OXIDATION OF C/SiC COMPOSITES AT REDUCED OXYGEN PARTIAL PRESSURES

Elizabeth J. Opila*, Jessica Serra^
NASA Glenn Research Center, Cleveland, OH 44135
^The Pennsylvania State University, University Park, PA, 16802

Carbon-fiber reinforced SiC (C/SiC) composites are proposed for leading edge applications of hypersonic vehicles due to the superior strength of carbon fibers at high temperatures (>1500°C). However, the vulnerability of the carbon fibers in C/SiC to oxidation over a wide range of temperatures remains a problem. Previous oxidation studies of C/SiC have mainly been conducted in air or oxygen[1-3], so that the oxidation behavior of C/SiC at reduced oxygen partial pressures of the hypersonic flight regime are less well understood. In this study, both carbon fibers and C/SiC composites were oxidized over a wide range of temperatures and oxygen partial pressures to facilitate the understanding and modeling of C/SiC oxidation kinetics for hypersonic flight conditions.

T-300 carbon fiber and C/SiC coupons were oxidized at temperatures of 816°, 1149°, 1343°, and 1538°C (1500°, 2100°, 2450°, and 2800°F) and in gas mixtures containing 50% O_2/Ar, 5% O_2/Ar, 0.5% O_2/Ar, and 0.1% O_2/Ar at one atmosphere total pressure. The T-300 fibers were held in slotted alumina crucibles for the oxidation testing. Oxidation kinetics were monitored using thermogravimetric analysis. Post test characterization of selected coupons included optical microscopy, x-ray diffraction, scanning electron microscopy, and energy dispersive spectroscopy.

Results of the T-300 carbon fiber oxidation are shown in Figure 1. The oxidation rates reported are instantaneous rates when 50% of the fibers are consumed. It can be seen from Figure 1 that the oxidation kinetics are only weakly dependent on temperature, but strongly dependent on oxygen partial pressure. The weak temperature dependence and oxygen pressure dependence shown in Figure 2 are both consistent with oxidation limited by gaseous transport.

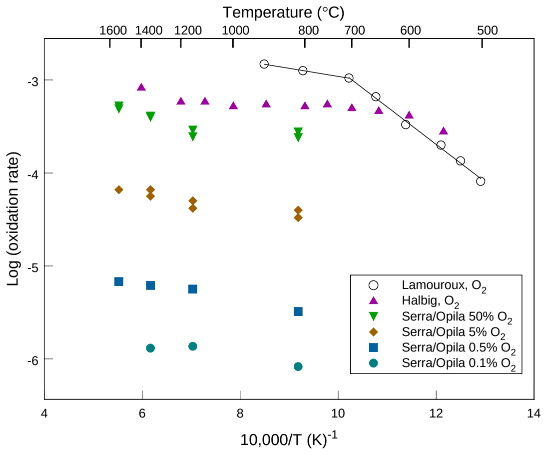


Figure 1. Oxidation rates of T-300 carbon fibers as a function of temperature and oxygen partial pressure.

The results in Figure 1 include oxidation rates for T-300 fibers in 100% oxygen that are found in the literature[1,4]. The results of Halbig et al.[4] were obtained in the same laboratory and show consistent pressure dependence with the new results as shown in Figure 2.

Kinetic results for C/SiC coupon oxidation are shown for all temperatures in 50% O_2/Ar in Figure 3. Weight loss is typically observed indicating that oxidation of carbon fibers rather than oxidation of SiC dominates the kinetics even at the highest oxygen partial pressure studied. Weight loss is largest at 816°C where cracks in the SiC coating and matrix are open allowing ingress of oxygen and complete consumption of the C fibers. As the temperature is increased thermal expansion and oxidation of the SiC both contribute to crack closure. The variation in the observed weight change is explained by variation in the number and size of cracks in the SiC seal coat as well as varying extents of crack closure. At lower oxygen partial pressures and higher temperatures crack closure is attributed exclusively to thermal expansion rather than formation of silica in the cracks.

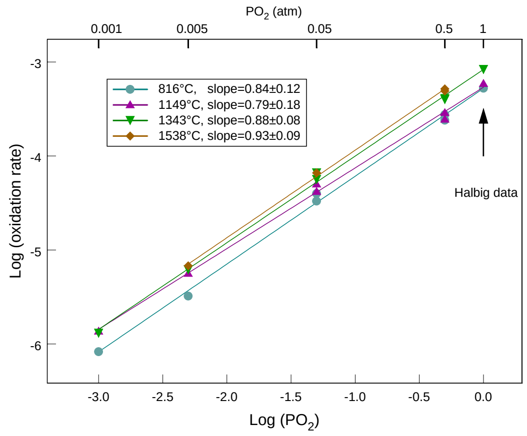


Figure 2. Oxygen partial pressure dependence of T-300 fiber oxidation rates obtained at all temperatures.

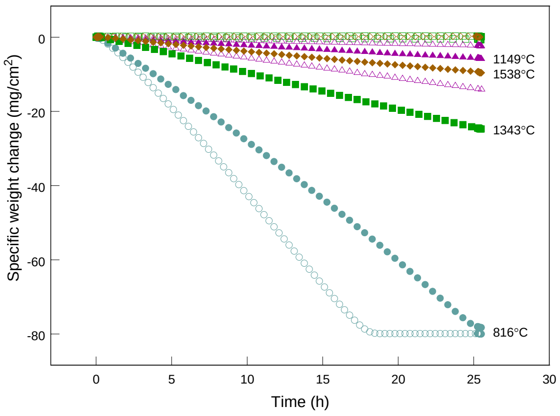


Figure 3. Oxidation weight loss of C/SiC composites in 0.4 cm/sec flowing 50% O_2/Ar as a function of temperature.

At the highest temperature (1538°C) and lowest oxygen partial pressure (0.1% O_2/Ar) the C/SiC coupon was rapidly consumed due to active oxidation of the SiC and oxidation of the C fibers as they were exposed.

Acknowledgment

This work was funded by the NASA Aeronautics Research Mission Directorate/Fundamental Aeronautics Program in Hypersonics.

References

[1] F. Lamouroux, X. Bourrat, and R. Naslain, “Structure/Oxidation Behavior Relationship in the Carbonaceous Constituents of 2D-C/PyC/SiC Composites,” Carbon 31 [8] 1273-1288 (1993).

[2] F. Lamouroux, G. Camus, J. Thebault, “Kinetics and Mechanism of 2D Woven C/SiC Composites: I, Experimental Approach,” J. Am. Ceram. Soc. 77 [8]2049-57 (1994).

[3] F. Lamouroux, R. Naslain, J.-M. Jouin, “Kinetics and Mechanism of 2D Woven C/SiC Composites: II, Theoretical Approach,” J. Am. Ceram. Soc. 77 [8]2058-68 (1994).

