

DURABILITY OF SILICA-PROTECTED CERAMICS IN COMBUSTION ATMOSPHERES

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INTRODUCTION

Silicon-based ceramics and composites are unstable in air and rely on a thin silica film for protection. Limited interaction of these materials with their operating environment is essential. This paper is divided into two parts: (I) External effects dealing with the stability of the silica film and (II) Internal effects dealing with attack of oxygen on internal components such as the fiber and fiber coating. These are shown schematically in Figure 1. Most of the emphasis is on a SiC fiber-reinforced SiC matrix, however the conclusions apply to other silica protected materials such as Si_3N_4 and $MoSi_2$.

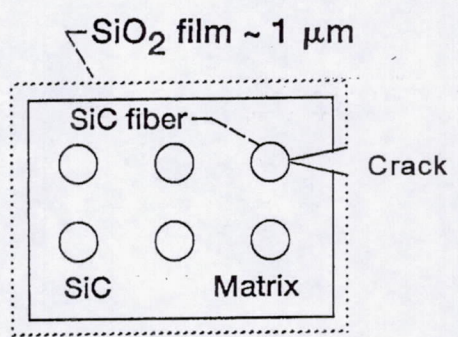


Figure 1. Schematic of composite.

Figure 2 shows the parabolic rate constants for silica as compared to other common oxides [1-5]--note the slow growth rate of silica and its low activation energy. For temperatures above 1300 K, silica is actually slower growing than alumina, which is the most common protective oxide on superalloys. Silica forms as a thin film, which is highly stable, dense, and self-healing--all desirable properties for a high temperature oxide. Thus corrosion resistance is often listed with the other promising properties of silicon-based ceramics.

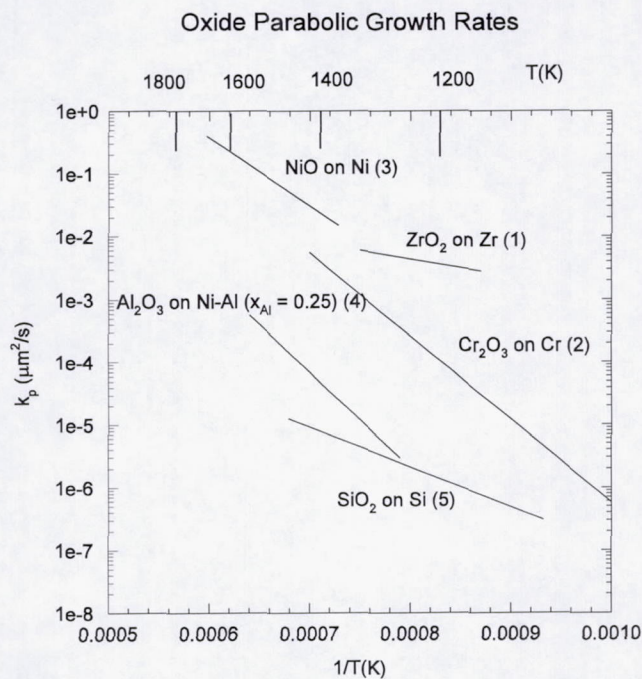


Figure 2. Parabolic rate constants for some common oxides.

However, in actual applications and complex gas atmospheres, silica scales are subject to degradation.[6] Ceramic matrix composites are under consideration for applications such as heat engines, heat exchanger tubes in furnaces, heat exchanger tubes in coal-fired environments, chemical process environments, and re-entry shields. Clearly each of these has a unique environment. This paper will focus on combustion environments and their interactions with silica scales. Where possible,

the conclusions will be generalized to other applications. Figure 3 shows the equilibrium products of a typical jet aircraft engine hydrocarbon fuel and air over a range of equivalence ratios. This figure shows a number of features critical to SiO_2 stability, such as high water vapor content and large amounts of CO and H_2 for equivalence ratios greater than one (fuel rich). In addition to the products shown in the figure, there are various low level impurities such as sulfur oxides, sodium, potassium and vanadium oxides, depending on the purity of the fuel. Four critical interactions can be identified between the silica scale and these constituents of the combustion environment:

- Ease of reduction to SiO(g) .
- Water vapor effects.
- Impurity effects.
- Dissolution by basic molten salts.

Each of these will be discussed and some possible solutions proposed.

