National Aeronautics and Space Administration

Compositional and microstructural effects in the protection of SiC components in water vapor

Benjamin Kowalski, Bryan Harder

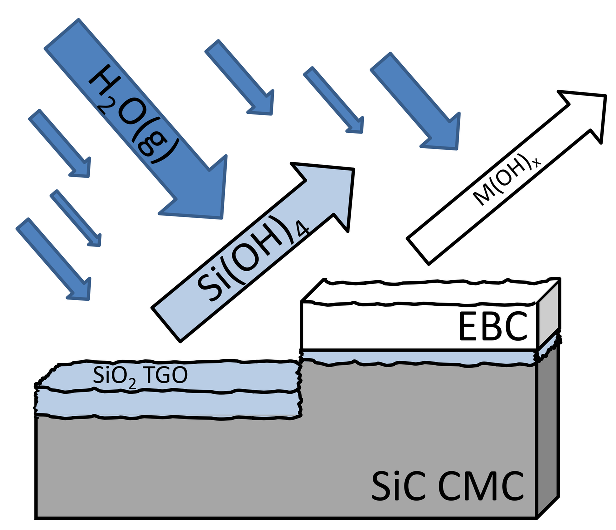
NASA Glenn Research Center, Cleveland, OH 44135, USA

Motivation:

To realize greater efficiencies in gas turbine engines, it is necessary to increase the operating temperature. To that end, silicon-based ceramics, composites, and coatings have shown great promise as replacements for current hot-stage alloy components of gas turbine engines. However, these Si-based materials are susceptible to a multitude of deleterious effects at elevated temperature. Water vapor plays a role in both the oxidation of the SiC ceramic-matrix composite (CMC) as well as the recession of the environmental barrier coating (EBC) meant to protect the underlying substrate. It is necessary to understand how the interaction with water vapor affects the life of both the CMC and EBC. This work primarily focuses on degradation of the CMC.

Background:

- Opila *et al* demonstrated that Si-based composites were vulnerable to recession by water vapor as depicted to the right with corresponding chemical equations.
- Oxidation and recession of SiC were described by a paralinear model (i.e. a combination of parabolic oxidation and linear recession as shown below.) with rates ascribed to each.
- These rates are affected by a multitude of factors, often overlapping, such as: diffusion rate, crystallinity, density, porosity, and doping among others, shown in graphs below.
- An EBC slows the rate of oxidation, but failure modes can appear due to the new interface that forms owing to chemical compatibility effects and thermal expansion mismatch.



$$SiC + 3/2\,O_2(g) \rightarrow SiO_2 + CO(g)$$
$$SiO_2 + 2H_2O(g) \rightarrow Si(OH)_4(g)$$