[4] M.C. Halbig, D.N. Brewer, and A.J. Eckel, “Degradation of Continuous Fiber Ceramic Matrix Composites Under Constant Load Conditions,” NASA TM-2000-209681.

Oxidation of C/SiC Composites at Reduced Oxygen Partial Pressures

Elizabeth Opila
NASA Glenn Research Center
Cleveland, OH

Jessica Serra
The Pennsylvania State University
University Park, PA

216th Meeting of the Electrochemical Society Meeting
Vienna Austria
October 8, 2009

Introduction

- C/SiC is proposed for leading edges, hot structure control surfaces, and acreage thermal protection systems for hypersonic vehicles
- Re-entry and hypersonic cruise environments: high temperatures, low oxygen partial pressures

Introduction: C/SiC oxidation

- Oxidation of C/SiC and carbon fibers studied in air or oxygen
  - Ismail, Carbon 29 [6] 777-792 (1991).
  - Lamouroux et al., Carbon 31 [8] 1273-1288 (1993).
  - Lamouroux, et al., J. Am. Ceram. Soc. 77 [8] 2049-57 (1994).
  - Halbig et al., NASA TM-2000-209681.
- Bulk carbon oxidation studied at reduced oxygen partial pressures
  - Walker et al., Adv. Catal., Vol. XI, 133-221 (1959).
  - Gulbransen et al., J. Electrochem. Soc. 110 [6] 476-483 (1963).
- Three reactions to consider

$C + 1/2\ O_2(g) = CO(g)$

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

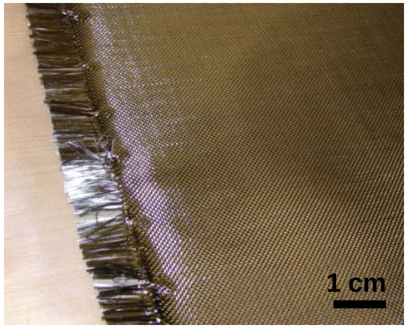
$SiC + O_2(g) = SiO(g) + CO(g)$ active oxidation

Objectives

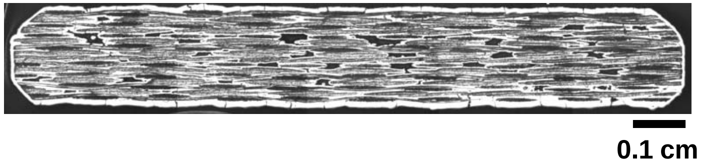
- Quantify the oxidation rates of the constituent carbon fibers and C/SiC composites at high temperatures and low oxygen partial pressures
- Understand the dominant oxidation mechanisms
- Provide input to a finite element model for predicting the life expectancy of C/SiC in hypersonic vehicle applications

Experimental materials

- T-300 carbon fibers
  - 1k tow
  - heat treated to 1538°C (2800°F)
  - 0.5 g batches of material
  - fibers bundled in slotted alumina crucible



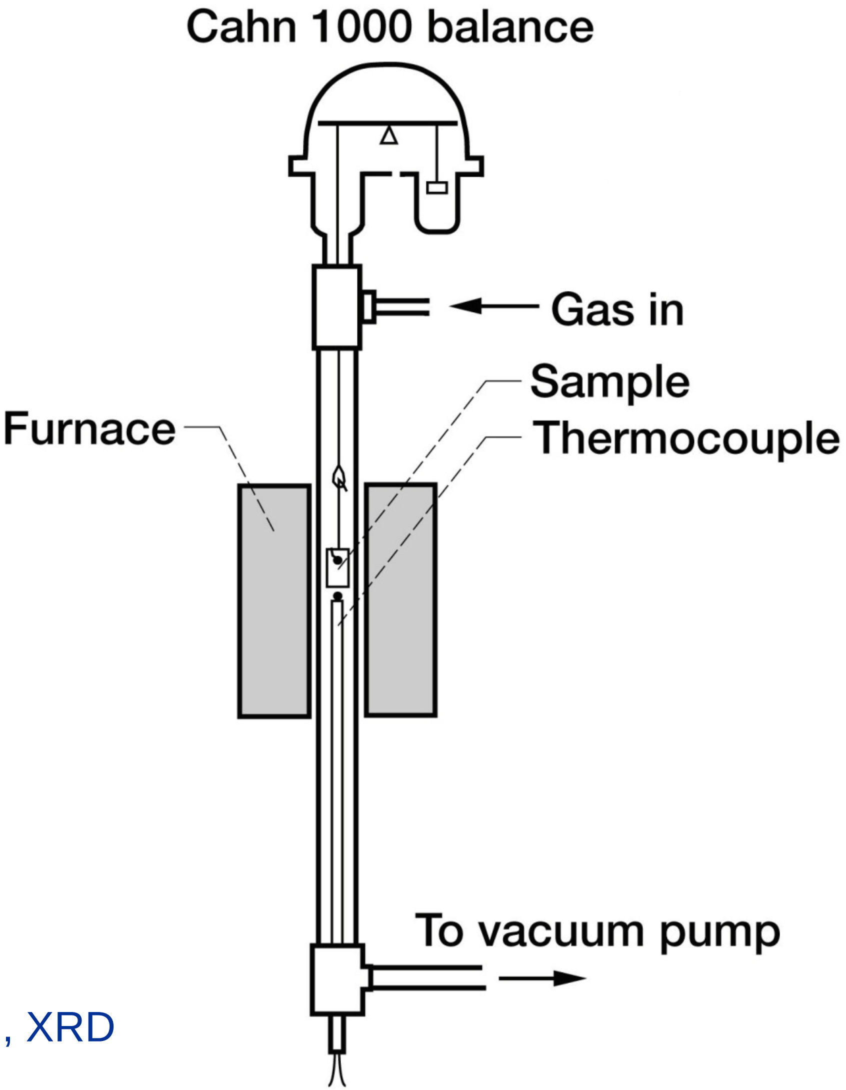
- C/SiC composite coupons
  - GE Power Systems
  - 1538°C heat treated T-300 fibers
  - CVI SiC matrix
  - 2.5 cm x 1.3 cm x 0.25 cm coupons
  - 0.25 cm dia hole
  - CVD SiC seal coat



