Oxidation of SiC Fiber-Reinforced SiC Matrix Composites With a BN Interphase

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SiC-fiber reinforced SiC matrix composites with a BN interphase were oxidized in reduced oxygen partial pressures of oxygen to simulate the environment for hypersonic vehicle leading edge applications. The constituent fibers as well as composite coupons were oxidized in oxygen partial pressures ranging from 1000 ppm O$_2$ to 5% O$_2$ balance argon. Exposure temperatures ranged from 816°C to 1353°C (1500°F to 2450°F). The oxidation kinetics of the coated fibers were monitored by thermogravimetric analysis (TGA). An initial rapid transient weight gain was observed followed by parabolic kinetics. Possible mechanisms for the transient oxidation are discussed. One edge of the composite coupon seal coat was ground off to simulate damage to the composite which allowed oxygen ingress to the interior of the composite. Oxidation kinetics of the coupons were characterized by scanning electron microscopy since the weight changes were minimal. It was found that sealing of the coupon edge by silica formation occurred. Differences in the amount and morphology of the sealing silica as a function of time, temperature and oxygen partial pressure are discussed. Implications for use of these materials for hypersonic vehicle leading edge materials are summarized.
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Motivation

Technical challenge for hypersonic vehicles
Develop lightweight, durable, reusable, 3000°F (1650°C) structurally-integrated Thermal Protection Systems (TPS) to carry both thermal and mechanical loads using ceramic matrix composite materials
Objectives

• Characterize the oxidation resistance of BN-coated SiC fiber-reinforced SiC composites at temperatures and oxygen partial pressures relevant for hypersonic environments

• Develop understanding of oxidation degradation kinetics and mechanisms

• Provide data to Materials Research and Design, Inc. for incorporation in FEM for SiC/SiC degradation
Oxidation reactions

Oxide formation

\[ \text{SiC} + \frac{3}{2} \text{O}_2(\text{g}) = \text{SiO}_2 + \text{CO}(\text{g}) \]
\[ 2 \text{ BN} + \frac{3}{2} \text{O}_2(\text{g}) = \text{B}_2\text{O}_3 + \text{N}_2(\text{g}) \]
\[ \text{SiO}_2 + \text{B}_2\text{O}_3 = \text{borosilicate glass} \]

Oxide volatilization

\[ \text{B}_2\text{O}_3 = \text{B}_2\text{O}_3(\text{g}) \]
\[ \text{B}_2\text{O}_3 + \frac{1}{2} \text{O}_2(\text{g}) = 2 \text{ BO}_2(\text{g}) \]
\[ \text{B}_2\text{O}_3 + \text{H}_2\text{O}(\text{g}) = 2 \text{ HBO}_2(\text{g}) \]
Materials

• Sylramic iBN fibers
  – Stoichiometric polycrystalline $\beta$-SiC
  – 3 wt% TiB$_2$, 1.3 wt % B$_4$C, 0.7 wt% BN*
  – $\sim$10 $\mu$m diameter
  – Heat treated in N$_2$ to form in situ BN surface layer (iBN), <100 nm
  – 800 fibers/tow

• SiC/BN/SiC composites
  – Sylramic iBN fibers
  – CVI Si-doped BN-coated fabric
  – CVI SiC matrix

Experimental Procedure

• ThermoGravimetric Analysis (TGA)
  – 5% O₂/Ar or 1000 ppm O₂/Ar, 100 sccm (0.4 cm/sec)
  – 816, 1149, 1343°C (1500, 2100, 2450°F)
  – 100h maximum time, shorter times to investigate kinetics
• Fibers twisted into “lanyards” that can be suspended directly from sapphire hangers to prevent reaction with containers
  – 8 cm length, 6 “lanyards” 800 fibers each, ~235 cm², 0.17 g
• SiC/BN/SiC coupons with seal coat on bottom edge ground off
  – 2.5 cm x 1.3 cm x 0.3 cm, ~9 cm², 2 g
• SEM, EDS to characterize oxidation products

ground off edge
Fiber oxidation
Oxidation weight change for Sylramic iBN fibers

- Rapid transient weight gain followed by slow oxidation rate
- Variation in weight gain during transient phase at 1343°C
“Parabolic” oxidation kinetics observed after transient

- Low rates and balance drift result in large uncertainty in measured slopes, rate constants
- Apparent parabolic rates are slower than those predicted for oxidation of pure SiC
Reduced fiber oxidation rates at low $P(O_2)$