[1]Oxidation of Si @ 84% H_2O

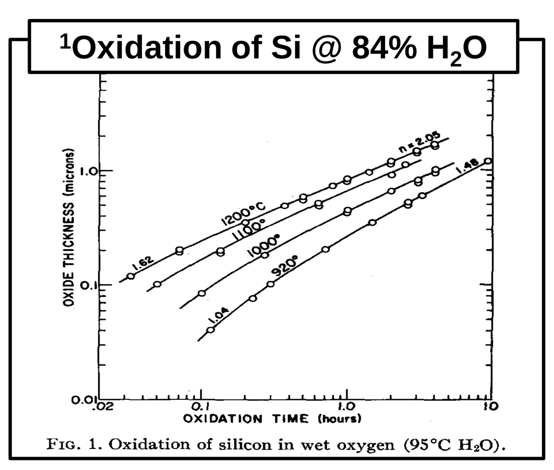
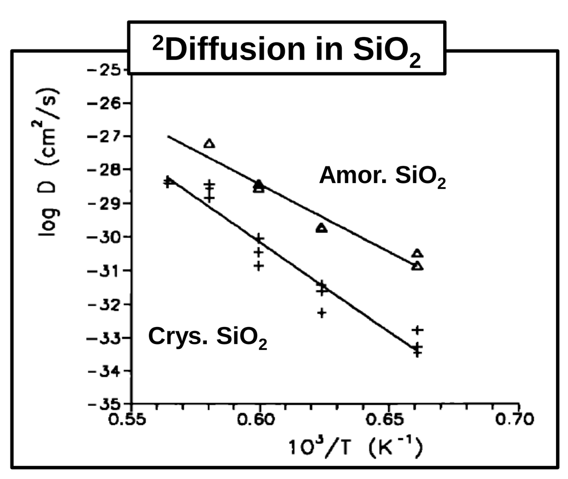
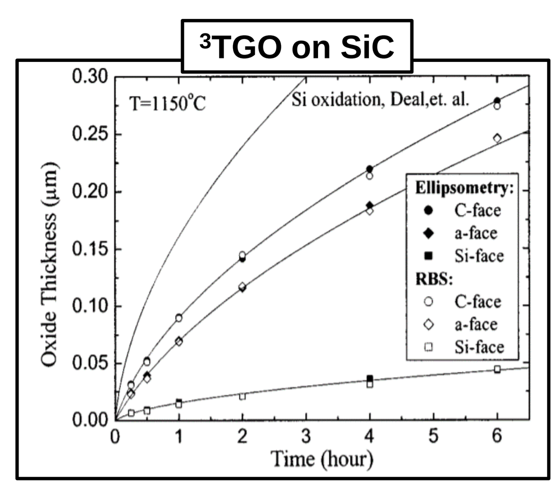


Fig. 1. Oxidation of silicon in wet oxygen (95°C H_2O).

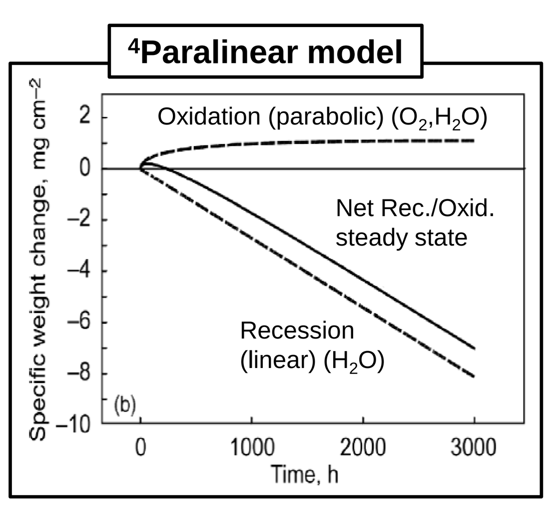
[2]Diffusion in SiO_2



[3]TGO on SiC



[4]Paralinear model



[5]TGO on CVD SiC

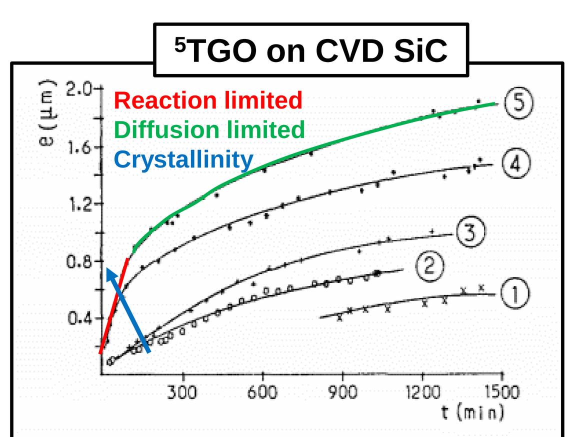


Fig. 5. Oxide thickness vs. time: curve 1, 1250°C; curve 2, 1310°C; curve 3, 1360°C; curve 4, 1420°C; curve 5, 1475°C.