Experimental technique

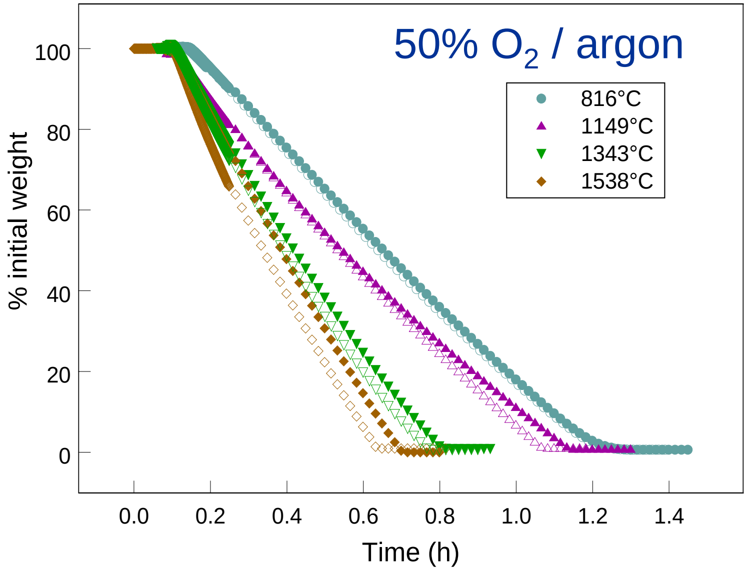
Thermogravimetric Analysis (TGA)

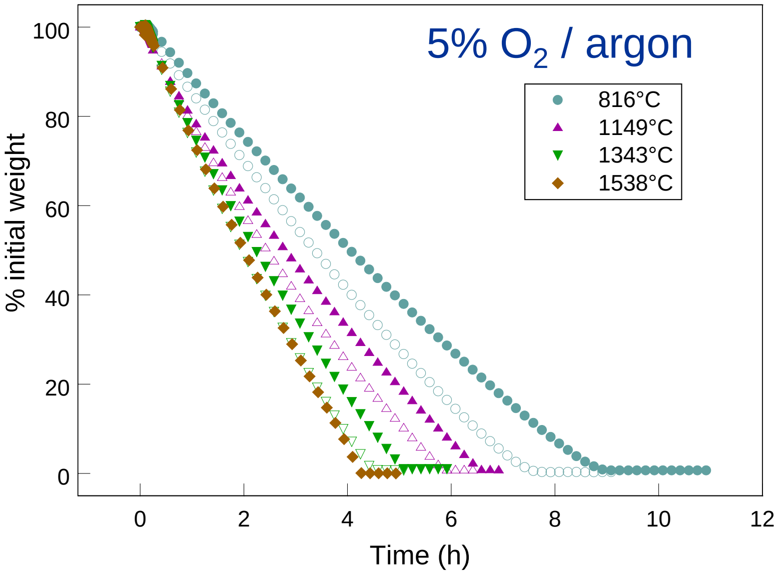
- Temperatures studied
  - 816°C (1500°F)
  - 1149°C (2100°F)
  - 1343°C (2450°F)
  - 1538°C (2800°F)
- Total pressure 1 atm
- Oxygen partial pressures
  - 50% O_2 / argon
  - 5% O_2 / argon
  - 0.5% O_2 / argon
  - 0.1% O_2 / argon
- Flow rate: 100 ccm, 0.4 cm/sec
- Exposure times
  - C fibers oxidized to completion
  - C/SiC coupons 25 or 100h
- Post-exposure microscopy, SEM/EDS, XRD



