High temperature oxidation of ceramic matrix composites

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Abstract: Ceramic matrix composites are developmental high temperature materials. We focus on composites with SiC matrices, SiC fibers, and BN fiber coatings. High temperature oxidation/corrosion reactions are discussed for each of these constituents. SiC forms a highly protective SiO_2 scale in pure oxygen, but problems arise in complex gas mixtures. These include: SiO(g) formation, Si-O-H(g) formation, impurity enhanced SiO_2 formation, and fluxing of SiO_2 in molten salts and slags. Refractory oxide coatings may minimize these effects. The major issue with these composites is oxidation of the BN fiber coating. The key reactions here are borosilicate glass formation, potential gettering of oxygen by SiC, and volatilization. We conclude with an oxidation study of an actual composite, which illustrates some of these effects.

INTRODUCTION

There has long been interest in ceramics as potential high temperature materials. A great deal of effort has gone into developing silicon carbide (SiC) and silicon nitride (Si_3N_4) ceramics. These materials can operate at higher temperatures than conventional superalloys and are substantially lighter in weight. The major block to their application has been their low fracture toughness.

Ceramic matrix composites (CMCs) have been developed in response to this issue (ref. 1). Additional phases, such as platelets, chopped fibers or whiskers, or continuous fibers, are used to impart fracture toughness. The most promising are the continuous fibers reinforced ceramics. A schematic is shown in Fig. 1, illustrating the major constituents. Development of ceramic fibers has been a major area of research and recently a number of extremely high strength nearly pure SiC fibers have been reported (ref. 2). In order to avoid fiber bonding with the matrix, a fiber coating or interphase is needed. This interphase is a critical constituent which must be nonreactive with both the fiber and the matrix, and serve as a path for deflected cracks. This is attained with weak bonding in the crystallographic direction perpendicular to the fiber. Current interphase compounds are graphite or hexagonal boron nitride.

In applications these materials would be exposed not only to severe mechanical stresses, but also to aggressive gases at high temperatures. The specific high temperature environment is dependent on application. For example, a hydrocarbon fuel combustion chamber contains N_2, O_2, CO_2, and H_2O gases as well as sodium sulfate and vanadate deposits, depending on the purity of the fuel and intake air. A spacecraft re-entry environment contains both monatomic and diatomic oxygen and nitrogen at reduced overall pressures and very high velocities. We have examined each constituent in Fig. 1 in such aggressive gases. This allows identification of the major corrosion reactions. These effects are then combined to interpret the behavior of the entire composite.
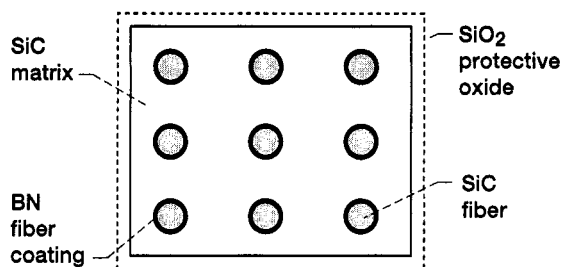
Figure 1.—Schematic of composite.

SiC MATRIX AND FIBER

Oxidation of SiC

Silicon carbide forms a dense, protective oxide scale according to the following passive oxidation process:

$$SiC + 3/2 \, O_2 = SiO_2 + CO \tag{1}$$

Oxygen must diffuse through the oxide scale, react at the SiC/SiO_2 interface, and some type of carbon-containing species must diffuse outward through the scale (ref. 3). The kinetics of reaction (ref. 1) can be followed by monitoring oxide scale thickness as a function of time. This can be done either via optical techniques or a continuous recording microbalance (Thermogravimetric apparatus—TGA). Fig. 2 is a typical TGA trace for high purity SiC in pure oxygen. Note the kinetics are parabolic, i.e. the reaction slows as thickness increases, indicating diffusion is rate limiting. This could be either oxygen inward or the carbon-containing species outward. It has been reported by several investigators that rate constants vary with the partial pressure of oxygen, indicating that diffusion of oxygen inward is rate controlling (refs. 4 and 5).
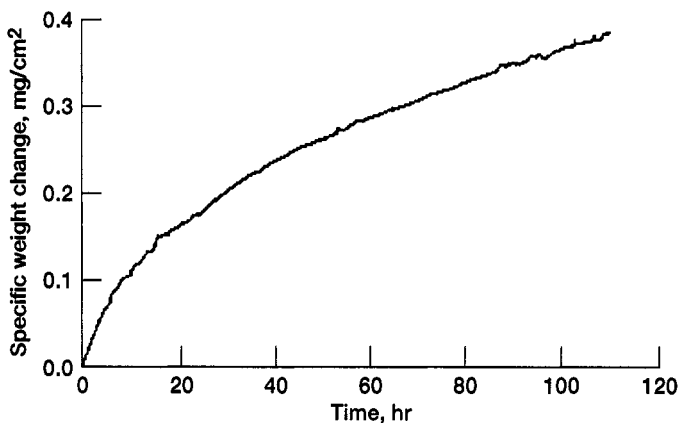
Figure 2.—TGA for CVD SiC at 1300 °C in pure oxygen.

