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

$SiC + 3/2\ O_2(g) = SiO_2 + CO(g)$

$2\ BN + 3/2\ O_2(g) = B_2O_3 + N_2(g)$

$SiO_2 + B_2O_3 = \text{borosilicate glass}$

Oxide volatilization

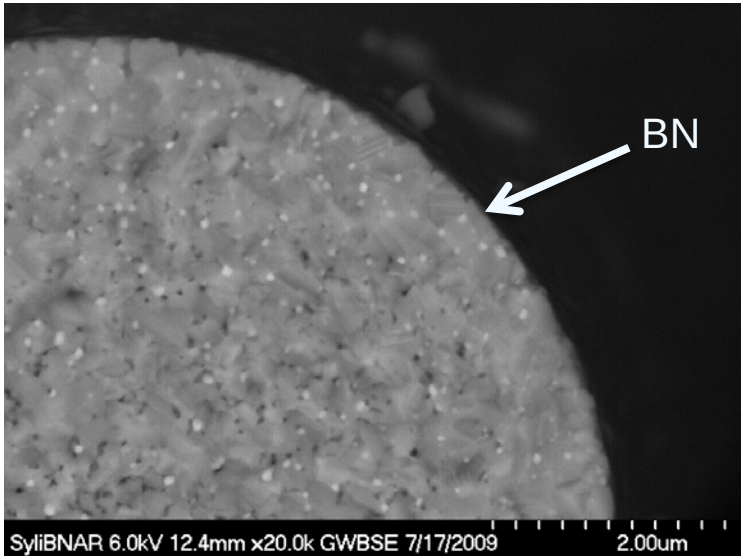
$B_2O_3 = B_2O_3(g)$

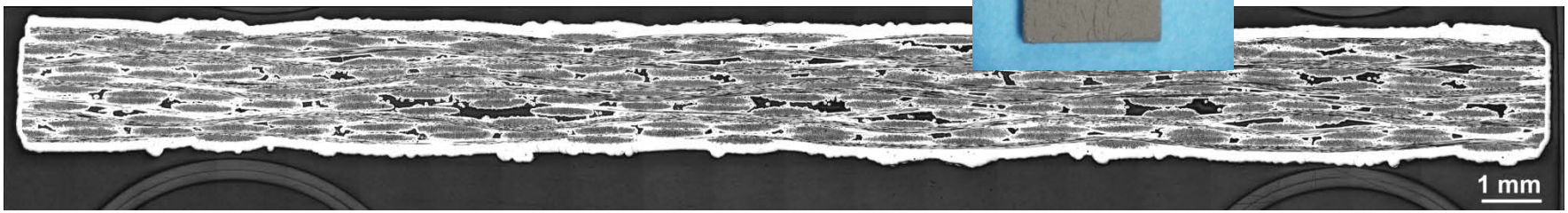
$B_2O_3 + ½\ O_2(g) = 2\ BO_2(g)$

$B_2O_3 + H_2O(g) = 2\ HBO_2(g)$

Materials

- Sylramic iBN fibers
  - Stoichiometric polycrystalline β-SiC
  - 3 wt% TiB_2, 1.3 wt % B_4C, 0.7 wt% BN*
  - ~10 μm 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

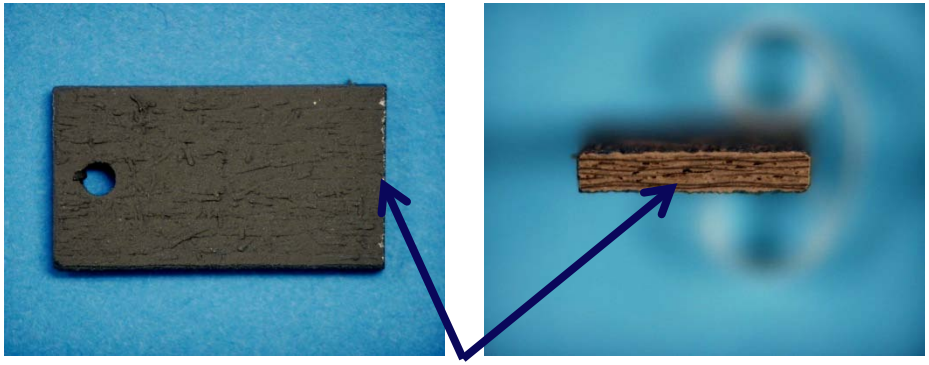




*Lipowitz et al, Cer Eng & Sci Proc. 18 [3] 147 (1997).

Experimental Procedure

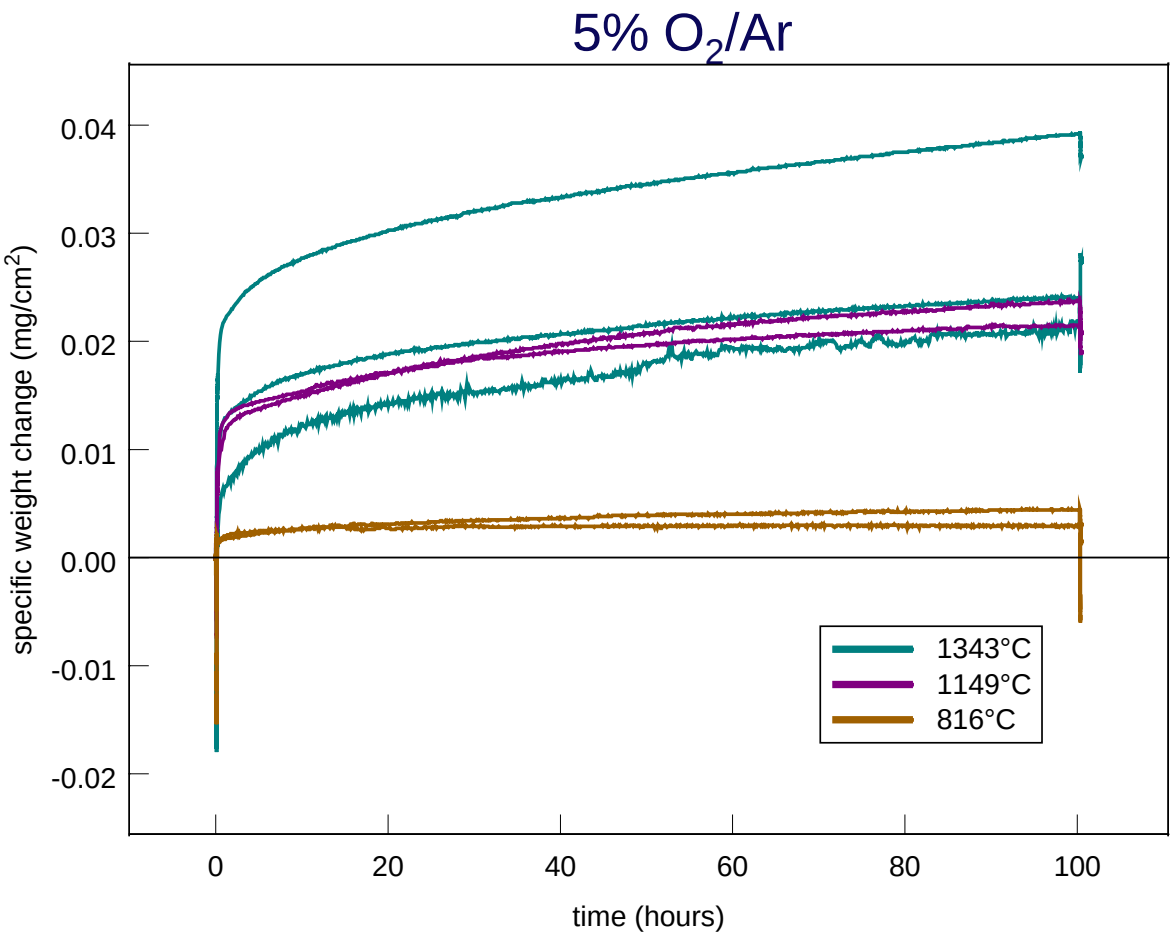
- ThermoGravimetric Analysis (TGA)
  - 5% O_2/Ar or 1000 ppm O_2/Ar, 100 sccm (0.4 cm/sec)
  - 816, 1149, 1343°C (1500, 2100, 2450°F)
  - 100h maximum time, shorter times to investigate kinetics
- Fibers twisted into “lanyards” that can be suspended directly from sapphire hangers to prevent reaction with containers
  - 8 cm length, 6 “lanyards” 800 fibers each, ~235 cm^2, 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 cm^2, 2 g
- SEM, EDS to characterize oxidation products