[6]B doping in Si

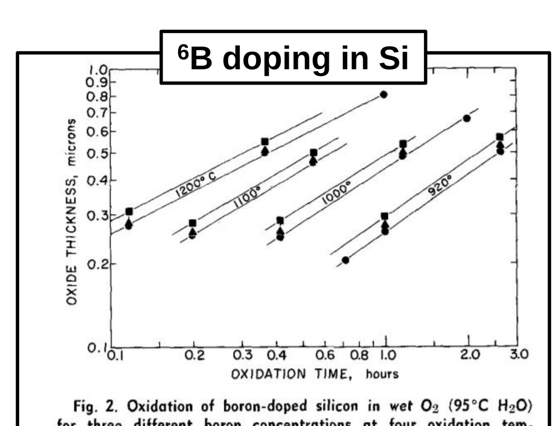
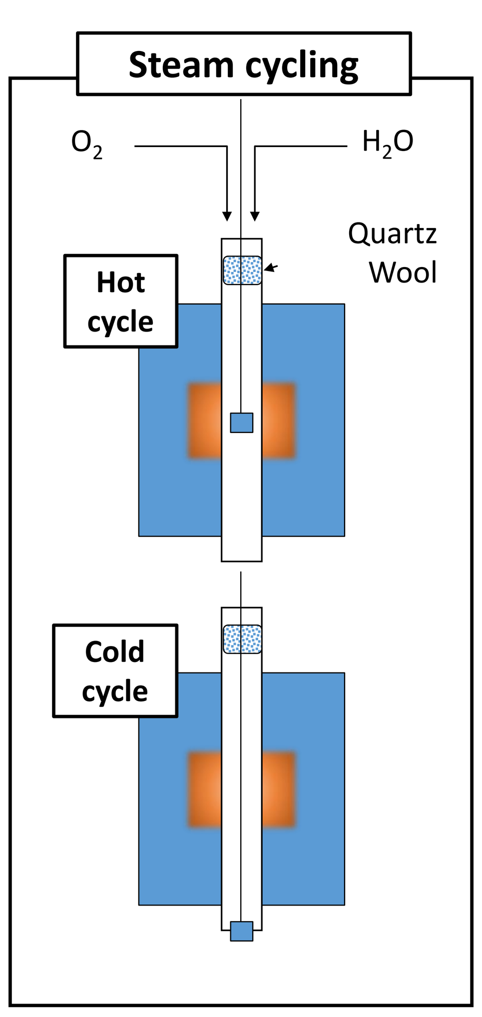


Fig. 2. Oxidation of boron-doped silicon in wet O_2 (95°C H_2O) for three different boron concentrations at four oxidation temperatures.

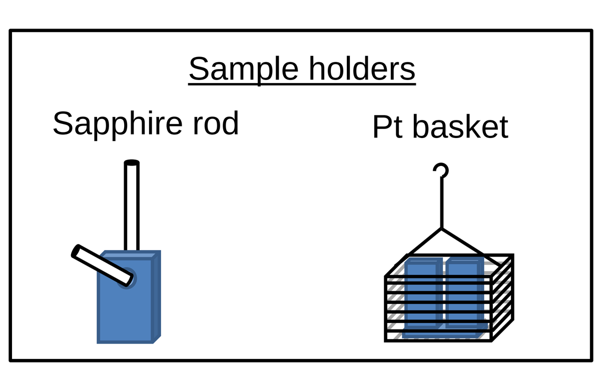
Experimental Setup:

- To understand the efficacy of the EBC as well as the influence of the material parameters in different SiC types, measurements of weight changes are performed *in situ* at a particular temperature (i.e. Thermogravimetric analysis (TGA)) or *ex situ* after temperature cycling (i.e. Steam cycling)