Fig. 3 compares the rate of silica growth on Si to that of other common oxides on different metals. The rate of Si oxidation is very close to that of SiC (ref. 3), so it is taken as a basis of comparison. Not only is SiO_2 growth the slowest, but it also has the lowest activation energy. Thus in pure oxygen, SiO_2 is a remarkably protective oxide scale.
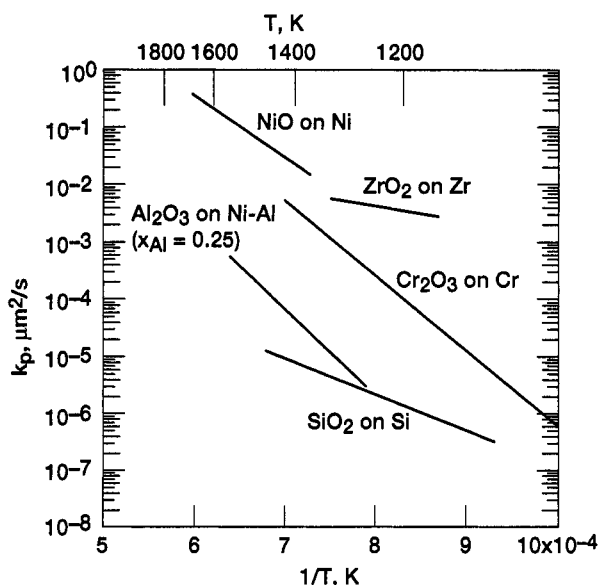
Figure 3.—Comparison of oxidation rates (parabolic rate constant, k_p) for several common oxides (6).

Behavior of SiO_2 in Complex Environments

As discussed in the introduction, actual applications involve complex environments. Current research indicates that four areas of concern: (1) Formation of SiO(g), (2) Water vapor interactions, (3) Enhancement of oxidation rates due to impurities and (4) Fluxing of the silica scale with molten salts and oxide slags. Each of these will be briefly discussed.

(1) Formation of SiO(g). Silica is a unique protective oxide in that it has a highly stable volatile suboxide, SiO(g). This can easily form via two mechanisms. The first is from classic active oxidation, first discussed by Wagner (ref. 7), where the partial pressure of oxygen (or any oxidant) is too low for a protective oxide film to form. Hence the oxygen reacts directly with the SiC surface in this active oxidation reaction:

$$SiC + O_2(g) = SiO(g) + CO(g) \tag{2}$$

Wagner has derived the conditions for the active-to-passive oxygen transition pressure based on the supply of oxygen to the SiC surface. These considerations extend to SiC as well (ref. 8). The passive-to-active transition pressure is determined from SiO_2 decomposition and is about four orders of magnitude lower than the active-to-passive transition (ref. 7).

In the second mechanism for SiO(g) formation, a stable SiO_2(s) layer actually forms, but is easily reduced by the reducing gases (H_2 and CO) in the environment. This may occur in a hydrocarbon fuel-rich situation, where the oxidants CO_2 and H_2O form SiO_2, but the reductants H_2 and CO are also present. The overall kinetics are paralinear—parabolic kinetics from silica growth and linear kinetics from SiO(g) formation (refs. 8 and 9).