ground off edge

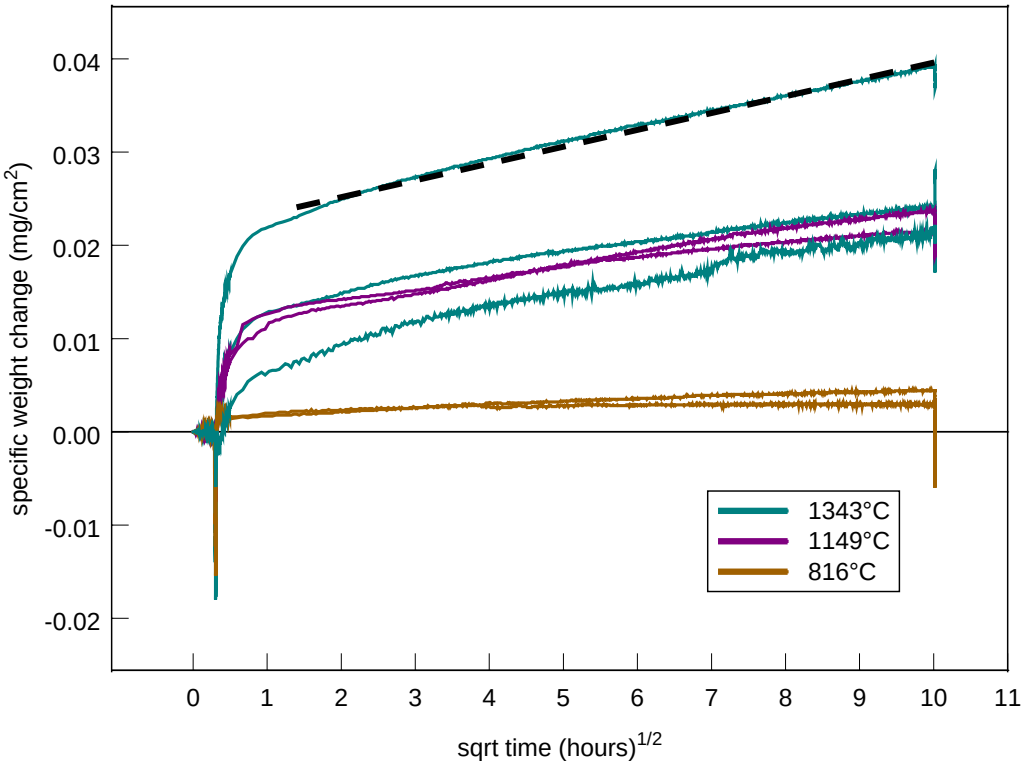
Fiber oxidation

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

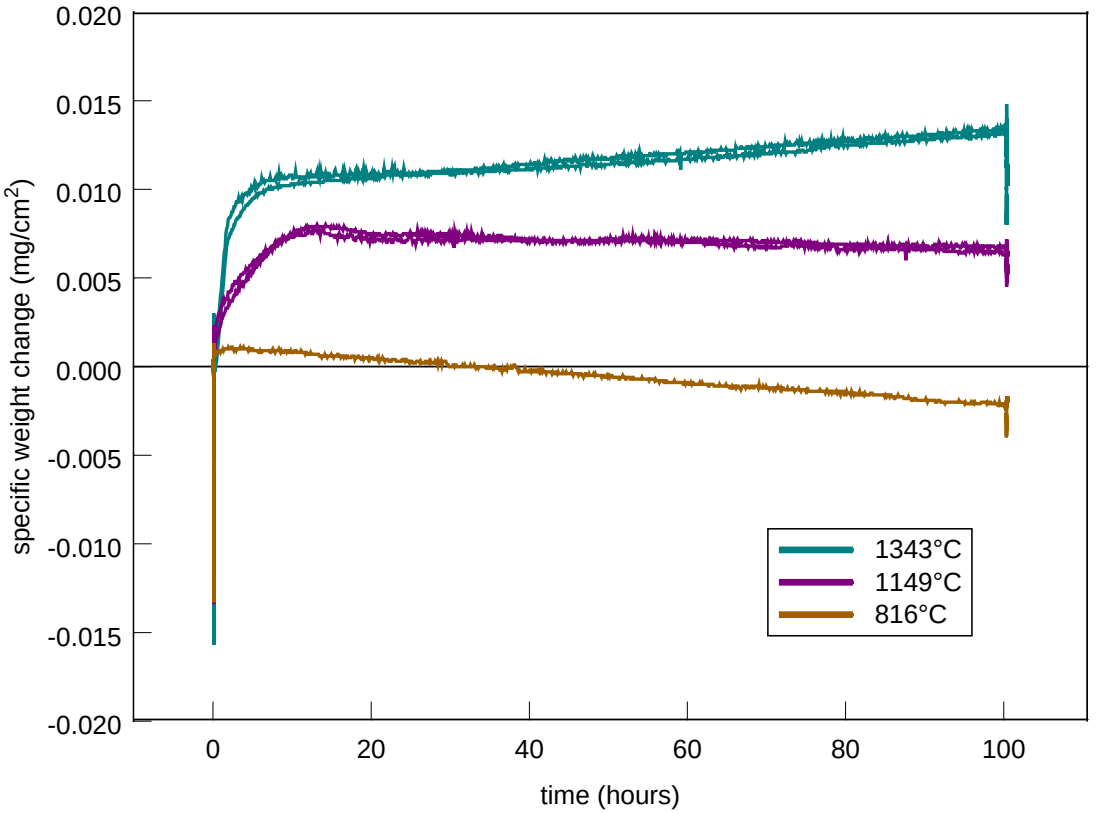
“Parabolic” oxidation kinetics observed after transient