1000 ppm $O_2$

- Rapid transient oxidation rates also observed at low oxygen partial pressures
- Weight loss observed at 816°C
Microstructure of oxidized fibers
plan view and fracture sections, 5% O₂/Ar, 100 hr

Thickness of oxide scales consistent with weight change
Microstructure of oxidized fibers
plan view and fracture sections, 5% O$_2$/Ar, 0.5 hr

No obvious oxidation after 0.5 hr exposure at 816°C

Thick oxide scales observed after oxidation at short times consistent with rapid transient weight change
Microstructure of oxidized fibers
plan view and fracture sections, 1000 ppm O₂/Ar

Oxide formation observed at 1149 and 1343°C
even at this low oxygen partial pressure
Chemical composition of oxide scales: SiO$_2$

1. Light phase in scale is SiO$_2$.

2. Dark phase in scale is BN surrounded by SiO$_2$?

Insignificant boron detected in SiO$_2$ by EDS even after 1 hr exposure, 1343°C, 1000 ppm O$_2$/Ar when rapid transient is midway. Boron doping of silica rather than borosilicate glass formation is hypothesized.

Aluminum in spectra from fiber cross-sections is from mounting stub.
Possible mechanism for Sylramic iBN fiber oxidation

- Thin film of boria, borosilicate or B-doped silica forms on fiber
- Rapid transport of oxygen through B-affected silica scale leads to rapid initial transient in oxidation kinetics
- BN layer consumed
- B-species diffuses out of scale and is volatilized
- Kinetics slow to those found for oxidation of pure SiC
Sylramic iBN Fiber Oxidation Summary

- Oxidation of iBN fibers occurs for all conditions studied except for 816°C in 1000 ppm O₂
- Rapid transient oxidation of BN results in rapid growth of silica layer
- Borosilicate glass is not observed
- B-doping of silica scale proposed to explain initial rapid oxidation rate of fibers
- Rapid initial oxidation rate may be beneficial to composite performance in hypersonics environment
  – Rapid sealing of exposed BN interphase to limit degradation
SiC/BN/SiC composite oxidation
Oxidation weight change of SiC/BN/SiC coupons

Weight change for SiC/BN/SiC coupons (bottom edge SiC seal coat ground off) in 5% O$_2$/Ar environment is minimal at all temperatures for 24 and 100 hr exposures

- $\Delta m < 0.4 \text{ mg}$
- $\Delta m$ on the order of expected drift in TGA signal
- Rely on SEM/EDS of SiO$_2$ formed/BN consumed in coupons exposed for 24h and 100h to characterize oxidation kinetics
- Section coupons and look for distance of oxygen ingress, loss of BN from open edge
Oxidation weight change of SiC/BN/SiC coupons

Weight loss observed in 1000 ppm O\textsubscript{2}/Ar environment at all temperatures studied. BN loss without SiO\textsubscript{2} formation? Need SEM/EDS characterization.
Microscopy of SiC/BN/SiC composites

- All samples polished with non-aqueous procedures to preserve any B$_2$O$_3$ in scale – B$_2$O$_3$ sensitive to moisture
- BN interphase polishes more easily than SiC
  - Interphase recessed relative to surrounding SiC and SiO$_2$
  - BN EDS signal obtained where shadowing of surrounding fibers/matrix is minimal
- Interaction volume of 6kV electron beam in SiC/BN/SiC prevents EDS sampling of BN interphase alone
  - BN: $\sim$1 $\mu$m interaction volume, interphase width is $\sim$0.3 $\mu$m
  - SiC & SiO$_2$: $\sim$0.5 $\mu$m interaction volume
- In cases where SiO$_2$ formation is minimal and BN is lost to oxidation, difficult to distinguish between BN and epoxy: same phase contrast, same appearance. Must use point EDS in selective areas where shadowing is not a problem.
Microstructure of Oxidized Coupons
1343°C, 5% \( \text{O}_2/\text{Ar} \), 100h

Oxygen ingress into ground edge of composite coupon can be measured for both fibers perpendicular and parallel to the plane of polishing.
Interface between SiO₂ and BN observed. Nitrogen is present with boron. No B-rich borosilicate glass.
Microstructure of Oxidized Coupons

1149°C, 100h, 1000 ppm O₂: intermittent SiO₂ formation

816°C, 5% O₂: minimal SiO₂ plugging at ground edge, but SiO₂ forms on SiC fibers next to BN
Summary of oxygen ingress/loss of BN for SiC/BN/SiC composites