(2) Water Vapor Interactions. In general, combustion environments contain about 10% water vapor. Thus a 1 bar combustion process contains 0.1 bar water vapor; higher pressures contain proportionally higher water vapor pressures. It is well-known that silicon oxidation is enhanced by the presence of water vapor (ref. 10); this appears to occur for SiC as well. However the major issue for SiC in combustion environments is the formation of Si-O-H volatiles. There is measured thermodynamic data on $Si(OH)_4(g)$ in the literature (ref. 11) and estimated data on other volatile Si-O-H(g) species (ref. 12). Fig. 4 is a plot of the principal vapor species over SiO_2 and 1 bar of $H_2O(g)$ (ref. 13). An important issue is the pressure dependence—
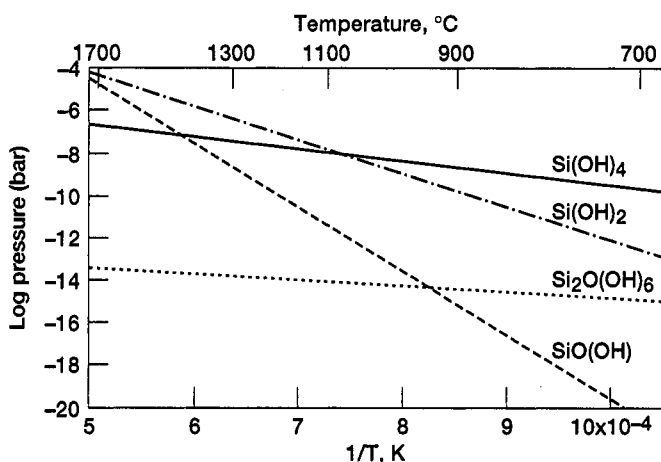
Figure 4.—Vapor species over SiO_2 + 0.9 bar O_2/0.1 bar H_2O.

$P[SiO(OH)_2] \propto [P(H_2O)]$ and $P[Si(OH)_4] \propto P[H_2O)]^2$. Thus the higher the pressure, the more important these species are.

(3) Enhancement of oxidation rates. It appears that silica scales are more sensitive to low-level impurities than other protective oxides. In any application, small amounts of metallic impurities are common in the gas stream, particularly alkali metals. It has been shown that small amounts of Na or K can enhance SiO_2 formation by an order of magnitude or more (refs. 14 and 15). The mechanism by which alkali metals open up the silica network is an important area of research.

(4) Fluxing of SiO_2 by molten salts and slags. Silica is a strongly acidic oxide and can easily accept an anion from a basic salt or slag (ref. 3):

$$SiO_2 + O^= = SiO_3^= \qquad (3)$$
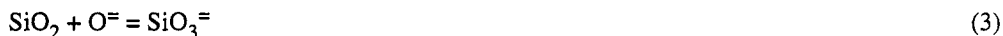
Thus the protective silica scale becomes a liquid silicate. Most of our research has centered on the effects of Na_2SO_4, which is a common deposit in heat engines. However silica can also accept an oxide anion from a basic oxide slag as well. In the case of Na_2SO_4, the critical factor is the activity of Na_2O, which is set by the $P(SO_3)$:

$$Na_2SO_4 = Na_2O + SO_3 \qquad (4)$$
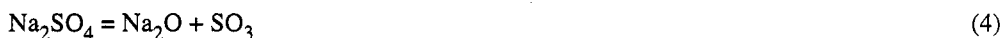
There is a threshold Na_2O activity above which SiO_2 is fluxed and below which SiO_2 is stable. This activity and corresponding $P(SO_3)$ can be calculated. In a combustion situation, the small amounts of sulfur in hydrocarbon fuels lead to overpressures of SO_3. We have predicted SiO_2 dissolution and found good agreement with a burner operating under controlled conditions (ref. 16).

Often a pure Na_2SO_4 deposit is not formed. Mixed salts such as Na_2SO_4-$MgSO_4$-$CaSO_4$ may be deposited and molten salt solution models are necessary to calculate the resultant oxide anion activity (ref. 17). Another important factor is carbon in the Na_2SO_4, which dramatically increases Na_2O activity (ref. 16). This is significant since SiC often has excess carbon.

Summary. The potential difficulties with silica as a high temperature protective oxide are:

1. SiO(g) formation
     A. $SiC + O_2(g) = SiO(g) + CO(g)$
     B. $SiO_2 + H_2 = SiO(g) + H_2O(g)$
2. Volatilization due to steam: $2SiO_2 + 3H_2O = SiO(OH)_2 + Si(OH)_4$

3. Oxidation enhancement by impurities
4. Dissolution by molten salts and slags: $SiO_2 + O^= = SiO_3^=$

Coatings

An examination of the above reactions indicates that many can be minimized by eliminating the silica as an outer film or reducing the chemical activity of the silica. Coatings have long been used with conventional superalloys to achieve improved resistance to aggressive gases. A refractory oxide coating on a SiC-based composite should produce a material with the durability of the former and desirable mechanical properties of the latter. Mullite has a remarkably close CTE to SiC and makes a desirable coating (ref. 18). Recent studies indicate improved resistance to fluxing by Na_2O, as compared to pure silica (ref. 19). This is due to the formation of high melting sodium-alumino-silicates, as opposed to low melting sodium silicates. However the activity of silica in mullite is still rather high and hence the reactions above which produce volatile species are not substantially inhibited. Other refractory oxides may be more effective—this is an important area for further research (ref. 20).