- 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 $P(O_2)$

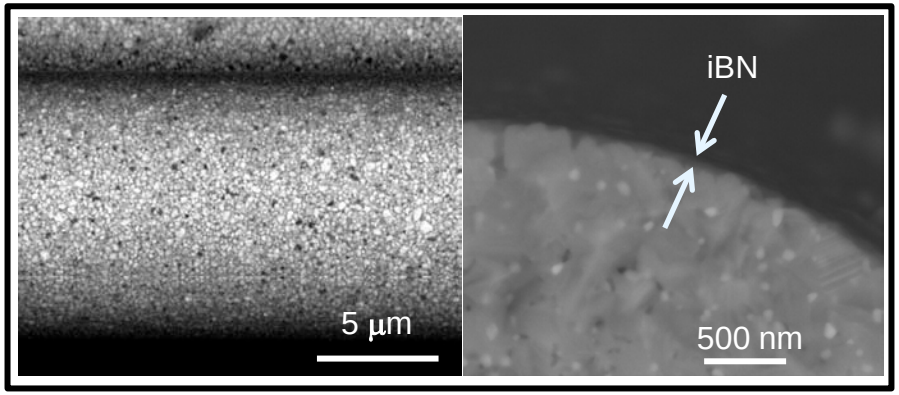
1000 ppm O_2



- 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% O_2/Ar, 100 hr



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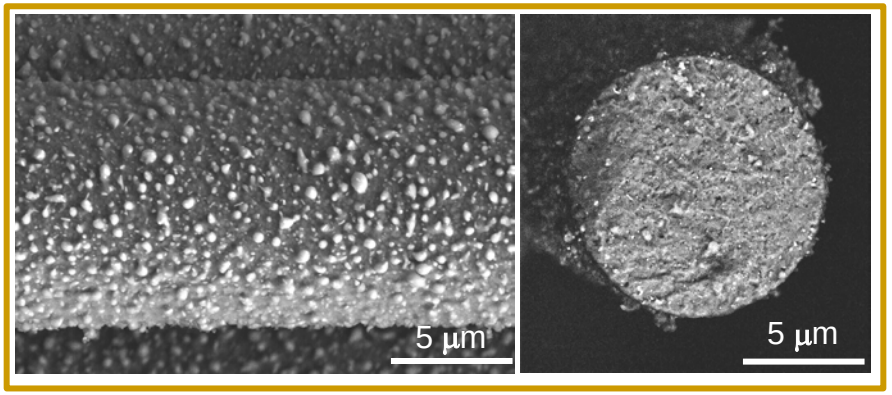
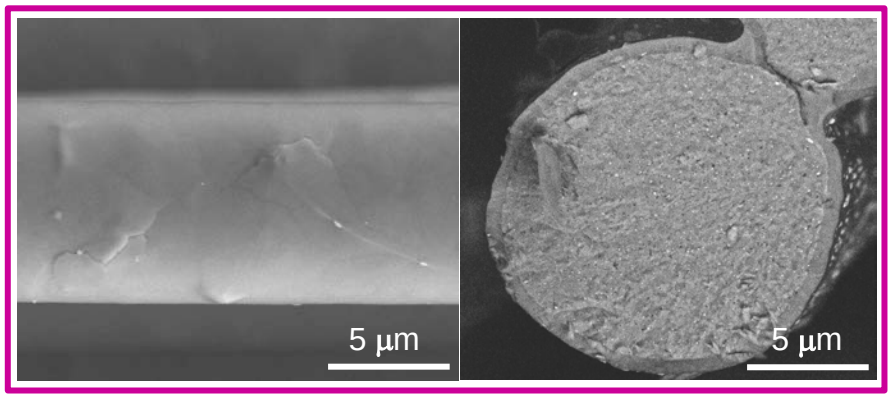
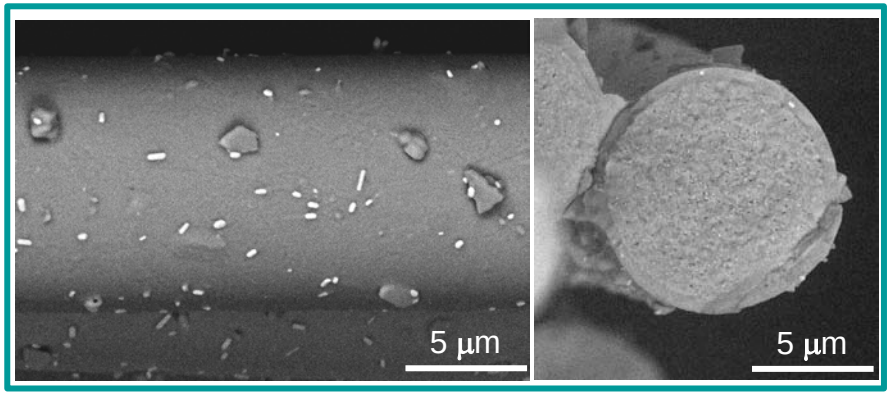


