx 1 - \frac{1}{4.4X_{O_2}}$$  \hspace{1cm} (5)

where $X_{O_2}$ is the ratio of the moles of $O_2$ introduced to the moles of SiC that are present. The assumptions used to obtain Eq. (5) also lead to the following expression:

$$P_{CO} \approx \frac{1}{4.4X_{O_2}}$$  \hspace{1cm} (6)

Thus, Eqs. (4)–(6) give values for $P_{O_2}$, $P_{N_2}$, and $P_{CO}$, which can then be used to determine the other partial pressures (e.g., Eq. (3) gives $P_{B_2O_3}$).

### Absence of Solid Carbon Formation

The experimental results in Fig. 1 do not show any evidence of the solid carbon formation that is predicted in Fig. 3. It is possible that this image was taken when the sample was at the transition point between stage II and stage III (i.e., where essentially all of the carbon was converted to CO, but condensed $B_2O_3$ was not present). However, this is unlikely to coincide, particularly because regions similar to Fig. 1 were observed on multiple occasions. Solid carbon layers have been observed at fiber/matrix interfaces after the synthesis of glass-ceramic matrix composites, where they are usually attributed to limited oxidation (similar to the results in Fig. 3).\(^1\)\(^,\)\(^2\)\(^,\)\(^3\) The formation of these layers has been analyzed with thermochemical and flux arguments associated with the multicomponent oxide matrix.\(^1\)\(^,\)\(^8\)\(^,\)\(^23\) In contrast, the results in Fig. 1 are consistent with conventional SiC oxidation from an $O_2$-containing gas (e.g., air) where solid carbon does not form.\(^24\)\(^,\)\(^25\) To consider oxidation...
in this situation, equilibrium calculations were performed without solid carbon. These results, presented in Fig. 4, show that the oxidation of SiC first proceeds to completion, before significant BN oxidation occurs (analogous to stage I in Fig. 3). In the absence of solid carbon, SiC oxidation can be described by the following equilibrium reaction:

$$\text{SiC}(s) + \frac{1}{2}\text{O}_2(g) \leftrightarrow \text{SiO}_2(s) + \text{CO}(g)$$

$$K_1, K_2 = P_{\text{CO}} P_{\text{O}_2}^{-3/2}$$

(7)

During stage I in Fig. 4 the CO formed during SiC oxidation is a significant fraction of the gas phase (similar to stage II in Fig. 3). If the gas phase consists primarily of N\(_2\) and CO,

$$P_{\text{CO}} = \frac{X_{\text{O}_2}}{X_{\text{O}_2} + 1.5X_{\text{N}_2}}$$

(8)

This assumes that all other gas species have low partial pressures (i.e., $\ll$0.01 atm), which is consistent with the numerical calculations. For oxidation in air, Eq. (8) gives $P_{\text{CO}} = 0.15$ atm.

The oxidation of BN during stage III in Fig. 4 is identical to stage III in Fig. 3. In both cases, liquid B\(_2\)O\(_3\) begins to form according to Eq. (4) only after all of the Si oxides to form SiO\(_2\) and all of the carbon oxides to form CO.

(4) B-Si-O Solid Solution

The preceding calculations assume that SiO\(_2\) and B\(_2\)O\(_3\) form as independent condensed phases with negligible solubility. The simultaneous oxidation of SiC and BN may also produce a borosilicate glass. To consider this possibility, the calculations in Figs. 3 and 4 were extended by assuming that SiO\(_2\) and B\(_2\)O\(_3\) form an ideal solution with complete miscibility, such that

$$a_{\text{SiO}_2} + a_{\text{B}_2\text{O}_3} = 1$$

(9)

For stages I and II, numerical calculations with this solution model give results that are essentially identical to those in Figs. 3 and 4 (at 1100°C). This occurs because the solution model predicts the formation of almost pure SiO\(_2\) with a negligible boron content (i.e., $a_{\text{SiO}_2} \sim 1$ and $a_{\text{B}_2\text{O}_3} \ll 1$). With solid carbon present, $a_{\text{B}_2\text{O}_3} = 1.54(10)^{-3}$ during stage I at 1100°C. During stage II, $a_{\text{B}_2\text{O}_3}$ increases as oxidation proceeds, with a maximum value of $a_{\text{B}_2\text{O}_3} = 4.57(10)^{-3}$ at the end of stage II. When solid carbon does not form, $a_{\text{B}_2\text{O}_3} = 1.14(10)^{-3}$ during stage I.

