Oxidation of SiC/BN/SiC Composites in Reduced Oxygen Partial Pressures

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SiC fiber-reinforced SiC composites with a BN interphase are proposed for use as leading edge structures of hypersonic vehicles. The durability of these materials under hypersonic flight conditions is therefore of interest. Thermogravimetric analysis was used to characterize the oxidation kinetics of both the constituent fibers and composite coupons at four temperatures: 816, 1149, 1343, and 1538°C (1500, 2100, 2450, and 2800°F) and in oxygen partial pressures between 5% and 0.1% (balance argon) at 1 atm total pressure. One edge of the coupons was ground off so the effects of oxygen ingress into the composite could be monitored by post-test SEM and EDS. Additional characterization of the oxidation products was conducted by XPS and TOF-SIMS. Under most conditions, the BN oxidized rapidly, leading to the formation of borosilicate glass. Rapid initial oxidation followed by volatilization of boria lead to protective oxide formation and further oxidation was slow. At 1538°C in 5% oxygen, both the fibers and coupons exhibited borosilicate glass formation and bubbling. At 1538°C in 0.1% oxygen, active oxidation of both the fibers and the composites was observed leading to rapid SiC degradation. BN oxidation at 1538°C in 0.1% oxygen was not significant.
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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

Materials and Procedure
- Sylramic iBN fibers
  - Stoichiometric polyacrylamide-SiC
  - 3 wt% TiB2, 1.3 wt% B4C, 0.7 wt% BN
  - Heat treated in N2 to form a silica BN surface layer (BN) <100 nm
  - TiB2 Nanotubes, 0.1-100 μm
- SiC/SiC matrixes
  - CVI SiC
  - β-SiC
- Sylramic iBN film

Summary of SiC/BN/SiC composite oxidation

Possible reactions
Oxide formation
SiC + 3/2 O2(g) + 3SiO2 + CO(g)
2 BN + 3/2 O2(g) = B2O3 + N2(g)

Oxide volatilization
B2O3 = B2O3(g)
B4C + 1/2 O2(g) = 2 BO2(g)
B2O3 + 3H2O(g) = 2 BO2(g)

Active Oxidation
SiC + O2(g) = SiO2(g) + CO2(g)

Summary and Conclusions
- Minimal oxidation of Sylramic iBN fibers or SiC/BN/SiC composites occurs at 816°C
- Transient borosilicate glass formation occurs at 1149 and 1343°C followed by boria volatility, leaving a protective silica scale on both fibers and composites
- Destructive oxidation of fibers and composites occurs at 1538°C
  - 5% O2, excessive borosilicate glass formation, SiC fluxing, and glass bubble formation
  - 0.1% O2, active oxidation of SiC to form SiO2(g) observed

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Fiber Oxidation
- Rapid transient weight gain followed by slow oxidation rate
- Oxidation weight change for Sylramic iBN fibers, 5% O2/Ar, 100h

Microstructure of oxidized fibers
- Plan view and fracture sections, 5% O2/Ar, 100 hr

TOF-SIMS and XPS analysis of oxide scale
Sylramic iBN fibers
- No obvious oxidation after 10 hr exposure at 816°C
- Thick oxide scales observed after oxidation at short times consistent with rapid transient weight change

Mechanism of oxidation of Sylramic iBN fibers
- Oxygen reacts with BN forming SiO(g)
- Borosilicate forms leading to rapid oxidation kinetics
- Boron volatilized from oxide surface
- BN is completely consumed by oxidation, Boron in glass is completely volatilized. Oxidation kinetics slow to those for pure SiC

Coupon Oxidation
- Weight change for SiC/BN/SiC coupons (bottom edge of SiC seal coat ground off) is minimal under most conditions
- Coupons sectioned and distance of oxygen ingress, loss of BN from open edge determined by microscopy

Oxidation of SiC/BN/SiC coupons
- Weight change for SiC/BN/SiC coupons (bottom edge of SiC seal coat ground off) is minimal under most conditions

Oxidation at 1538°C
- Loss of SiC seal coat observed due to active oxidation of SiC to form SiO2(g)

Oxidation of Sylramic iBN fibers, SiC/BN/SiC coupons
- Excessive formation and volatilization of borosilicate glass observed for both fibers and coupons

Active oxidation of Sylramic iBN fibers
- Rapid weight loss and degradation of fibers observed due to active oxidation of SiC to form SiO2(g)

Active oxidation of SiC/BN/SiC coupons
- Loss of SiC seal coat observed due to active oxidation of SiC to form SiO2(g)