816°C



1149°C

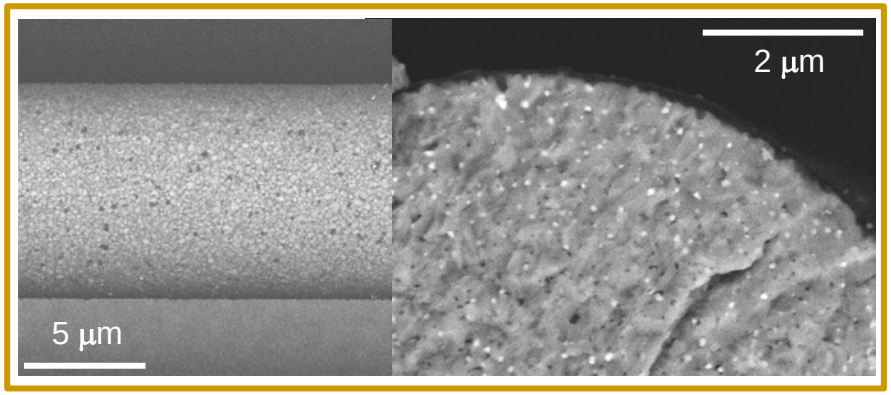


1343°C

Thickness of oxide scales consistent with weight change

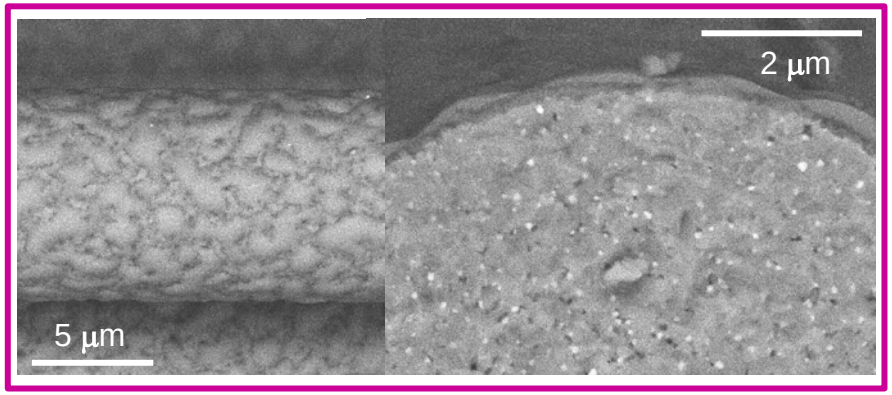
Microstructure of oxidized fibers

plan view and fracture sections, 5% O_2/Ar, 0.5 hr

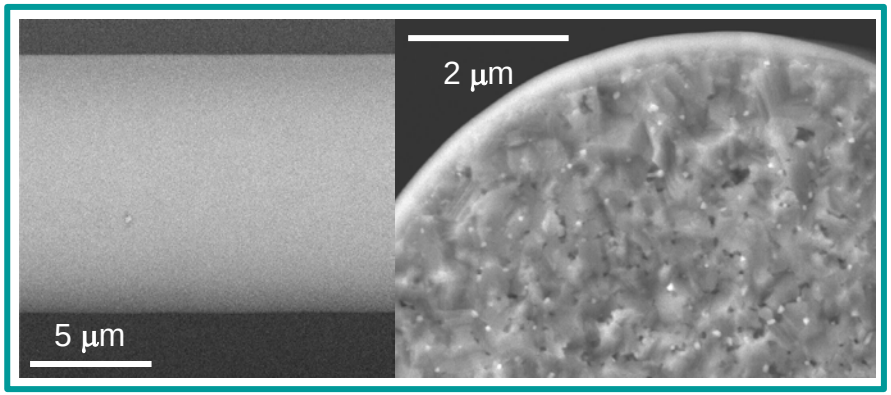


816°C

No obvious oxidation after 0.5 hr exposure at 816°C



1149°C

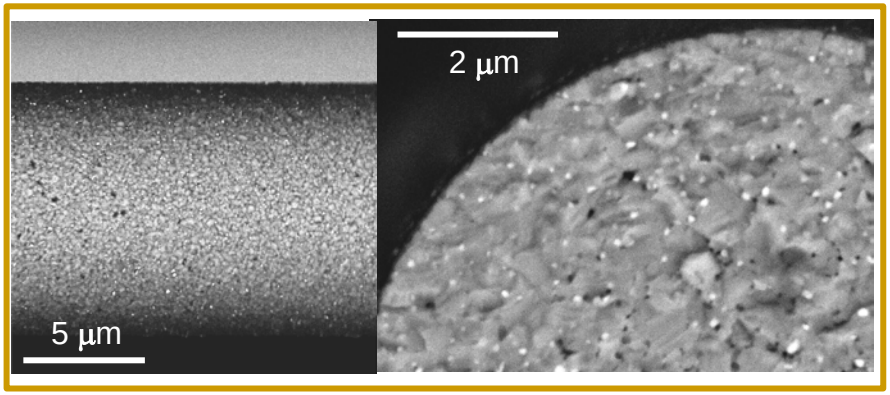


1343°C

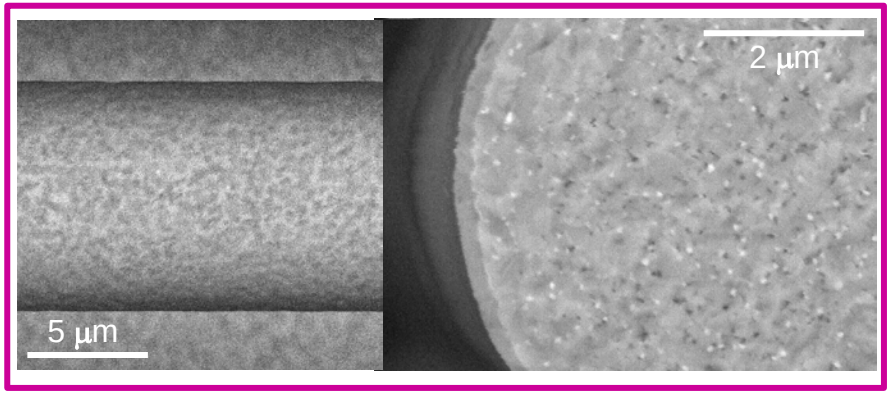
Thick oxide scales observed after oxidation at short times consistent with rapid transient weight change

Microstructure of oxidized fibers

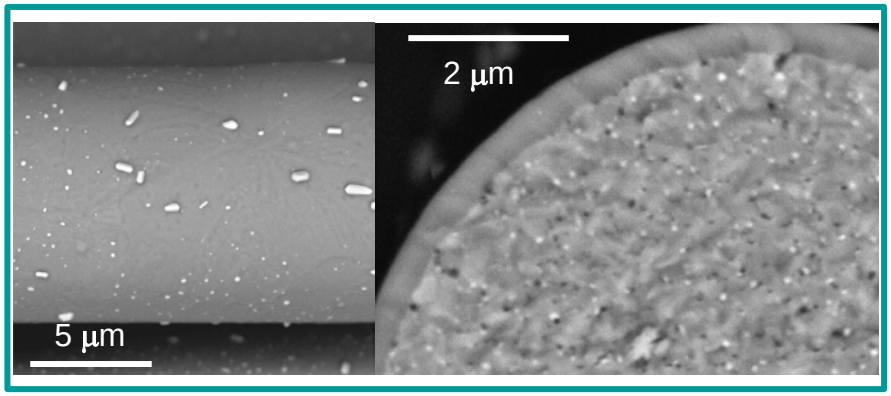
plan view and fracture sections, 1000 ppm O_2/Ar



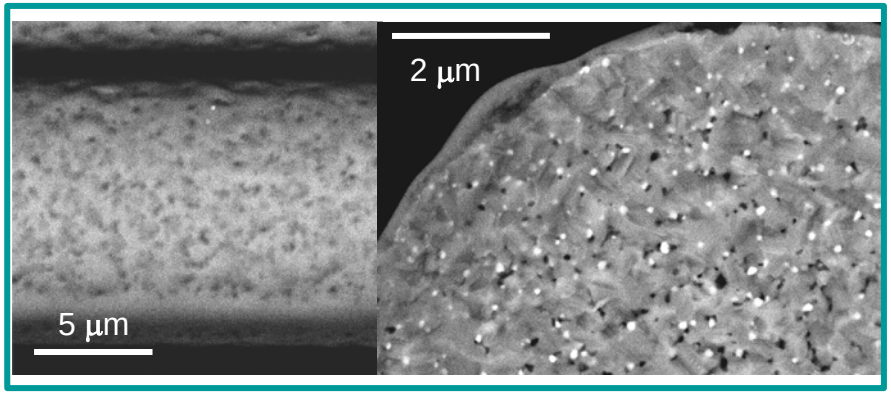
816°C, 100 hr



1149°C, 100 hr



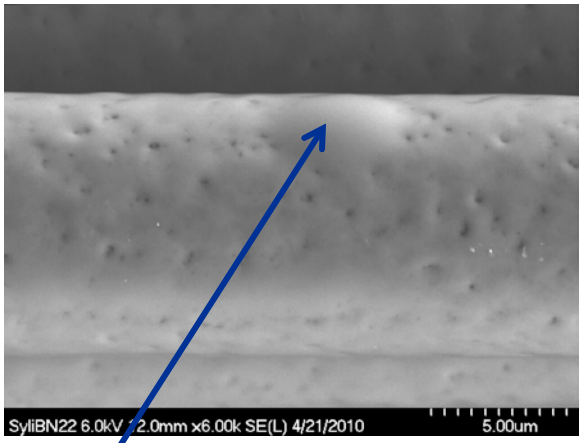
1343°C, 100 hr

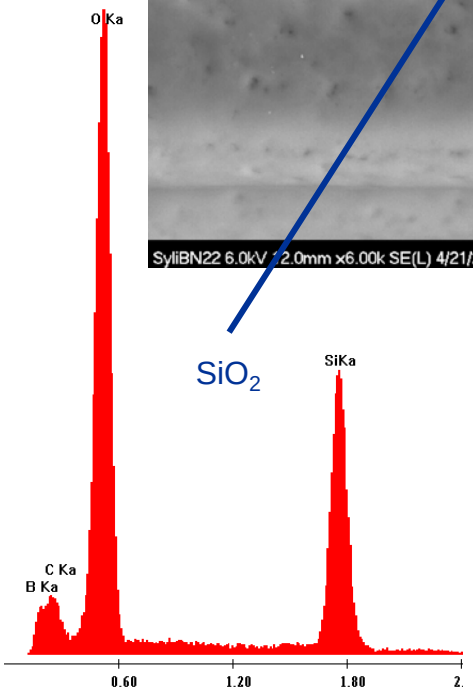


1343°C, 1 hr

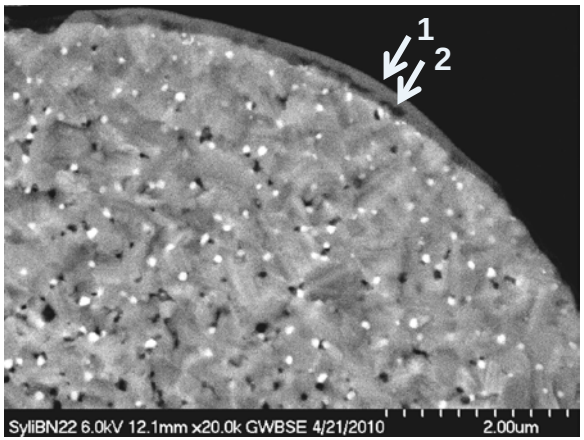
Oxide formation observed at 1149 and 1343°C
even at this low oxygen partial pressure