In stages I and II almost all of the oxygen reacts to form SiO\(_2\) and CO. For the nonsolution case, most of the additional oxygen added to the system during stage III reacts to form B\(_2\)O\(_3\) (see Fig. 3). With the ideal solution model, stage III oxidation corresponds to the formation of B\(_2\)O\(_3\) as part of the SiO\(_2\)-B\(_2\)O\(_3\) solution. The following approximate expression assumes that nearly all of the additional oxygen added during stage III is consumed by B\(_2\)O\(_3\) formation:

$$a_{\text{B}_2\text{O}_3} \approx 1 - \frac{3}{2X_{\text{O}_2}}$$

(10)

This increase in $a_{\text{B}_2\text{O}_3}$ decreases $a_{\text{SiO}_2}$, but does not change the condensed phases in Figs. 3 and 4, except that SiO\(_2\) and B\(_2\)O\(_3\) should now be interpreted as a single phase with a variable composition (i.e., a borosilicate solid solution). During stage III, the changes in $a_{\text{B}_2\text{O}_3}$ and $a_{\text{SiO}_2}$ that occur as oxidation proceeds lead to corresponding changes in the equilibrium partial pressures. For example, the O\(_2\) partial pressure is given by

$$P_{\text{O}_2} = \frac{[a_{\text{B}_2\text{O}_3} P_{\text{N}_2}^{2/3}]}{K_4}$$

(11)

The changes in $a_{\text{B}_2\text{O}_3}$ and $a_{\text{SiO}_2}$ also affect the other partial pressures in the system, even if the equilibrium expressions do not explicitly contain $a_{\text{B}_2\text{O}_3}$ and $a_{\text{SiO}_2}$. For example, $P_{\text{CO}}$ and $P_{\text{B}_2\text{O}_3}$ are now in equilibrium with the value of $P_{\text{O}_2}$ that is given in Eq. (11).

IV. Discussion and Conclusions

A concise summary of these calculations is that the oxygen partial pressure in equilibrium with SiC and SiO\(_2\), $P_{\text{CO}}^\text{SiC Outgast}$, is lower than the oxygen partial pressure that is necessary for B\(_2\)O\(_3\) formation, $P_{\text{CO}}^\text{BN Outgast}$. With this terminology, $P_{\text{CO}}^\text{BN Outgast}$ is given by Eq. (4) (using Eq. (5) to evaluate $P_{\text{CO}}$). $P_{\text{CO}}^\text{SiC Outgast}$ is given by Eq. (1) if solid C is present, and by Eqs. (7) and (8) if it is not present. In either case, solid SiO\(_2\) forms before condensed B\(_2\)O\(_3\). Thus, crack closure due to oxidation can limit the availability of oxygen and prevent condensed B\(_2\)O\(_3\) formation under some circumstances. This is an oversimplified view of the process depicted in Fig. 2, because it neglects key kinetic effects, such as solid-state diffusion through the SiO\(_2\) and the diffusion of gas-phase species along the crack.