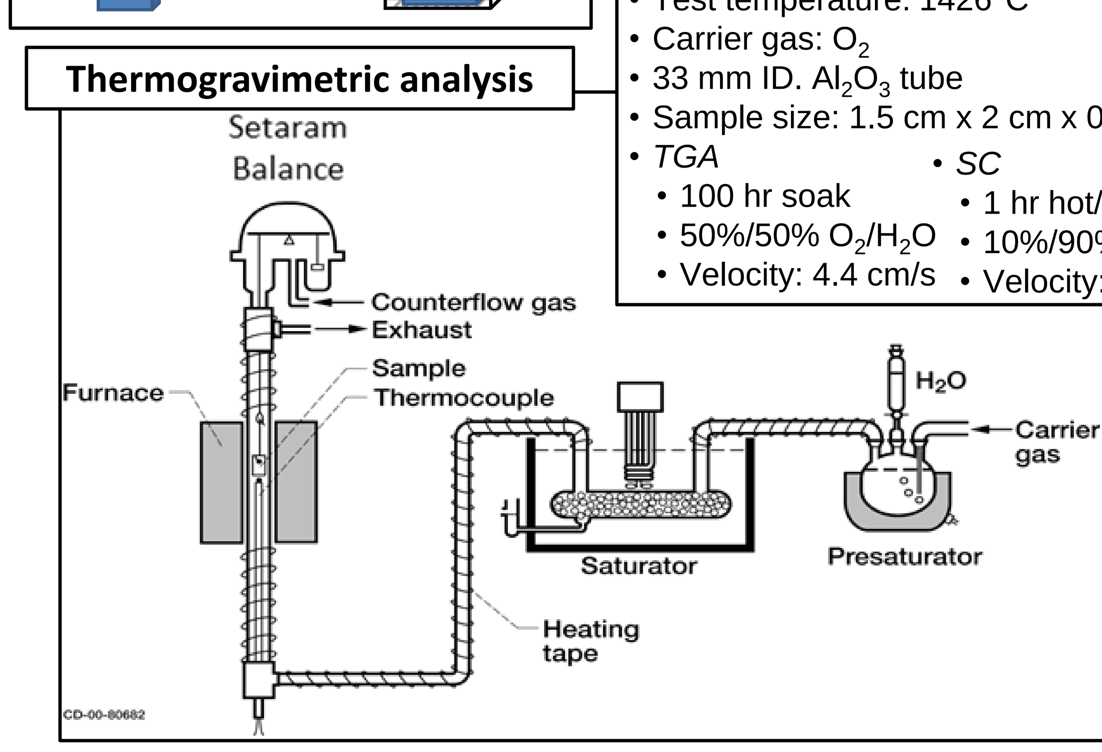
Steam cycling



Sample holders



Thermogravimetric analysis



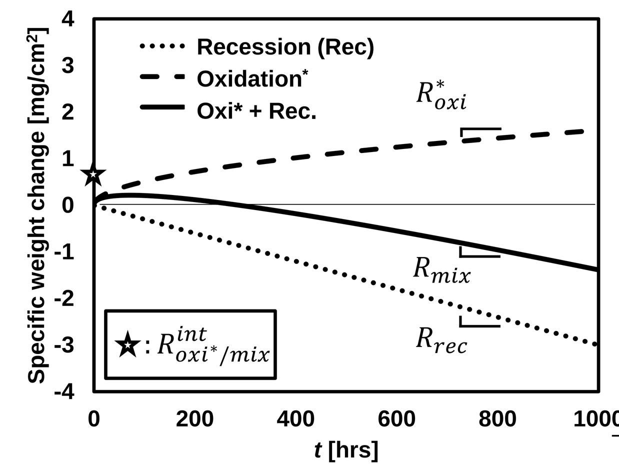
Materials Used

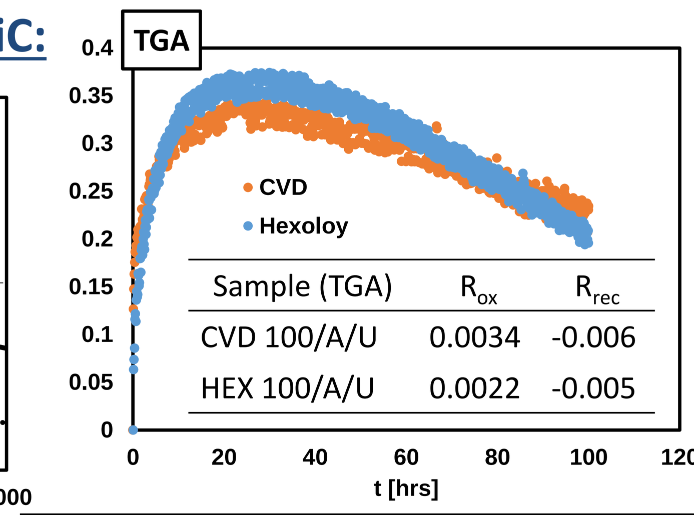
- *Hexoloy*: α-SiC, 5-8% porosity, contains (BC, BN, B, C)
- *CVD*: β-SiC, textured due to growth.
- *EBC*: $Yb_2Si_2O_7$