Chemical composition of oxide scales: SiO_2

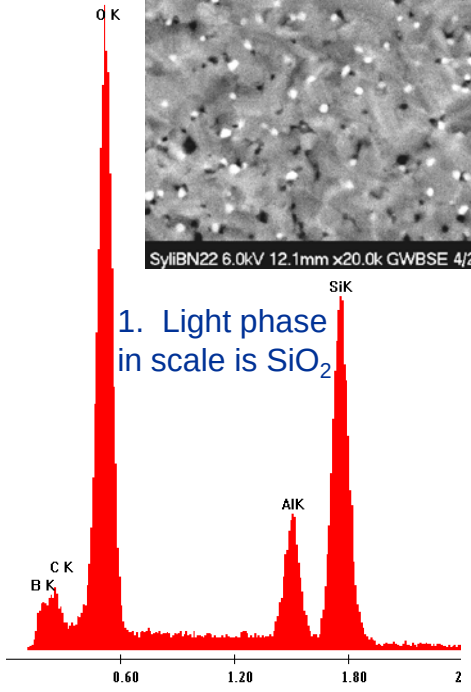


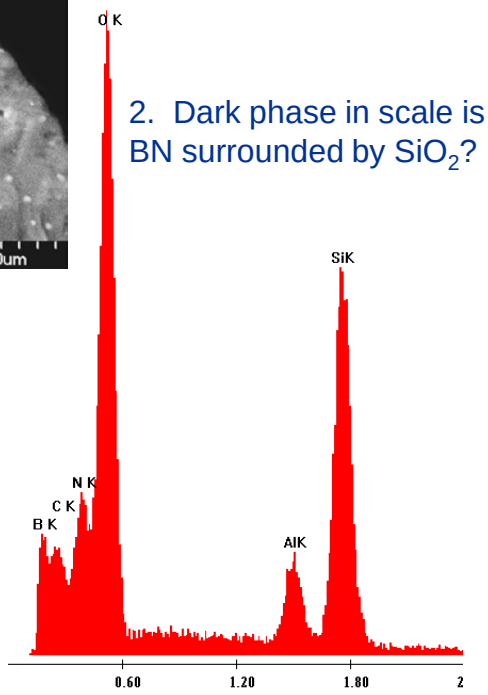


SiO_2



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

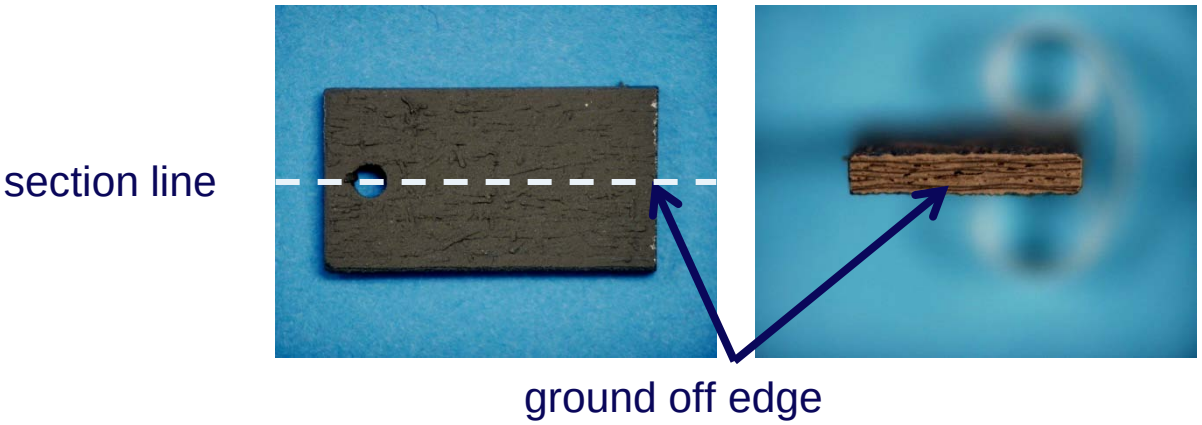
- Oxidation of iBN fibers occurs for all conditions studied except for 816°C in 1000 ppm O_2
- Rapid transient oxidation of BN results in rapid growth of silica layer
- Borosilicate glass is not observed
- B-doping of silica scale proposed to explain initial rapid oxidation rate of fibers
- Rapid initial 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

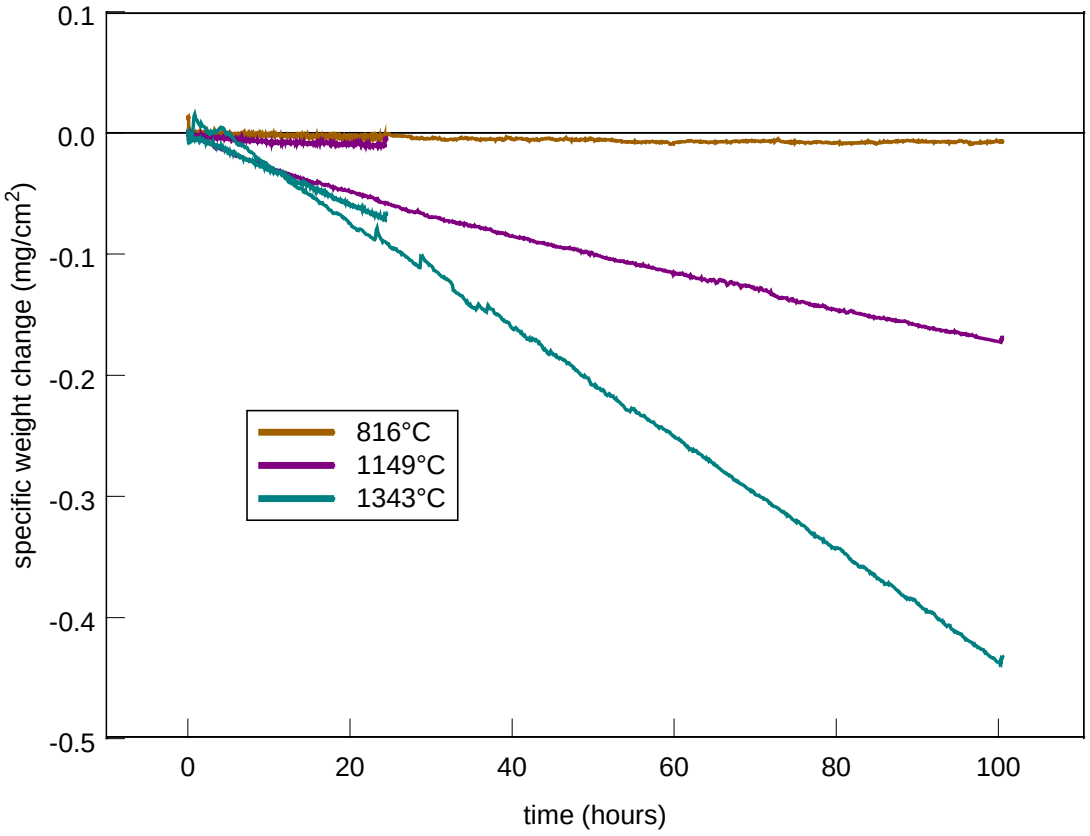
Weight change for SiC/BN/SiC coupons (bottom edge SiC seal coat ground off) in 5% O_2/Ar environment is minimal at all temperatures for 24 and 100 hr exposures

- $\Delta m < 0.4$ mg
- Δm 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_2/Ar environment at all temperatures studied. BN loss without SiO_2 formation? Need SEM/EDS characterization.