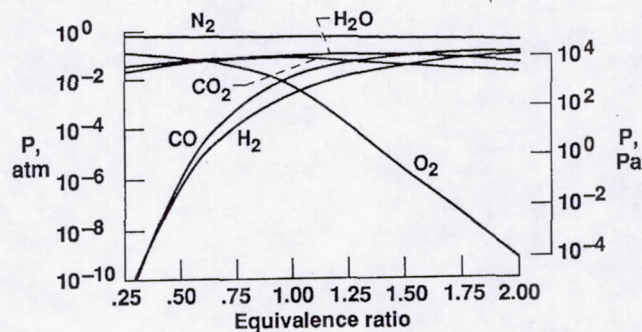


Figure 3. Equilibrium gas composition as a function of equivalence ratio.

Internal oxidation occurs when a crack is formed in the ceramic or composite providing a path for oxygen ingress. The slow growth rates of silica are then a problem, as the crack cannot heal fast enough. This is a particular problem at intermediate temperatures (873-1273 K). This problem will be discussed as well as some possible solutions.

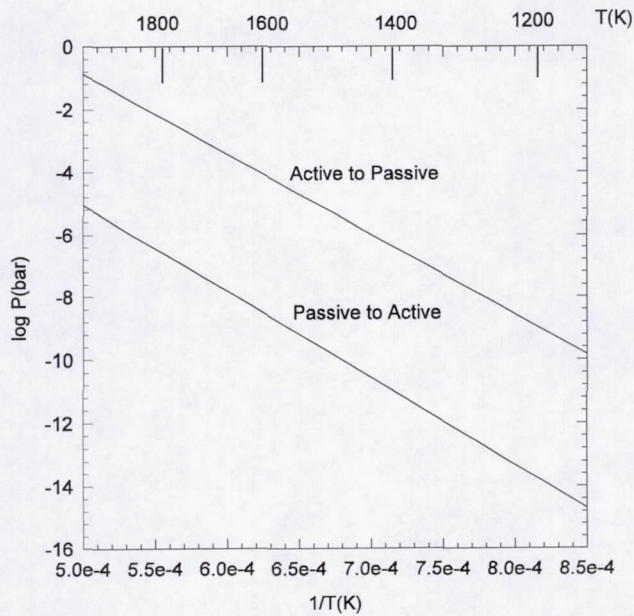
I. EXTERNAL OXIDATION/CORROSION

As discussed earlier, silica forms as a dense protective oxide via a reaction such as:



The formation of this stable SiO_2 film is termed 'passive oxidation'. It is generally accepted that the rate controlling step is oxygen diffusion inward through the silica film, and that the chemical reaction occurs at the scale/ceramic interface. [6,7] Note that $\text{CO}(\text{g})$ formed at this interface must escape rapidly through the silica film. Other silica formers behave generally the same. MoSi_2 forms $\text{MoO}_x(\text{v})$ volatile species in the early stages of oxidation and then a thin layer of Mo_5Si_3 between the SiO_2 and the MoSi_2 . [8] Si_3N_4 oxidation is complicated by the formation of $\text{Si}_x\text{N}_y\text{O}$ solid solution layers which may have even lower oxygen diffusivities than SiO_2 . [6,9]

I.a. Formation of $\text{SiO}(\text{g})$

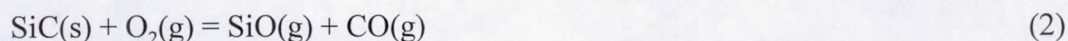


APPASIC

Figure 4. Active/Passive and Passive/Active transitions for SiC.

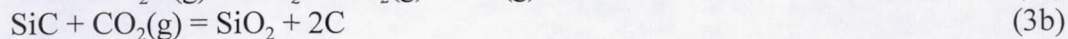
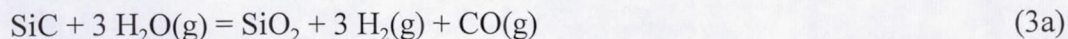
Silica is an unusual oxide as it has a stable gaseous sub-oxide (SiO(g)). The formation of this oxide leads to rapid material consumption rates, particularly in a high velocity combustion environment. SiO(g) may form via several mechanisms. The most well-known is active oxidation.

When the supply of oxygen to the SiC surface is insufficient to form a stable SiO₂ film, then SiO(g) forms in active oxidation.