<table>
<thead>
<tr>
<th>Temp., °C</th>
<th>orientation</th>
<th>5% O₂, 100 h</th>
<th>5% O₂, 24h</th>
<th>1000 ppm O₂, 100 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>1343</td>
<td>// fibers</td>
<td>119±24 µm (n=13)</td>
<td>61±32 µm (n=22)</td>
<td>15±8 µm (n=16)</td>
</tr>
<tr>
<td></td>
<td>⊥ fibers</td>
<td>3 fiber diameters</td>
<td>2 fiber diameters</td>
<td>1 to 2 fiber diameters</td>
</tr>
<tr>
<td>1149</td>
<td>// fibers</td>
<td>2.8±3.1 µm (n=16)</td>
<td>3.8±2.1 µm (n=35)</td>
<td>Intermittent SiO₂</td>
</tr>
<tr>
<td></td>
<td>⊥ fibers</td>
<td>&lt;1 fiber diameter</td>
<td>&lt;1 fiber diameter</td>
<td>Intermittent SiO₂</td>
</tr>
<tr>
<td>816</td>
<td>// fibers</td>
<td>0.3 µm (n=2), 5 µm (n=1)</td>
<td>2 µm (n=3)</td>
<td>14 µm (n=2)</td>
</tr>
<tr>
<td></td>
<td>⊥ fibers</td>
<td>&lt;1 fiber diameter</td>
<td>&lt;1 fiber diameter</td>
<td>1 fiber diameter</td>
</tr>
</tbody>
</table>

- Red = depth of SiO₂ formed, BN consumed, measured from ground edge
- Blue = depth of BN consumed without SiO₂ sealing edge, measured from ground edge
Stability of BN adjacent to SiO$_2$

- BN stability adjacent to SiO$_2$ has been observed previously

- Given limited amounts of oxygen, SiC will oxidize preferentially over BN since SiO$_2$ is thermodynamically stable relative to B$_2$O$_3$
Summary of SiC/BN/SiC oxidation

• SiO₂ formation is observed at all temperatures in 5% O₂ environment. Sealing of exposed BN interphase channels into composite occurs at 1343 and 1149°C.

• At 1000 ppm O₂ condition, some SiO₂ formation is observed, but weight loss of composite is observed, indicating loss of BN without sealing composite.
Unanswered questions: SiC/BN/SiC composite oxidation

- Microstructure of composite oxidized at 1343°C in 1000 ppm O\textsubscript{2} indicates SiO\textsubscript{2} sealing of composite, inconsistent with largest observed weight loss.
- Weight loss of composites at 1343°C, 1149 °C in 1000 ppm O\textsubscript{2} is inconsistent with observed weight gain of fibers under same conditions.
- What occurs at SiO\textsubscript{2}/BN interface? How is oxygen transported down interphase region to SiO\textsubscript{2}/BN interface? What oxidation reaction occurs at interface? How are B and N transported from interface?
Conclusions

• Beginning to understand the oxidation behavior of SiC/BN/SiC composites in low oxygen partial pressure environments

• Rapid B-affected oxidation transient of SiC fibers provides mechanism for sealing exposed fibers in composite

• Sealing of exposed fibers in composites occurs for exposures in 5% O_2 environments at 1149 and 1343°C.

• Inward progression of oxidation (SiO_2 formation/loss of BN interphase) is <200 µm, usually much less: minimal degradation for 100 h exposure
Further work

• Continue to characterize the oxidation of both Sylramic iBN fibers and SiC/iBN/SiC composites, more repeats, higher temperatures (1538°C, 2800°F), intermediate oxygen partial pressure (0.5% O₂).

• Characterize oxidation of woven Sylramic iBN fabric with CVI Si-doped BN coating (intermediate processing step)

• Better characterize B-content in thermally grown SiO₂. SIMS?

• Role of atomic oxygen in hypersonic environment on SiC/BN/SiC oxidation should be considered, arc-jet exposures?
Acknowledgment

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Backup charts
Initial transient weight gain attributed to oxidation of BN, doping of SiO$_2$ scale

- Initial transient is variable, especially at 1343°C, possibly due to variable fiber spacing, oxide bridging between fibers, changes of exposed surface area.
Comparison of oxidation rates at various P(O_2)

Transient oxidation extended to longer times for 1149 and 1343°C exposures.

Oxidation not observed at 816°C in 1000 ppm O_2.