BN INTERPHASES

As discussed, durability of the interphase is the single most critical issue in the development of this type of composite. Current candidate interphases are graphite and boron nitride, which both oxidize easily. Graphite oxidizes to a gas and several detailed models have been developed for oxidation of graphite interphases (refs. 21 and 22). However boron nitride is more likely to remain intact and hence the focus of this discussion will be on boron nitride.

Monolithic BN Oxidation

Although BN is an internal constituent, cracks and porosity could provide easy oxygen access. The oxidation properties of BN are quite dependent on microstructure, crystallinity, and water vapor content of the gas stream (ref. 23). Fig. 5 shows the 900 °C oxidation behavior of two different CVD BN materials, deposited from BCl_3 and NH_3 at at high (>1800 °C) and low temperature (<1400 °C). Both are oriented along the c-axis, however the material deposited at the high temperature is substantially more crystalline. Note the dramatic difference in oxidation behavior. The less crystalline material exhibits nearly linear kinetics and a thick, glassy B_2O_3 layer forms. The more crystalline material oxidizes much more slowly.

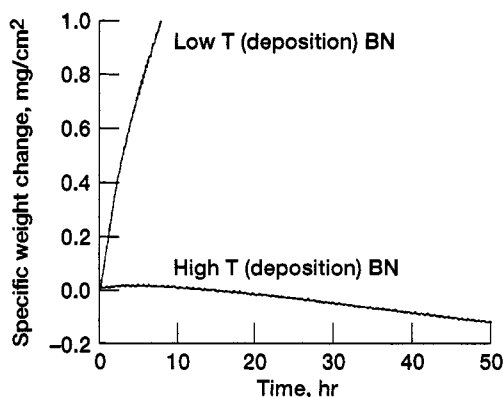Figure 5.—Oxidation of CVD BN at 900 °C in oxygen
with 20 ppm H_2O.

The more crystalline BN shows a small initial weight gain followed by a weight loss. This is combined parabolic/linear or paralinear kinetics. The parabolic component is due to the oxidation of BN:

$$2\,BN + 3/2\,O_2(g) = B_2O_3(l) + N_2(g) \tag{5}$$

The linear component is due to the reaction of B_2O_3 with residual water vapor in the gas stream:

$$B_2O_3(l) + H_2O = HBO_2(g), \ H_3B_3O_6(g), \ H_3BO_3(g) \tag{6}$$
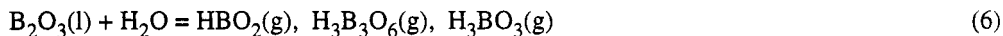
These boron hydroxy species are thermochemically highly stable, and even ppm levels of water are sufficient to produce measurable quantities. Larger amounts of water vapor can lead to substantial material consumption. These observations are important because we wish to fabricate a composite with the most oxidation resistant BN available. The difficulty is that the high CVD temperatures for the better boron nitrides may not fully coat all the fibers during processing.

Oxidation of BN in a Composite

An understanding of monolithic BN oxidation is a basis to examine BN interphase oxidation in a composite. As BN and SiC oxidize, there are numerous interactions between the oxidation products. We have examined a series of model compounds and identified three basic mechanisms (ref. 24): (1) Formation of borosilicate glass, (2) Gettering of oxygen by SiC and preservation of the BN, and (3) Volatilization of the BN via B_2O_3 and $H_xB_yO_z(g)$ formation.

(1) Formation of borosilicate glass. It is well known that small amounts of boron will enhance silica growth (ref. 25). The silica from SiC oxidation will readily react with B_2O_3 from BN oxidation to form borosilicate glass. In order to examine this, we have oxidized a coupon of SiC coated with ~2 μm BN in pure oxygen. Oxidation rates increase roughly a factor of three. The borosilicate glass also lost weight as time progressed, which was attributed to the reaction of B_2O_3 with residual water vapor to form volatile species.