The classic description of this process is from Wagner [10]. He points out the difference between the active-to-passive (increasing pressure) and passive-to-active (decreasing pressure) transition points. The active-to-passive transition point is derived from the condition for a stable SiO₂ film on SiC; the passive-to-active transition point is derived from the decomposition of SiO₂. Figure 4 shows the calculated values for these points.[11] Although we have presented these transition pressures in terms of oxygen, they are the same for any oxidant (e.g. H₂O and CO₂). [12] Low oxidant potentials occur in certain heat treating environments [13], but most combustion environments contain sufficient oxidant so that active oxidation does not occur.

A second mechanism for SiO(g) formation occurs when a stable SiO₂ layer forms, but there is a sufficient amount of reducing gases present so that it is immediately reduced to SiO(g).[12] This occurs in an oxidizing/reducing mixture of gases such as CO₂/CO [14] and H₂O/H₂. [15] The oxidation step, which exhibits parabolic kinetics, occurs as:



The reduction step, which exhibits linear kinetics, occurs as:



This leads to a mixture of parabolic and linear kinetics, producing overall parabolic behavior. Parabolic oxide growth curves generally show a period of oxide growth, followed by a linear volatilization region in which the scale thickness remains

constant but net material consumption is occurring.[12] This has been observed for CO_2/CO [12,14], $\text{H}_2\text{O}/\text{H}_2$ [12, 15] and a synthetic fuel rich combustion gas mixture which contains both CO_2/CO and $\text{H}_2\text{O}/\text{H}_2$ [16].

I.b. Water Vapor Effects

It is well known that steam enhances the oxidation of silicon [5], with the parabolic rate constant proportional to the amount of water vapor in the gas stream. However silica is also known to volatilize in steam environments. [17] Figure 5 shows a TGA trace of a pre-oxidized SiC coupon in a 50% steam/oxygen environment. The linear weight loss clearly indicates the formation of a volatile Si-O-H molecule. The exact identity of this molecule had been in question. Recent transpiration experiments indicate a $[\text{P}(\text{H}_2\text{O})]^2$ dependence, suggesting the following reaction [18]:

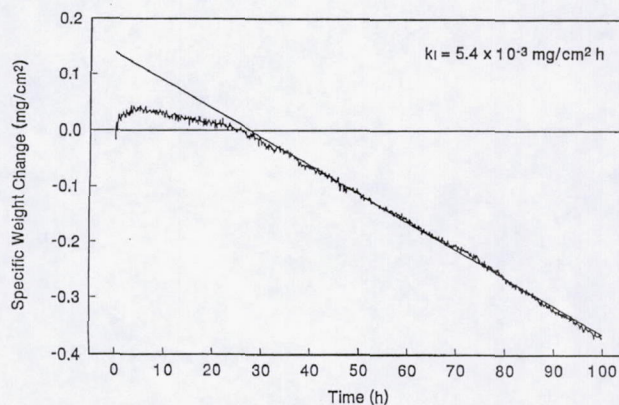
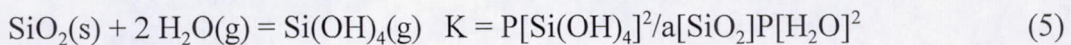


Figure 5. Volatilization of a SiO_2 scale on pre-oxidized SiC--1473 K, 50% $\text{H}_2\text{O}/\text{O}_2$, 4.4 cm/sec, initial scale thickness $\sim 8 \mu\text{m}$.

Recently the $\text{Si}(\text{OH})_3^+$ ion has been observed in a specialized sampling mass spectrometer at NASA Lewis.[19] This is most likely a fragment of the $\text{Si}(\text{OH})_4(\text{g})$ molecule. According to Hashimoto's data [18] at 1400 K, the vapor pressure of $\text{Si}(\text{OH})_4$ is about 2×10^{-8} bar and 2×10^{-6} bar at 0.1 and 1 bar H_2O , respectively. As shown in Figure 3, combustion atmospheres typically contain about 10% water

vapor. For a 1 bar combustor, there is only enough water ($P(\text{H}_2\text{O}) = 0.1 \text{ bar}$) to generate a negligible amount of $\text{Si}(\text{OH})_4(\text{g})$; however for a 10 bar combustor there is enough water vapor ($P(\text{H}_2\text{O}) = 1 \text{ bar}$) to generate much more $\text{Si}(\text{OH})_4(\text{g})$.