Solid-state diffusion through the SiO\(_2\) is important because it is unlikely that all of the SiC in the system will be converted to SiO\(_2\) prior to the formation of condensed B\(_2\)O\(_3\), even though this behavior is predicted by equilibrium calculations. As SiO\(_2\) forms on the SiC, the diffusion of oxygen or some other species through the oxide will become rate-limiting when the silica layer is sufficiently thick. This will produce a gradient in the oxygen partial pressure across the oxide, with an oxygen partial pressure in the crack that is higher than the equilibrium value. When the thickness of the SiO\(_2\) layer reaches a critical value, the oxygen partial pressure in the crack will exceed $P_{\text{CO}}^\text{BN Outgast}$, and condensed B\(_2\)O\(_3\) should begin to form. This will be prevented if the formation of SiO\(_2\) closes off the crack before the oxygen concentration in the crack reaches $P_{\text{CO}}^\text{BN Outgast}$. In theory, oxygen could still enter the crack via solid-state diffusion; however, this will occur much more slowly than the gas-phase transport that occurs prior to crack closure. Note that the oxide which closes a crack near an external surface is likely to be thicker than the SiO\(_2\) layer that covers the SiC surfaces that are farther inside the material. Under some conditions, it is also interesting that an impurity in the SiO\(_2\) that increases the diffusion of oxygen and leads to faster SiO\(_2\) formation can limit B\(_2\)O\(_3\) formation because of two simultaneous effects: (1) the crack will close off faster, and (2) more of the SiC will oxidize before $P_{\text{CO}}$ in the crack reaches $P_{\text{CO}}^\text{BN Outgast}$.

Gas-phase diffusion will remove volatile byproducts, and thus alter the total rate at which certain reactions proceed. For example, the removal of CO can lower $P_{\text{CO}}$ inside of the crack, which could lead to less solid C compared to the calculations in Fig. 3. Also, prior to stage III oxidation the removal of BO\(_2\)(g) and B\(_2\)O\(_3\)(g) removes BN via an active oxidation process. These volatile species will diffuse out of the composite, as long as the local $P_{\text{CO}}$ in the crack is below $P_{\text{CO}}^\text{BN Outgast}$. This could completely remove the BN and prohibit the formation of any condensed B\(_2\)O\(_3\). The results in Figs. 3 and 4 indicate that active oxidation of BN interlayers should proceed at a much slower rate than the active oxidation of carbon interlayers, because $P_{\text{CO}}$ and $P_{\text{B}_2\text{O}_3}$ are far below the equilibrium $P_{\text{CO}}$ that should exist with carbon. For the region shown in Fig. 1, the partial pressures of BO and B\(_2\)O\(_3\) do not remove a significant amount of BN from the system. This is based on the observation that the BN coating thickness in the oxidized sample is reasonably close to the initial BN thickness (this is an approximate assessment because of the variability of the initial thickness). Filipuzzi’s analysis of the volatilization of carbon interlayers can be expanded to consider simultaneous SiC and BN oxidation; however, this requires modifications that account for the specific chemical reactions and mass-transport mechanisms that are occurring. In general, the length and width of the crack (or pore) are the key dimensions, with shorter and wider cracks more prone to both condensed B\(_2\)O\(_3\) formation and BN removal by active oxidation.

The oxidation of SiC that is described here does not treat the Si-O-C phase in the Nicalon fiber. Oxidation reactions presumably increase the oxygen content of this oxycarbide. This will affect the amount of oxygen consumed; however, it will not affect the general conclusion that SiO\(_2\) formation precedes B\(_2\)O\(_3\) formation. In some cases, the values of $P_{\text{CO}}^\text{SiC Outgast}$ and $P_{\text{CO}}^\text{BN Outgast}$ can...
be affected by the oxidation of the Si-O-C phase because of changes in the CO activity. The aforementioned mass transport effects can also alter these partial pressures because of CO removal.

Although the calculations presented here do not consider certain important effects, the results in Figs. 3 and 4 demonstrate that SiO oxidation should precede BN oxidation. This indicates that the oxidation of BN-coated SiC fibers will not necessarily lead to the formation of a low-melting oxide phase (i.e., B$_2$O$_3$(l) or a borosilicate glass). As already noted, a relatively pure SiO$_2$ phase that observed in Fig. 1 generally has a significantly higher viscosity and higher glass transition temperature than a borosilicate. Thus, the absence of passive BN oxidation could lead to superior high-temperature mechanical properties (compared to a composite where a condensed boron-containing oxide phase forms). While this by no means eliminates property degradation associated with oxidation at the fiber/matrix interface, it does show that BN coatings on SiC fibers will not always react to form a low-melting borosilicate glass under oxidizing conditions.

References