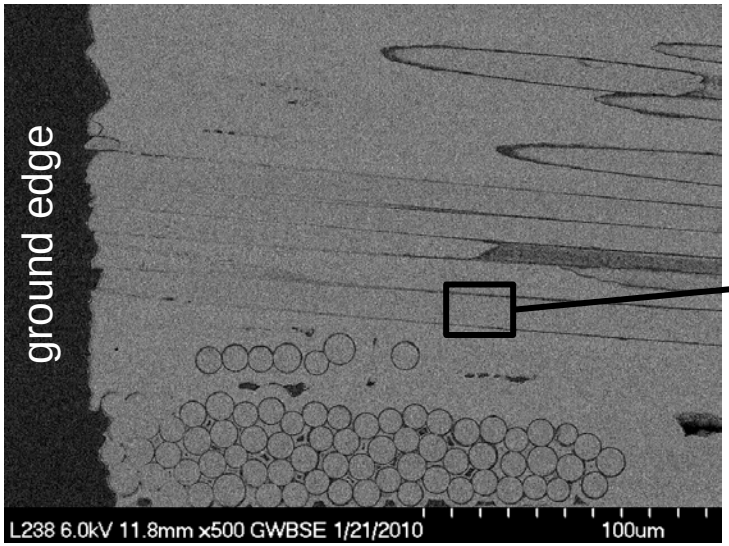


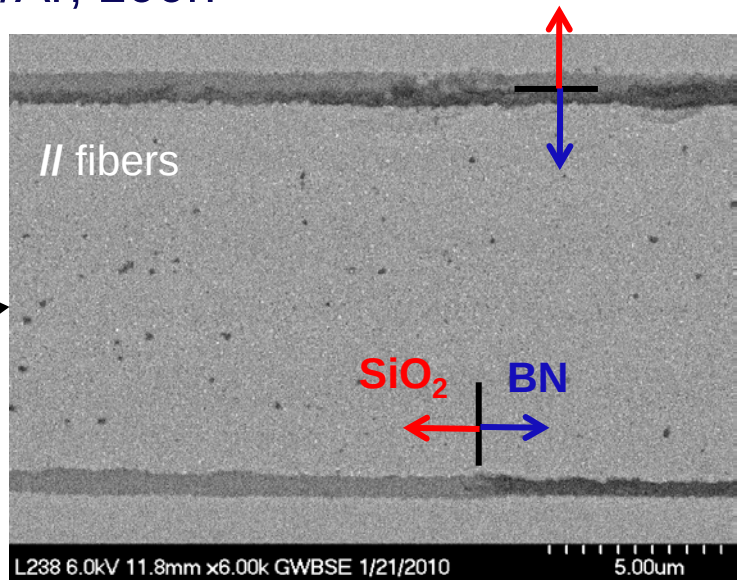
Microscopy of SiC/BN/SiC composites

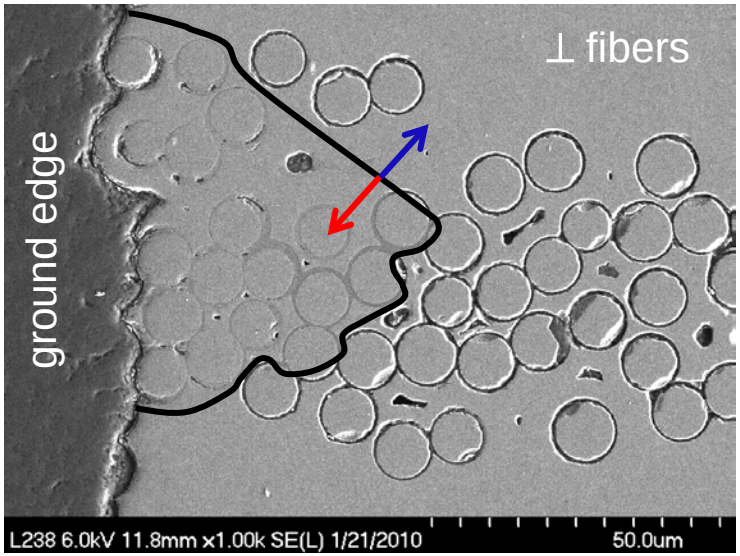
- All samples polished with non-aqueous procedures to preserve any B_2O_3 in scale – B_2O_3 sensitive to moisture
- BN interphase polishes more easily than SiC
  - Interphase recessed relative to surrounding SiC and SiO_2
  - BN EDS signal obtained where shadowing of surrounding fibers/matrix is minimal
- Interaction volume of 6kV electron beam in SiC/BN/SiC prevents EDS sampling of BN interphase alone
  - BN: ~1 μm interaction volume, interphase width is ~0.3 μm
  - SiC & SiO_2: ~0.5 μm 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% O_2/Ar, 100h



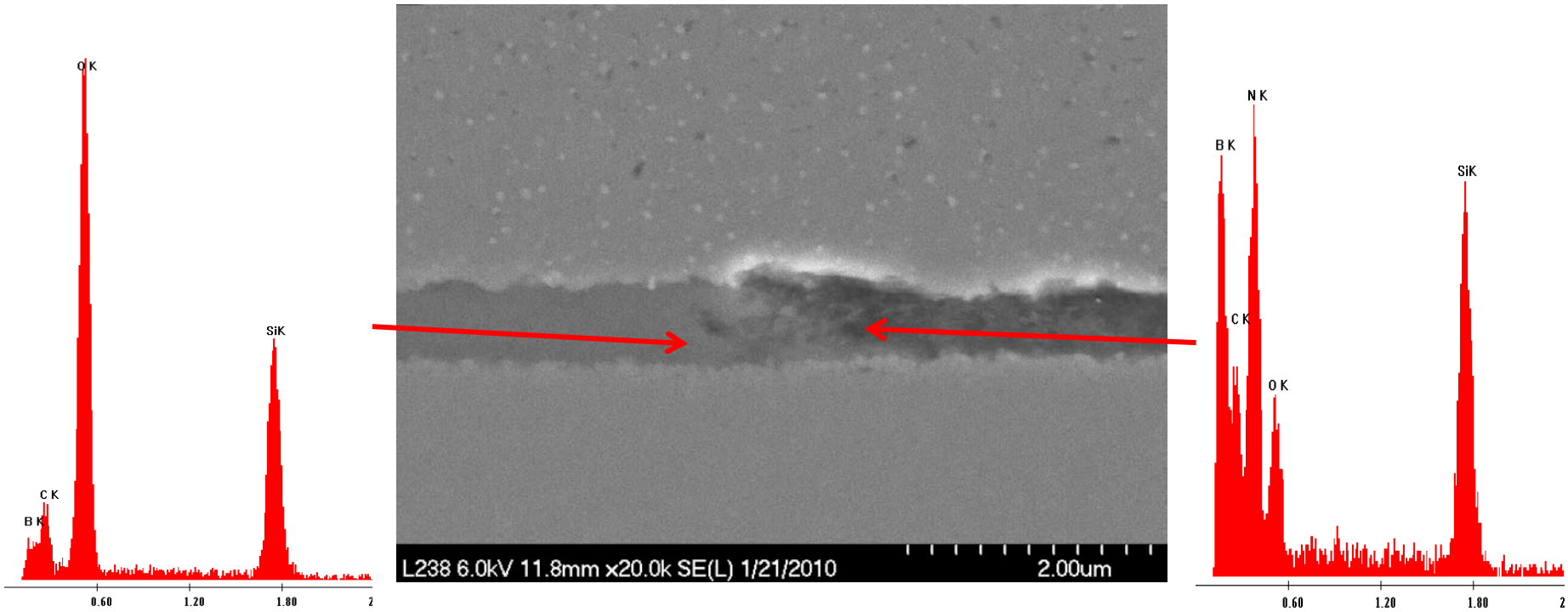




Oxygen ingress into ground edge of composite coupon can be measured for both fibers perpendicular and parallel to the plane of polishing

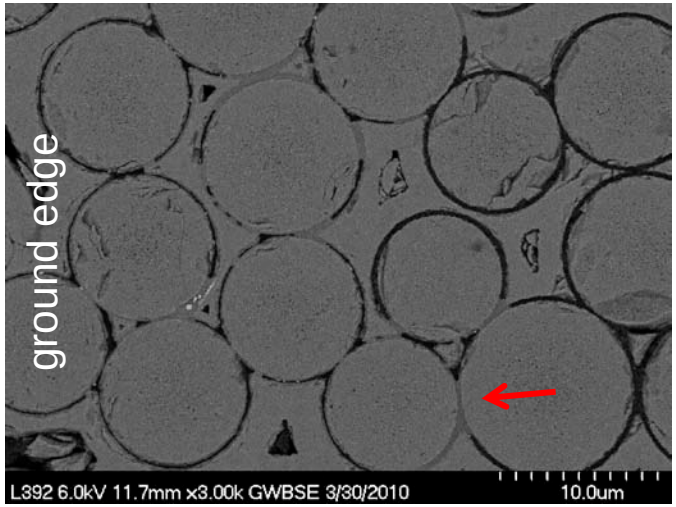
Microstructure/Composition of Oxidized Coupons