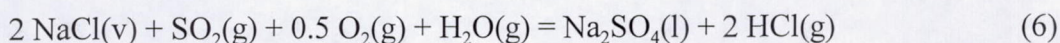
Again the parabolic oxidation behavior and linear volatilization behavior lead to overall parabolic kinetics. [20] Water vapor is a major combustion product and in a high pressure combustion situation, there will be a large amount of water vapor. This can lead to substantial matrix recession rates.

I.c. Impurity Effects

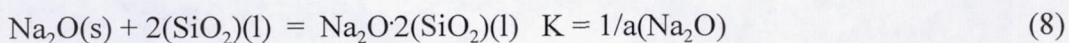
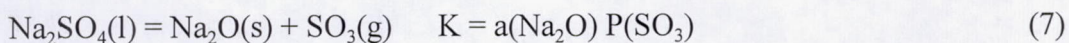
As discussed, in any combustion situation there will be metal ions in the atmosphere. The most common are sodium and potassium, but other group I, II and transition metals are also present. These may come from fuel impurities, combustion air in a marine environment, and/or degradation of metallic parts. These low levels (~ppm) can open up the silica network and allow faster transport of oxygen molecules. Oxidation rates are increased by up to an order of magnitude in such environments. [21,22]

I.d. Molten Salt Degradation

A well-known problem for gas turbines running near a marine environment and/or operating with dirty fuels is corrosive attack from Na_2SO_4 . [23] Na_2SO_4 is an extremely stable molecule formed from the reaction of NaCl with sulfur impurities in the fuel:



The Na_2SO_4 then partially decomposes and dissolves or fluxes the protective oxide on the engine component:



The process thus transforms a thin protective silica scale into a liquid non-protective silicate. The latter allows rapid influx of oxygen and formation of more silica by reaction (1). Continuous deposition of Na_2SO_4 leads to extensive silicate formation,

as shown in Figure 6, and ceramic consumption.

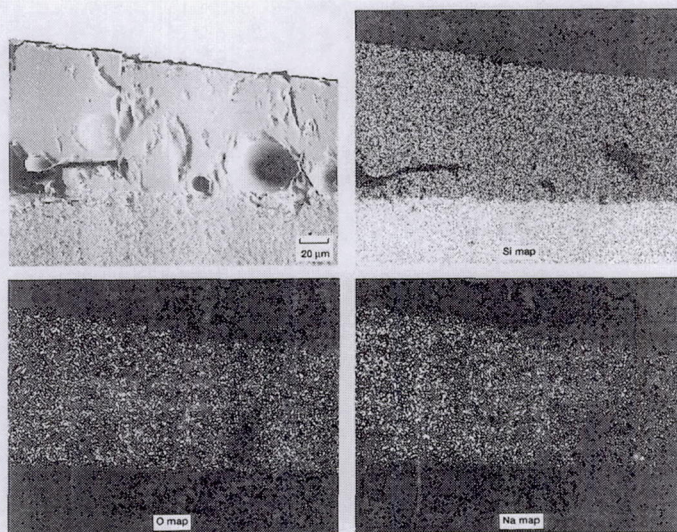


Figure 6. Polished cross section and Si, O, and Na dot maps of SiC corroded in burner--1273 K, 4 bar, Jet A fuel, 13.5 hr, 4 ppm Na

The critical quantity is the chemical activity of Na_2O , which is set by the partial pressure of SO_3 . A molten salt with a high activity of Na_2O is termed basic and one with a low activity of Na_2O is termed acidic. Silica is an acidic oxide--it will only react with a basic oxide. From reaction (8), the threshold $a(\text{Na}_2\text{O})$ for silica dissolution can be calculated to be 9×10^{-11} at 900°C . If the activity of Na_2O is greater than this, sodium silicate will form; if it is less than this, sodium silicate will not form. [24] In a 4 bar combustor with Jet A aviation fuel (0.05% sulfur), the calculated $P(\text{SO}_3)$ is 4×10^{-6} bar and corresponding $a(\text{Na}_2\text{O}) = 1.25 \times 10^{-10}$. Experiments with pure silica indicated silicate formation under these conditions. In the same combustor with No. 2 Diesel fuel (0.5% sulfur), a higher $P(\text{SO}_3)$ of 6.3×10^{-5} atm is calculated and a corresponding $a(\text{Na}_2\text{O})$ of 8×10^{-12} is established. Experimentally silica was found to form little silicate under these more acidic conditions.[24]