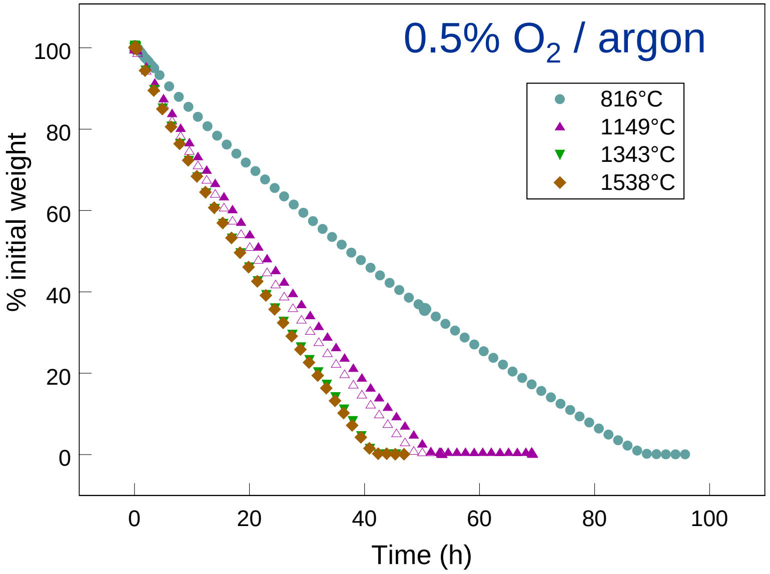
T-300 carbon fiber oxidation

T-300 fiber oxidation TGA results

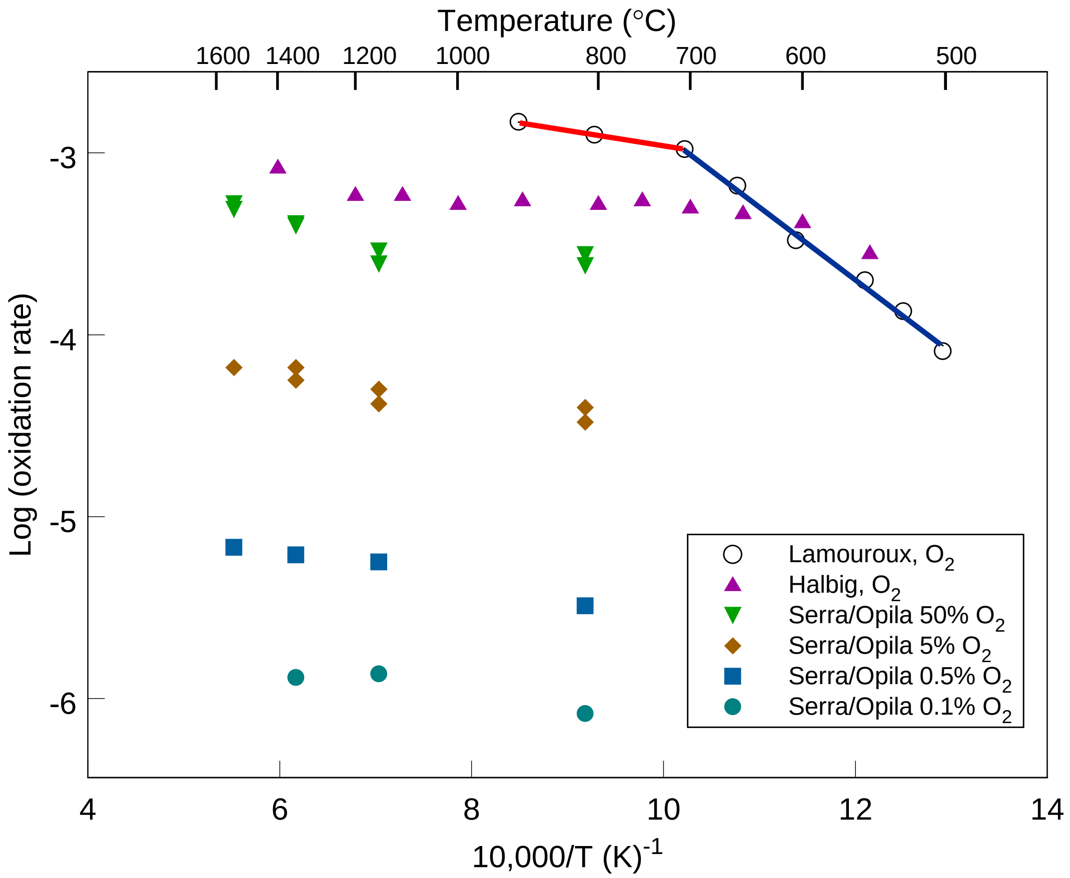


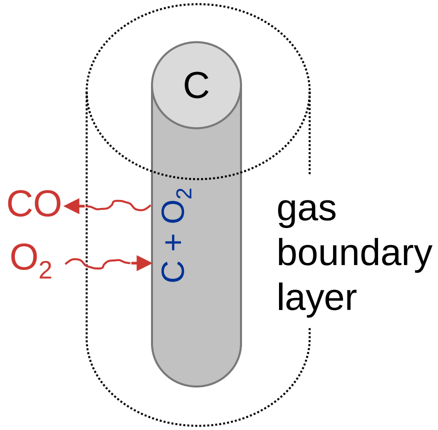


- Results fairly repeatable
- Reported rates - instantaneous rate at 50% consumed
- Oxidation rates vary by about a factor of two over temperature range of interest
- Oxidation rates vary by orders of magnitude over pressure range of interest