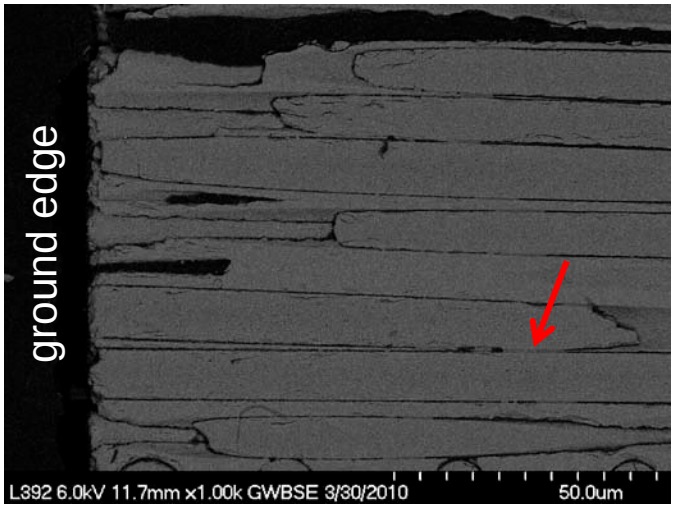
1343°C, 5% O_2/Ar, 100h



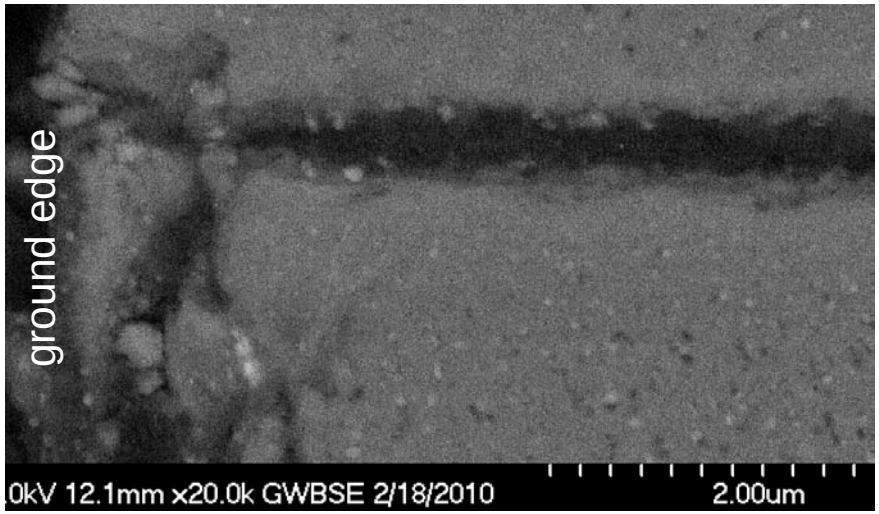
Interface between SiO_2 and BN observed. Nitrogen is present with boron. No B-rich borosilicate glass.

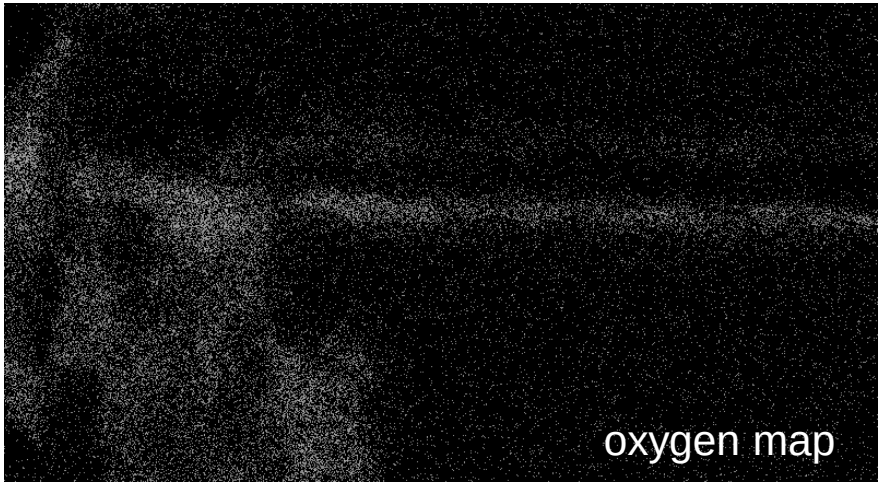
Microstructure of Oxidized Coupons





1149°C, 100h,1000 ppm O_2: intermittent SiO_2 formation



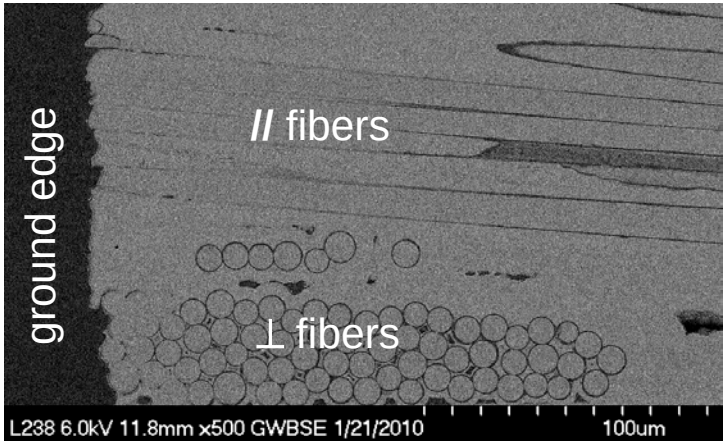


816°C, 5% O_2: minimal SiO_2 plugging at ground edge, but SiO_2 forms on SiC fibers next to BN

Summary of oxygen ingress/loss of BN for SiC/BN/SiC composites

Temp., °C	orientation	5% O_2, 100 h	5% O_2, 24h	1000 ppm O_2, 100 h
1343	// fibers	119±24 μm (n=13)	61±32 μm (n=22)	15±8 μm (n=16)
	⊥ fibers	3 fiber diameters	2 fiber diameters	1 to 2 fiber diameters
1149	// fibers	2.8±3.1 μm (n=16)	3.8±2.1 μm (n=35)	Intermittent SiO_2
	⊥ fibers	<1 fiber diameter	<1 fiber diameter	Intermittent SiO_2
816	// fibers	0.3 μm (n=2), 5 μm (n=1)	2 μm (n=3)	14 μm (n=2)
	⊥ fibers	<1 fiber diameter	<1 fiber diameter	1 fiber diameter

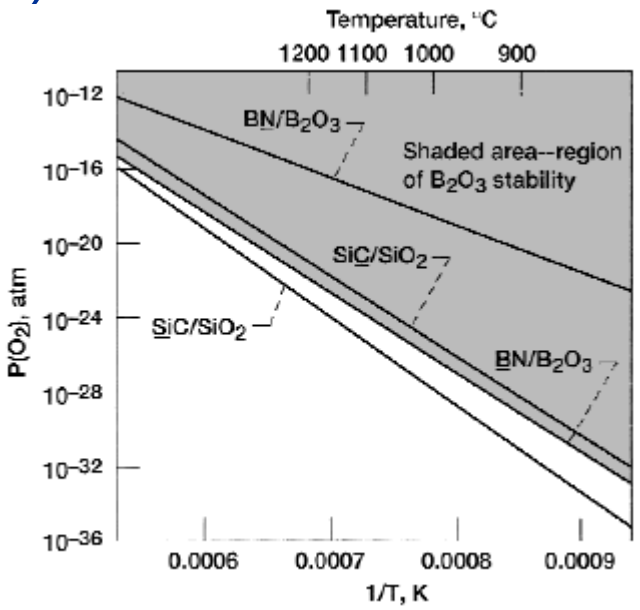
- Red = depth of SiO_2 formed, BN consumed, measured from ground edge
- Blue = depth of BN consumed without SiO_2 sealing edge, measured from ground edge



Stability of BN adjacent to SiO_2

- BN stability adjacent to SiO_2 has been observed previously
  - Fibrous Monoliths SiC/BN system, Baskaran & Halloran, JACerS 77 [5] 1249 (1994).
  - Oxidation of BN-Coated SiC Fibers in CMCs, Sheldon et al, JACerS 79 [2] 539 (1996).
  - High Temp Oxidation of BN Layers in Composites, Jacobson et al, JACerS 82 [6] 1473 (1999).