Other factors may alter the activity of Na_2O , such as the presence of carbon, which increases the activity of Na_2O in Na_2SO_4 and drives the salt more basic. [24] This is important since many ceramics and composites contain a second phase of pure

carbon. The concept of basic fluxing of SiO_2 is remarkably general and applies to many situations. Glass re-melt furnaces may deposit sodium silicate.[25] Unless this sodium silicate is silica-saturated, more silica will be fluxed. Combustion of coal leads to slag deposits which are mixtures of oxides. If the mixture contains primarily acidic oxides, limited attack occurs [26]; if the mixture contains primarily basic oxides, fluxing occurs.[27]

As mentioned, this fluxing attack can lead to substantial material consumption. This is not only in the form of even surface recession, but also as localized surface pitting, as shown in Figure 7.[28] This is particularly critical in the case of monolithic ceramics due their sensitivity to surface flaws and it leads to a reduction in strength. [29] Pitting has been shown to correlate with the salt chemistry, with the more aggressive salts leading to more extensive pitting.

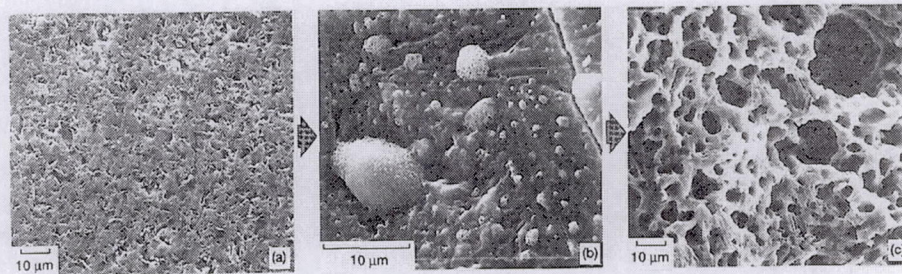


Figure 7. Sequence showing sintered SiC (B, C additive) before salt corrosion, after salt corrosion with $\text{Na}_2\text{SO}_4/(0.01\text{SO}_2/\text{O}_2)$ at 1273 K showing silicate product layer, and with product layer removed by HF, revealing pitted SiC.

Potential Solutions to the External Oxidation/Corrosion Problem

In the case of superalloys many oxidation/corrosion problems have been solved with coatings--particularly overlay coatings such as NiCoCrAlY. Therefore one approach may be coating silicon-based ceramic materials. Refractory oxides show the best corrosion resistance and a number of these have been evaluated as coatings for SiC. [30, 31]

Currently the most promising coating system for SiC is mullite. It has a remarkably close coefficient of thermal expansion (CTE) match to SiC and can be plasma sprayed on SiC. When steps are taken to roughen the SiC before coating and insure

that fully crystalline mullite goes on the SiC, the coating adheres well after thermal cycling. [32] A micrograph of this coating system is shown in Figure 8. It shows better performance over uncoated SiC in Na₂O-induced corrosion due to the formation of higher melting sodium-alumino-silicates, as compared to the low melting sodium silicates. [33]

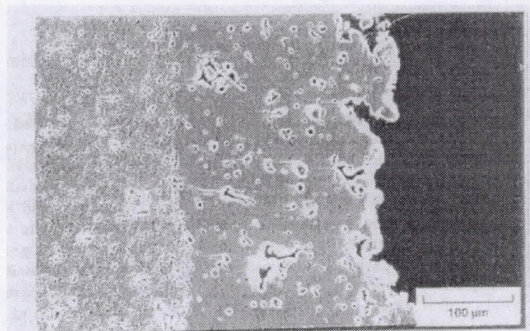


Figure 8. External mullite coating plasma sprayed onto SiC.

However alumina-saturated mullite still has a relatively high chemical activity of SiO₂--~0.4 at 1400 K. Examination of equations (4a), (4b) and (5) shows that to substantially reduce the amount of volatiles, the activity of silica should be reduced by an order of magnitude or more. One possible solution is an outer refractory oxide coating such as alumina or zirconia. However the CTE mismatch is so large between these oxides and mullite that cracking and spallation will occur. However, it may be possible to reduce the CTE mismatch stress by grading the coating from mullite to alumina or zirconia.

Another possible solution is the development of a low silica-activity binary or ternary silicate coating. Such a coating must meet the following criteria:

1. High silica activity at the ceramic/coating interface; low silica activity at the coating/gas interface.
2. Close CTE match to the ceramic substrate.
3. High melting.
4. Second and third metal and metal oxide(s) must have a low vapor pressure, minimal water vapor interactions.
5. Stable silicate--does not decompose.