Temperature dependence for T-300 fiber oxidation

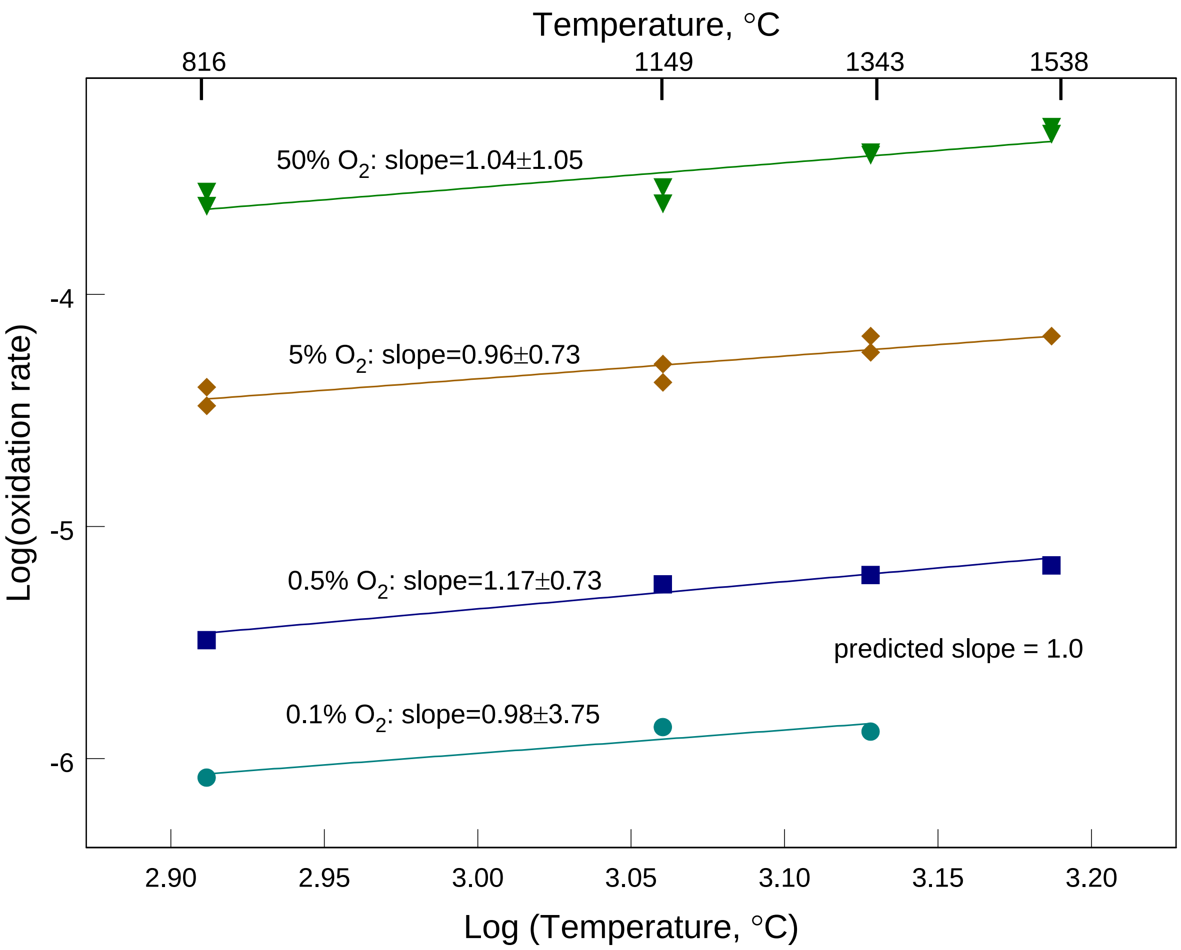




Low temperature (<700°C) surface reaction control

High temperature (>700°C): gas phase diffusion control

Temperature dependence for T-300 fiber oxidation



Gas boundary layer limited oxidation rate, k_{ox}

$$k_{ox} = \mathrm{Re}^{1/2} Sc^{1/3} \frac{D\rho_{ox}}{L}$$

$$Sc \propto D^{-1}$$

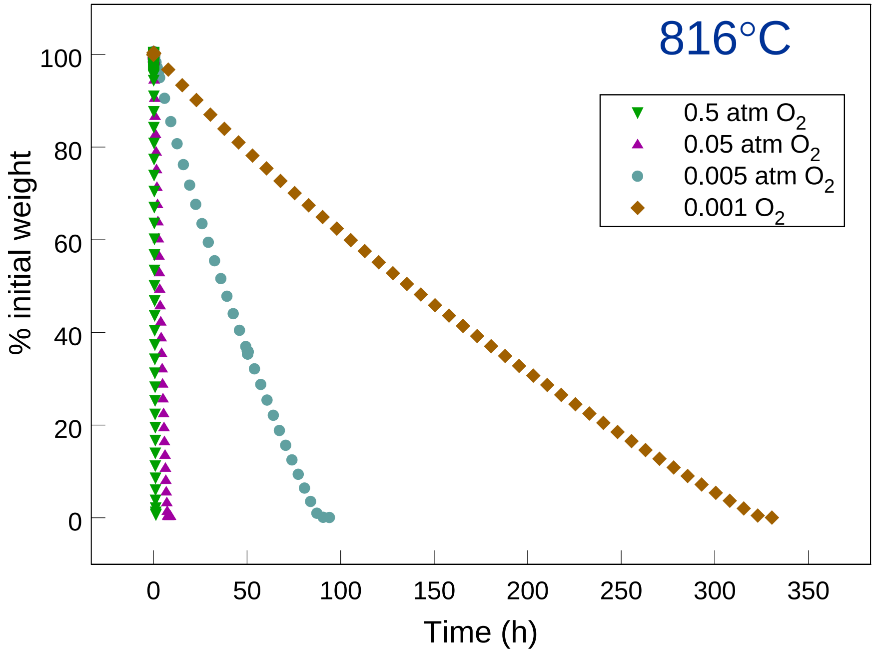
$$k_{ox} \propto D^{2/3}$$

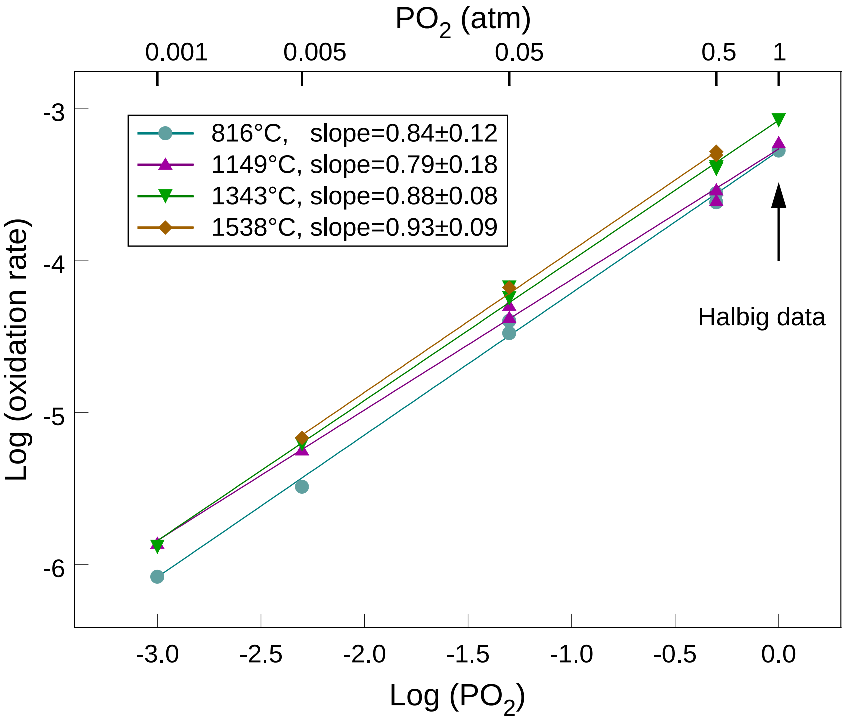
Kinetic theory of gases predicts $T^{3/2}$ dependence of gas phase interdiffusion, D

$$k_{ox} \propto T^{1}$$

Only considers temperature dependence of gas phase diffusion

Pressure dependence for T-300 fiber oxidation





Oxidation limited by gas diffusion through a laminar boundary layer:

$$k_{ox} = \mathrm{Re}^{1/2}\, Sc^{1/3} \frac{D\rho_{ox}}{L} \propto \frac{P_{ox}}{P_{total}^{1/2}}$$

Theory predicts P^n, n=1
Experiment: n=0.79 to 0.93

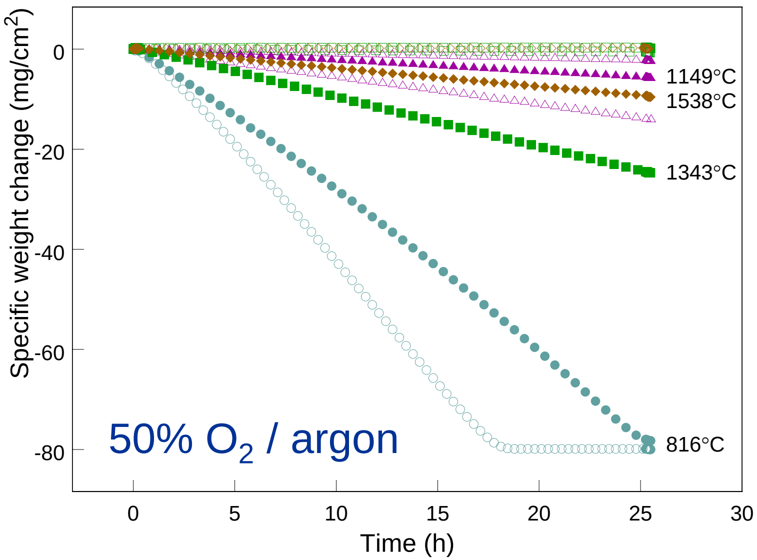
Summary of T-300 fiber oxidation

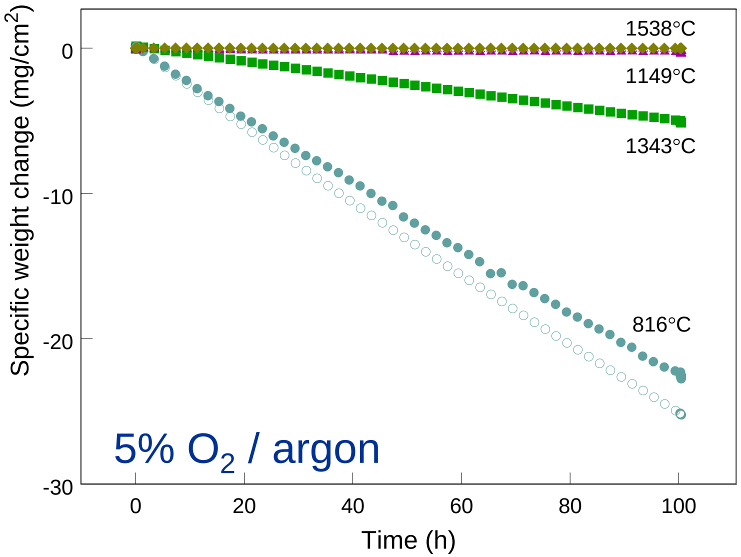
- T-300 fiber oxidation is limited by gas phase diffusion through the gas boundary layer