TGA/SC conditions

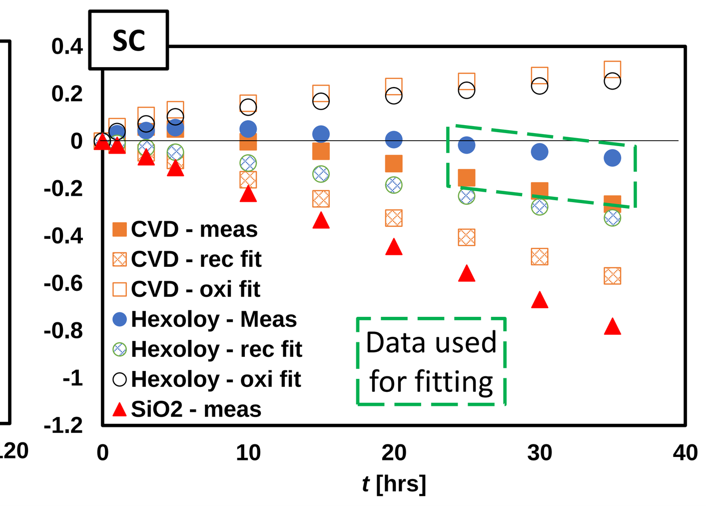
- Test temperature: 1426°C
- Carrier gas: O_2
- 33 mm ID. Al_2O_3 tube
- Sample size: 1.5 cm x 2 cm x 0.3 cm
- *TGA*
  - 100 hr soak
  - 50%/50% O_2/H_2O
  - Velocity: 4.4 cm/s
- *SC*
  - 1 hr hot/20 min cold
  - 10%/90% O_2/H_2O
  - Velocity: ~10 cm/s

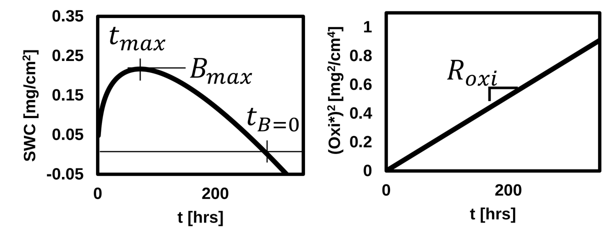
Oxidation & Recession of SiC:





Sample (TGA)	R_{ox}	R_{rec}
CVD 100/A/U	0.0034	-0.006
HEX 100/A/U	0.0022	-0.005





- As a consequence of the paralinear model, for long times the parabolic oxidation data fits to $x = R^*_{oxi} * t^2$, but it is possible to extract the rate constants from only a few data points.