We are currently methodically examining a range of silicate compositions for these

requirements. Generally the alkali and alkaline earth silicates have a low silica activity, but do not meet requirement 3 or 4. Ternary silicates may meet more of the requirements.

II. INTERNAL OXIDATION

Figure 9 shows a schematic of a crack in a SiC fiber-reinforced SiC matrix composite. Clearly this is a path for rapid oxygen ingress. The oxygen can then attack the SiC fiber and/or the fiber coating. Current fiber coatings are either carbon or boron nitride, which are quite susceptible to oxidation. Oxidation of these components will then lead to a substantial decrease in composite properties.

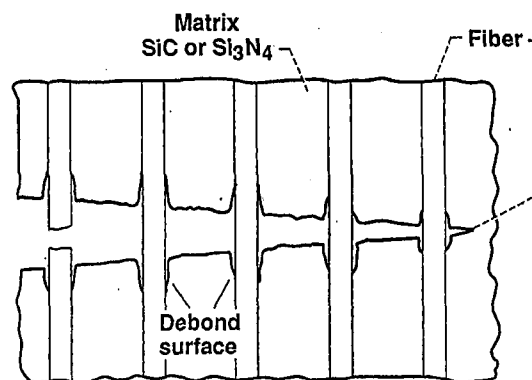


Figure 9. Schematic showing oxygen ingress through crack to fiber and fiber coatings.

In the event of a crack, a fiber could be directly exposed to 1 bar of air. At 1473 K under this pressure of oxygen, SiC will form about 0.5 μm of SiO_2 in 10 hrs. [34] This represents a substantial amount of material consumption for a fiber of several microns diameter. Carbon fiber coatings will form CO and CO_2 as an oxidation product and be removed. This is likely to be more of a problem at intermediate temperatures (873-1273 K), where concurrent growth of silica in the fiber/matrix annular region is minimal.[35-37] Boron nitride oxidizes to form liquid B_2O_3 , which then reacts with the SiO_2 in a fluxing-type reaction to form borosilicate glass. We have observed that this borosilicate can attack SiC, much as a molten salt does. Also, water vapor will deplete the B_2O_3 from the borosilicate by forming $\text{HBO}_2(\text{g})$. [38] Clearly, these internal oxidation effects are quite serious for current silicon-based composites.

The search for solutions to these internal oxidation effects is critical. Some solutions have been proposed, with a limited degree of success. These fall into two categories. The first is to produce a more fluid glass, which will readily fill the cracks. This approach has been used for SiC protected carbon/carbon on the Space Shuttle for many years. The CTE mismatch between carbon/carbon and SiC leads to extensive cracking of the SiC. An outer layer of a silica-saturated sodium silicate glass is applied to fill these cracks as they develop.[11] For SiC/SiC composites, other glasses, such as borosilicate [39] and perhaps germania-silicate [40] have been proposed. Borosilicate glasses have the problems which were discussed in the previous paragraph. Germania-silica glasses look promising for MoSi_2 , but little is known about their behavior in SiC materials or about the stability of germania in combustion environments.

A second approach is to provide a getter, to reduce the oxygen potential along the crack wall. A lower oxygen potential will provide less interaction with the internal components of the composite. Again, boron compounds have been tried for this approach.[39] The gettering material would have to be inert in the matrix and to the fiber.

SUMMARY AND CONCLUSIONS

This overview of oxidation and corrosion effects on silica-protected ceramics and composites is divided into two parts: (I). External effects and (II). Internal effects. In regard to the first part, the literature indicates silica the best of the common protective oxides in pure oxygen. However in actual applications, there are four major degradation routes which must be considered: (a) Formation of $\text{SiO}(\text{g})$ (b) Water vapor enhancement of oxidation rate and formation of $\text{Si}(\text{OH})_4$ volatiles (c) Low level metal cation enhancement of oxidation rate and (d) Molten salt and slag corrosion. Several protective coating concepts have been discussed, which may minimize these effects. Internal effects deal with a microcrack providing a path for oxygen ingress to the oxygen sensitive fiber and fiber coating. This is a critical area of study for these materials. Possible solutions involve a fluid glass to fill the cracks and/or oxygen gettering along the walls of the cracks.

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