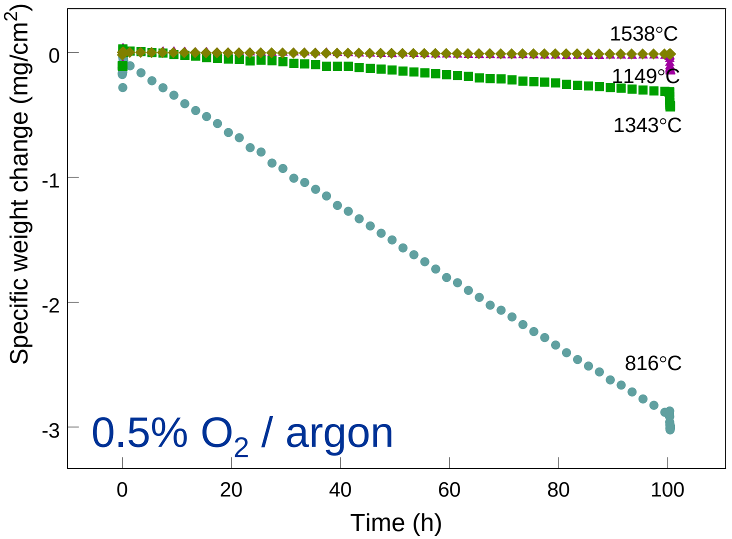
- Actual hypersonic environment will have reduced total pressure

C/SiC coupon oxidation

C/SiC coupon oxidation TGA results



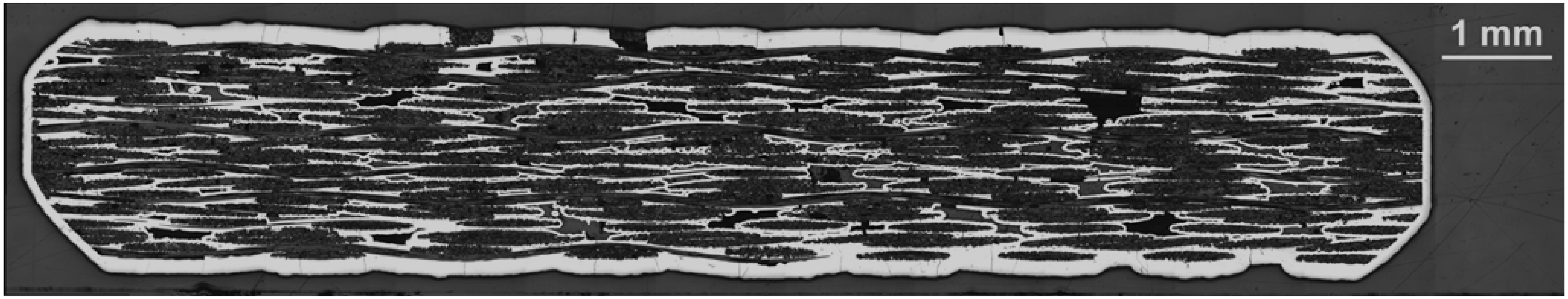




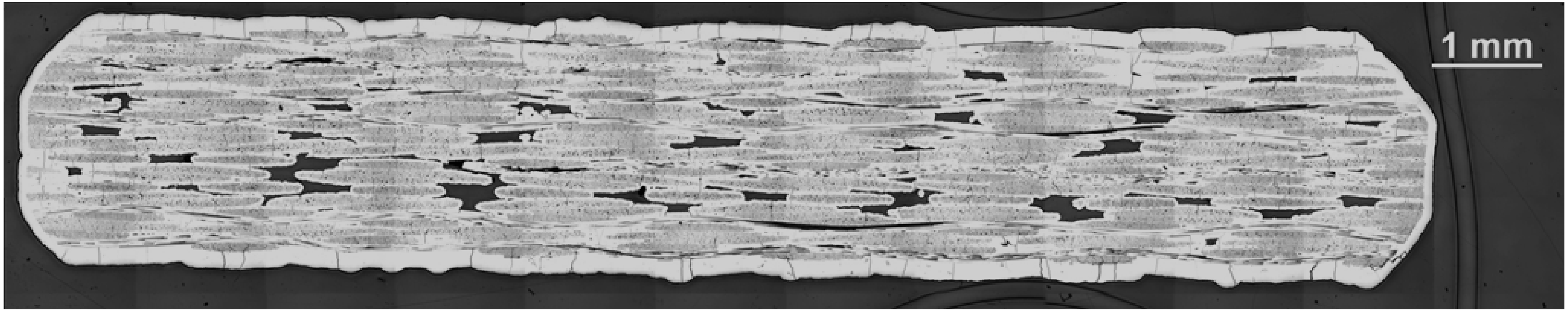
- Weight loss observed in almost all conditions: oxidation of carbon fibers through cracks in SiC seal coat
- Results show scatter due to varied crack structure in seal coat
- Weight loss rates are greatest at lowest temperatures, seal coat cracks open
- Weight loss rates are strongly dependent on oxygen partial pressure

C/SiC coupon oxidation: carbon oxidation

C/SiC composite, 816°C, 0.5 atm O_2 / argon, 100ccm, 25h



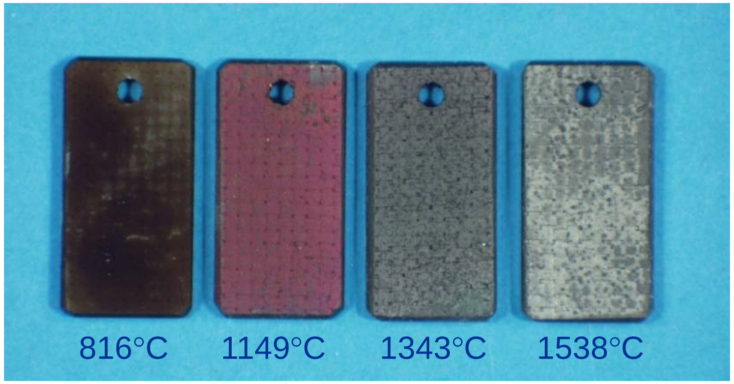
C/SiC composite, 1538°C, 0.5 atm O_2 / argon, 100ccm, 25h



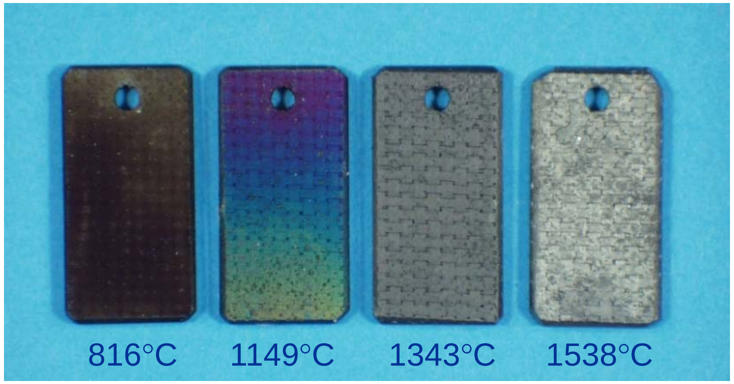
Complete C fiber oxidation at 816°C
Minimal C fiber oxidation at 1538°C