- Given limited amounts of oxygen, SiC will oxidize preferentially over BN since SiO_2 is thermodynamically stable relative to B_2O_3

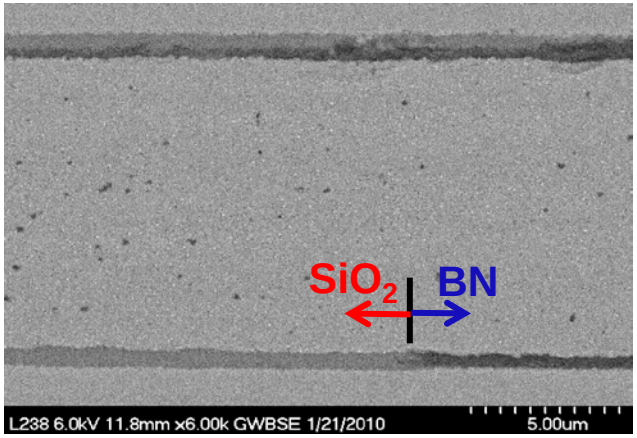


Summary of SiC/BN/SiC oxidation

- SiO_2 formation is observed at all temperatures in 5% O_2 environment. Sealing of exposed BN interphase channels into composite occurs at 1343 and 1149°C.
- At 1000 ppm O_2 condition, some SiO_2 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_2 indicates SiO_2 sealing of composite, inconsistent with largest observed weight loss.
- Weight loss of composites at 1343°C, 1149 °C in 1000 ppm O_2 is inconsistent with observed weight gain of fibers under same conditions.
- What occurs at SiO_2/BN interface? How is oxygen transported down interphase region to SiO_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

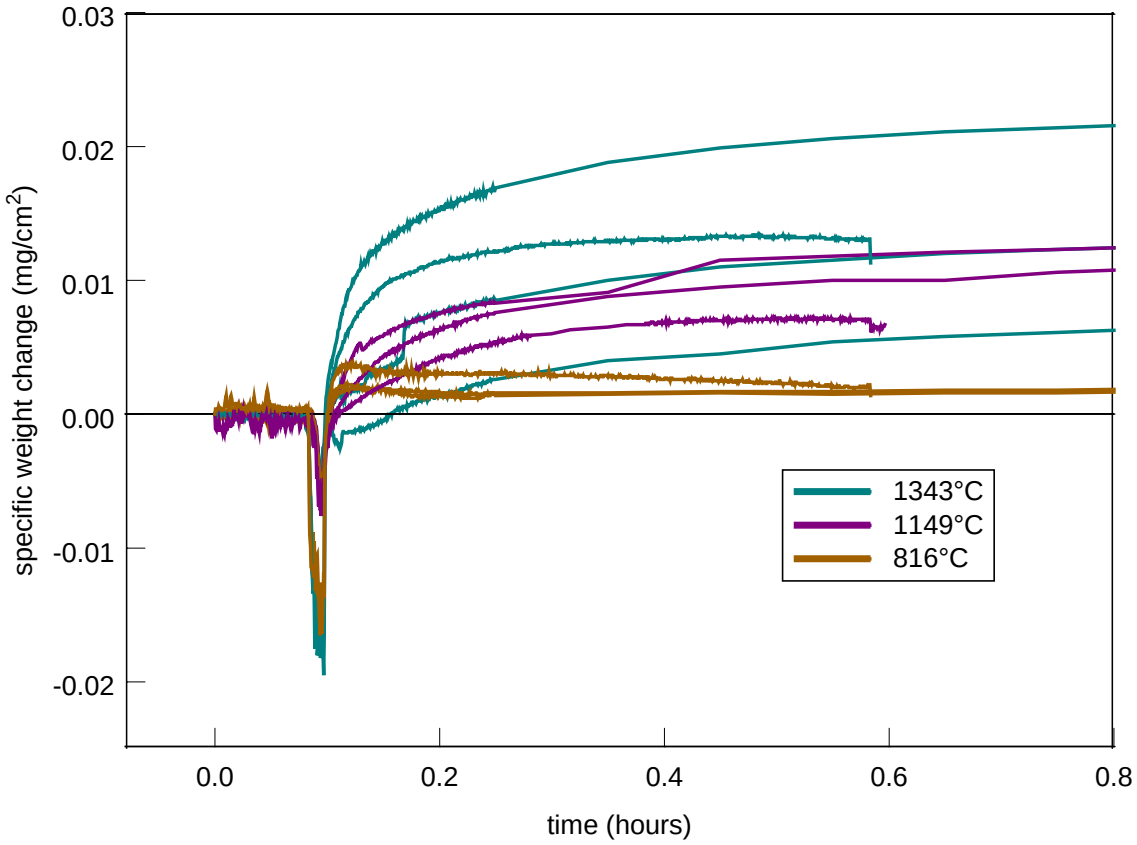
- Continue to characterize the oxidation of both Sylramic iBN fibers and SiC/iBN/SiC composites, more repeats, higher temperatures (1538°C, (2800°F)), intermediate oxygen partial pressure (0.5% O_2).
- Characterize oxidation of woven Sylramic iBN fabric with CVI Si-doped BN coating (intermediate processing step)
- Better characterize B-content in thermally grown SiO_2. SIMS?
- Role of atomic oxygen in hypersonic environment on SiC/BN/SiC oxidation should be considered, arc-jet exposures?

Acknowledgment

This work was funded by the NASA Aeronautics Research Mission Directorate, Fundamental Aeronautics Program on Hypersonics

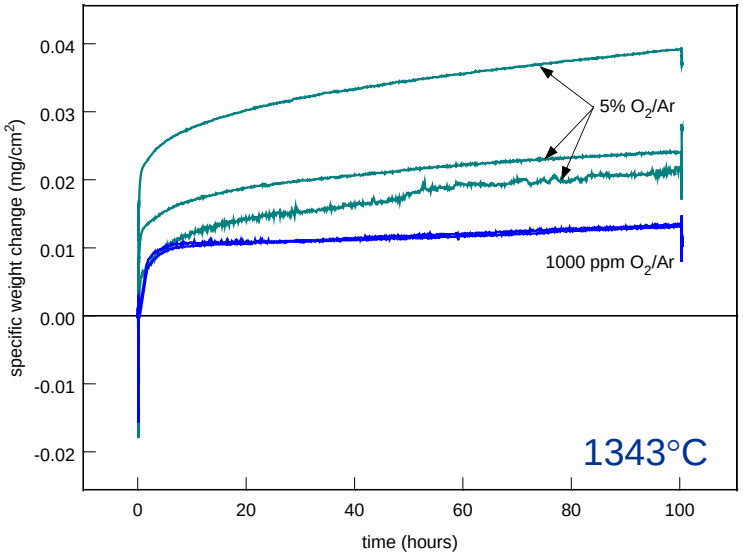
Backup charts

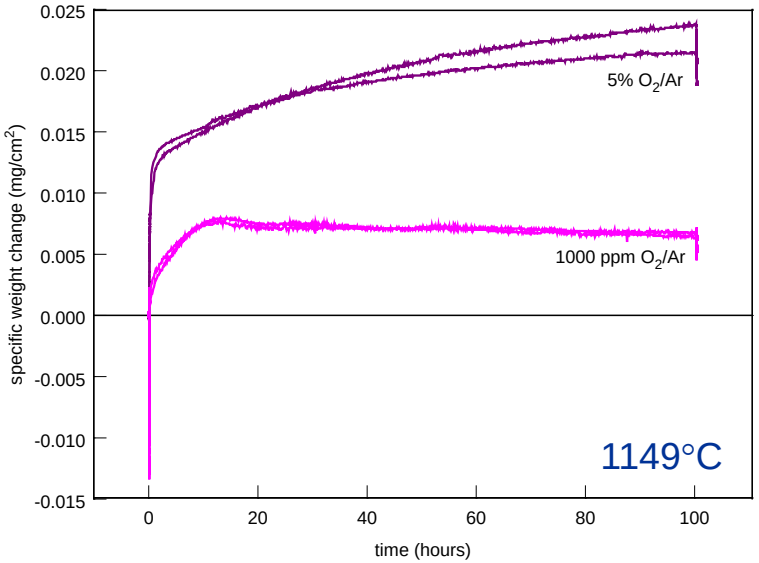
Initial transient weight gain attributed to oxidation of BN, doping of SiO_2 scale



- 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.