(2) Gettering of oxygen and preservation of BN. A layered SiC/BN/SiC was fabricated, ground so that BN was exposed, and oxidized in pure oxygen for 100+ hrs at 900 °C. The BN remained intact and the SiC in contact with it exhibited clear signs of oxide formation. A thermodynamic analysis of BN/B_2O_3 and SiC/SiO_2 indicates that the silicon-rich SiC in contact with SiO_2 sets a low oxygen potential, which is low enough so that the BN is preserved.

(3) Volatilization of BN. As discussed previously, the oxidation product of BN—whether as a distinct phase or in a borosilicate glass—reacts readily with water vapor to produce volatile $H_xB_yO_z(g)$ species. Thus the BN interphase can volatilize if exposed to a high water vapor/oxygen environment. This is shown schematically in Fig. 6. Several processes are operative here. The BN oxidizes to form B_2O_3 and water vapor diffuses inward through the boundary layer. This then reacts with the B_2O_3 to form volatile $H_xB_yO_z(g)$ species, which must diffuse through the pores and boundary layer. Diffusion through the boundary layer should lead to linear kinetics, which are not observed in this situation. Diffusion through the pores would lead to parabolic kinetics, which are closer to those measured. This indicates pore diffusion is important. As time progresses, pores also start to close off due to enhanced pore wall oxidation.
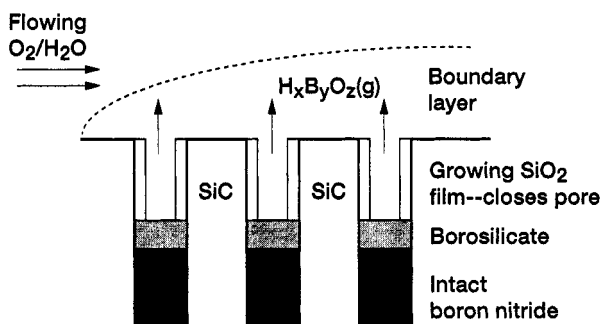

Figure 6.—Schematic of BN volatilization process in a SiC/SiC composite with BN fiber coatings.

ACTUAL COMPOSITES

We now combine all these effects and examine an actual composite. Some of the above reactions will dominate, others will not be detectable. Of course, the dominant reactions depend on the test environment. In a hot basic salt or slag environment, fluxing of silica is expected to dominate. In an environment with oxidants at a low potential, active oxidation is likely to dominate.

As an example, Fig. 7 illustrates a composite sample (SiC matrix/SiC fiber with BN fiber coatings) tested in air at 816 °C for 100 h. Under these conditions, BN interphase oxidation dominates. Kinetics are substantially faster than those of pure SiC at these temperatures—an effect due to both BN oxidation and boron-enhanced SiC oxidation. Note the substantial borosilicate glass formation around the fibers. As time progess, the B_2O_3 in the glass will volatilize due to reaction with the H_2O in air, leaving behind pure SiO_2.
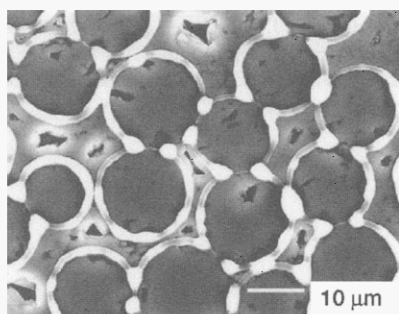

Figure 7.—Electron micrograph of oxidized composite showing exposed fiber ends.

SUMMARY AND CONCLUSIONS

High temperature oxidation/corrosion behavior of ceramic matrix composites has been discussed. Emphasis is on SiC matrices with SiC fibers and BN fiber coatings. It is useful to examine the behavior of each component individually. Baseline studies of CVD SiC provide information about the matrix and pure SiC fibers. In general, SiC shows excellent oxidation behavior in pure oxygen, but complex atmospheres lead to other issues. Particular areas of concern are production of SiO(g), volatilization of SiO_2 as $Si(OH)_4$ and $SiO(OH)_2$, impurity enhanced oxidation of SiC, and fluxing of SiO_2 by molten salts and slags. Refractory oxide coatings may minimize some of these reactions.

The most important issue for this type of composite remains the oxidation of the fiber interphase. The oxidation of pure BN is complex and highly dependent on the microstructure of the BN and water vapor content in the gas stream. High deposition temperature CVD BN is the most desirable, but may lead to problems in composite fabrication. In a composite, there appear to be three important mechanisms for BN oxidation/corrosion: borosilicate glass formation, gettering of oxygen by SiC, and volatilization. Research is needed into more effective preservation of the BN interphase.

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