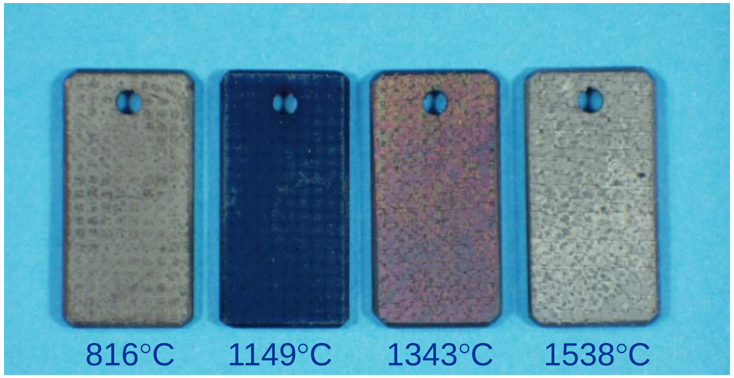
C/SiC coupon oxidation: SiC oxidation

0.5 atm O_2

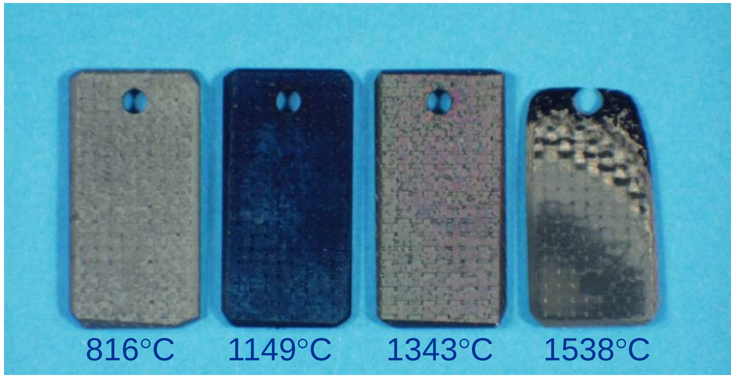


0.05 atm O_2





0.005 atm O_2



0.001 atm O_2

Colors indicate thin film of SiO_2 has formed on surface of SiC

C/SiC coupon oxidation: SiC oxidation

Predicted oxide thickness (μm) formed
on SiC at specified oxidation conditions

PO_2, atm	Temperature, °C				Time, h
	816*	1149*	1343^	1538^	
0.5	0.02	0.43	0.74	1.17	25
0.05	0.01	0.25	0.47	0.74	100
0.005	0.00	0.06	0.15	0.24	100
0.001	0.00	0.01	0.07	n/a	100

Low temperature, short times, thin scales: linear parabolic kinetics

High temperature, long times, thick scales: parabolic kinetics

$$x^2 + Ax = Bt$$

$$x = \sqrt{Bt}$$

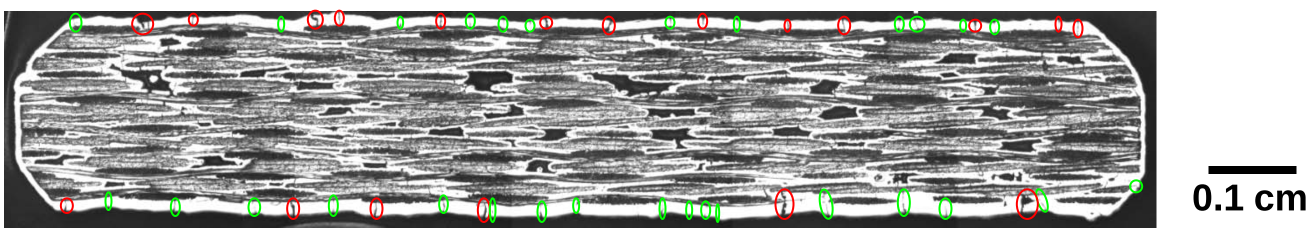
$$B \propto P_{O_2}$$

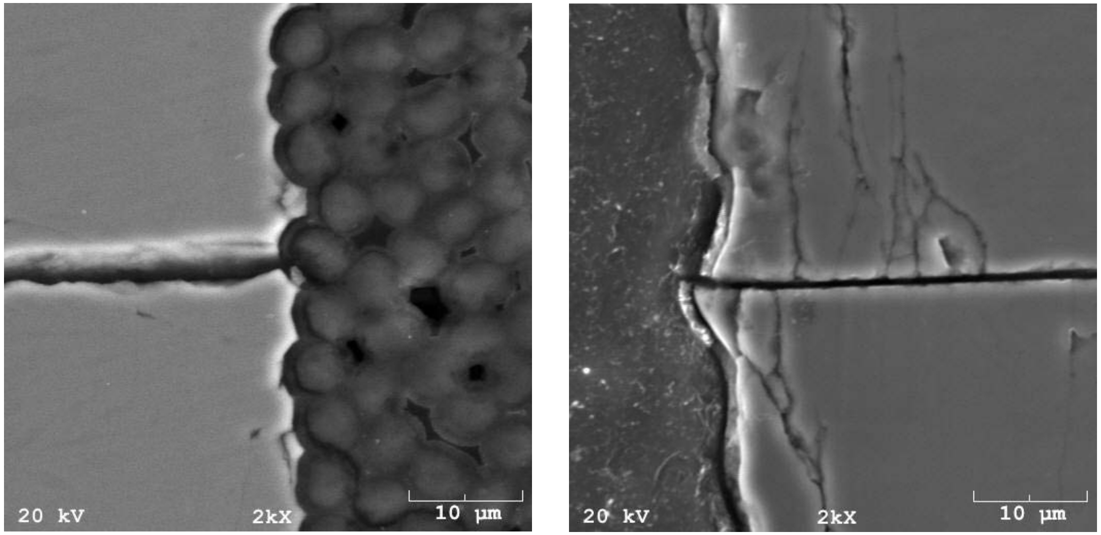
X=oxide thickness, B=parabolic rate constant, B/A=linear rate constant

*Ramberg et al., J. Am. Ceram. Soc. 79 [11] 2897-2911 (1996).
^Ogbuji et al., J. Electrochem. Soc. 142 [3] 925-930 (1995).

Transport of oxidant through cracks in SiC coating controls fiber oxidation rate

- Typical crack width on order of 1 μm (green)
- Significant number of wider cracks (red)
- Average spacing between cracks 73 μm





Crack closure mechanisms as temperature is increased

Thermal Expansion of SiC

%ΔL/L from Touloukian

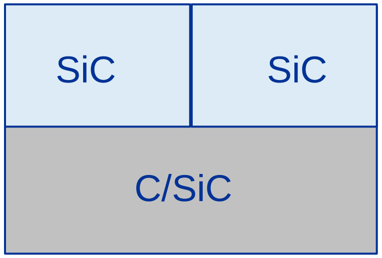
T, °C	% ΔL/L	ΔL (μm) for 73 μm segment
816	0.38	0.28
1149	0.57	0.41
1343	0.69	0.50
1538	0.81	0.59

Oxidation: growth of SiO_2

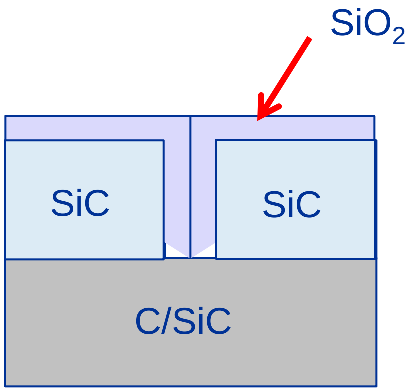
Silica thickness, μm

PO_2, atm	Temperature, °C				Time, h
	816*	1149*	1343^	1538^	
0.5	0.02	0.43	0.74	1.17	25
0.05	0.01	0.25	0.47	0.74	100
0.005	0.00	0.06	0.15	0.23	100
0.001	0.00	0.01	0.07	n/a	100

Dominant mechanism of crack closure



PO_2, atm	Temperature, °C			
	816	1149	1343	1538
0.5	TE	≈	ox	ox
0.05	TE	TE	≈	ox
0.005	TE	TE	TE	TE
0.001	TE	TE	TE	TE

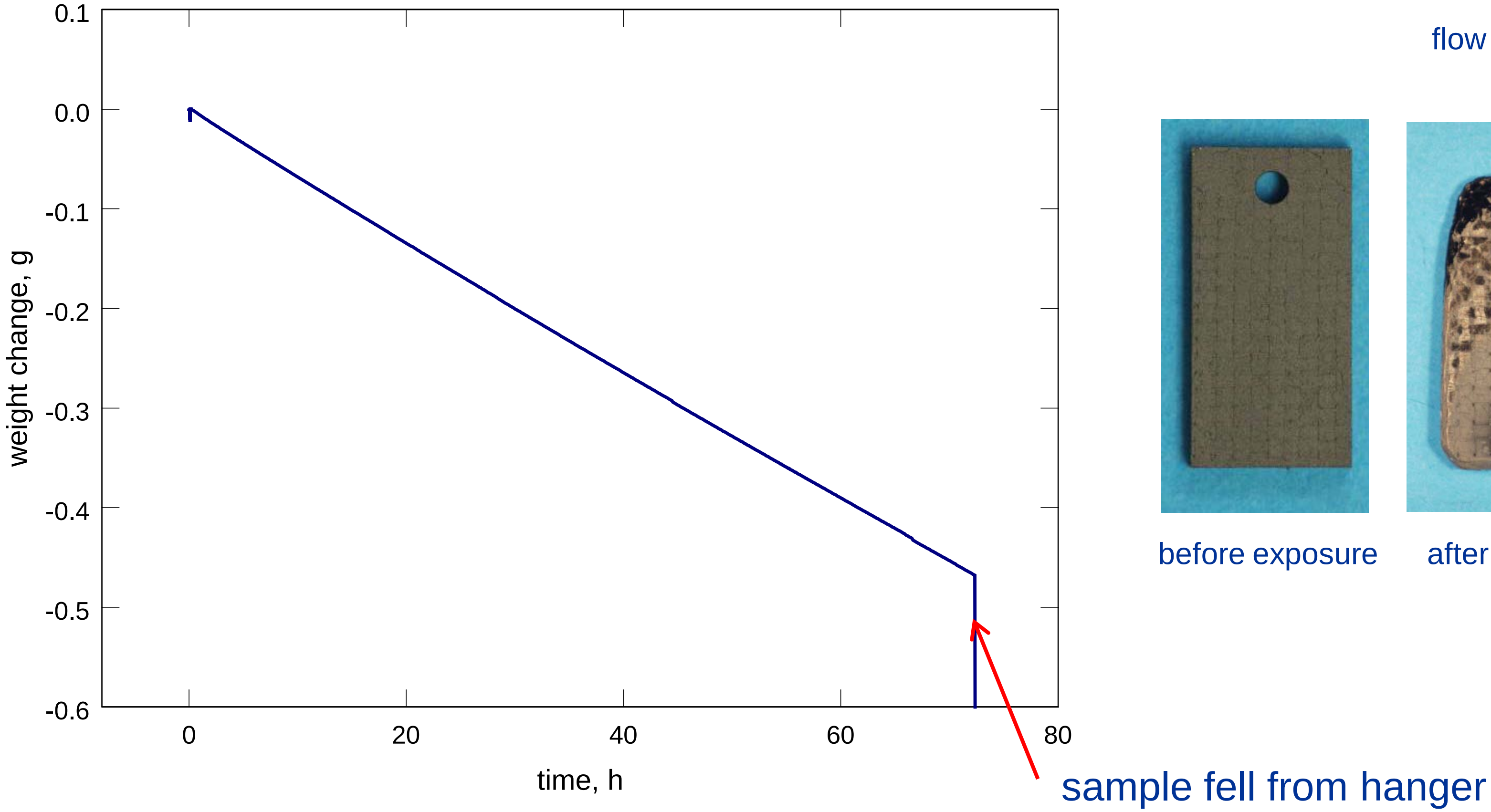


Neither mechanism can completely close cracks >~ 1 μm

Active oxidation of C/SiC

$SiC + O_2 = SiO(g) + CO(g)$

1538°C (2800°F), 1000 ppm O_2/Ar, exposure time: 72.3h
Sample fell from hanger when hole breached, weight loss 0.468g



before exposure

after exposure

sample fell from hanger

Summary of C/SiC oxidation

- C/SiC oxidation is dominated by carbon fiber oxidation through cracks in the coating
- Oxidation rates of C and SiC in actual hypersonic environments will differ due to the presence of atomic oxygen
- Active oxidation of SiC at low oxygen partial pressures and high temperatures is a major concern for C/SiC in hypersonic environments

Ongoing work

- Active oxidation of SiC under study
  - Determine conditions under which it occurs
  - Develop predictive capability for rate of attack
- C/SiC protective coating development task in place
  - Task objectives
    - 200h lifetime
    - T≥1650°C
    - leading edge environment
  - Coating needs
    - Seal cracks over all temperature ranges and under mechanical loading conditions
    - Mitigate SiC active oxidation

Acknowledgments

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

Thanks to
Bob Mattingly (NASA-GRC) for XRD
Matt Rowan (U. Toledo, Ohio)
Meredith Boyd (Rochester U., New York)