Equations and relations used to fit subset of data

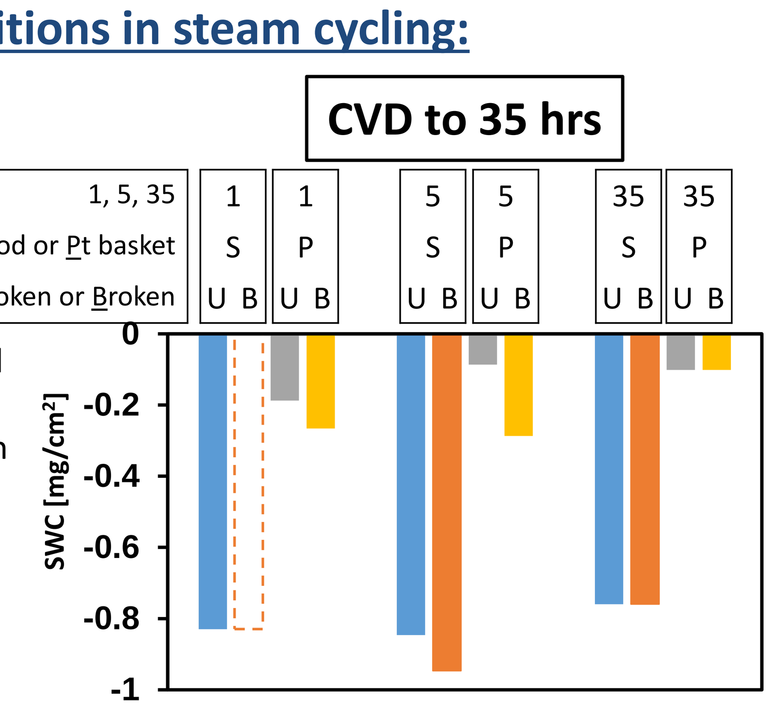
$$R_{mix} - R_{rec} = R^*_{oxi} \qquad R_{rec} \approx -\frac{B_{max}}{t_{max}}$$
$$t_{B=0} = 4 * t_{max} \qquad R_{ox} \approx \frac{(2 * B_{max})^2}{t_{max}}$$
$$t_{max} = \frac{R_{ox}}{4 * R^2_{rec}} \qquad R^{int}_{oxi^*/mix} \approx \left(\frac{t_{avg} * R_{ox}}{4}\right)^{0.5}$$
$$t_{B=0} = \frac{R_{ox}}{R_{rec}} \qquad R^*_{oxi} \approx \frac{\tan\left(R^{int}_{oxi^*/mix}\right)}{0.0174 * t_{avg}}$$

Sample (SC)	R_{ox} [mg²/cm⁴-h]	R_{rec} [mg/cm²-h]
CVD 5/P/B	0.0026	-0.017
HEX 5/P/B	0.0011	-0.007
CVD 5/A/B	0.0023	-0.032
HEX 5/A/B	0.0029	-0.027
SiO_2 5/P/B	--	-0.022
SiO_2 5/A/B	--	-0.044
EBC/HEX 1/A/U (100 hrs)	0.0033	--
E/H w/OxBC 1/A/U (100 hrs)	0.0009	--

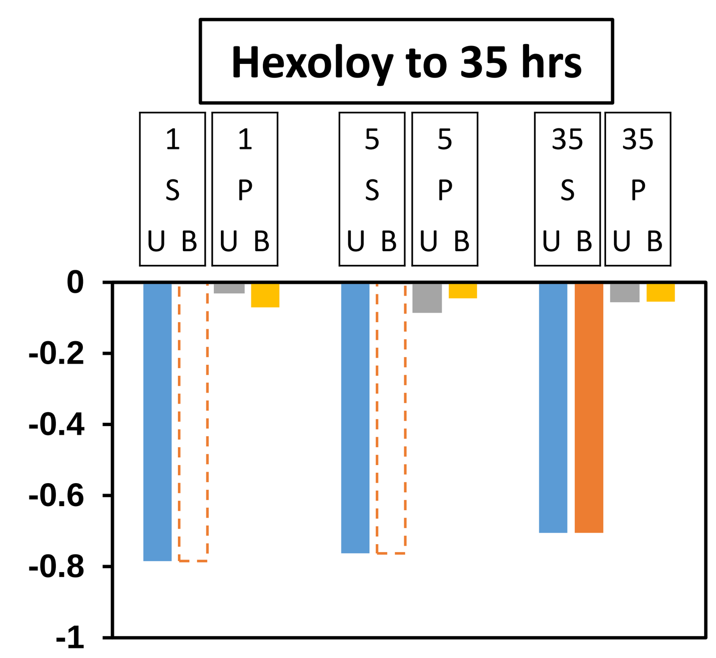
Effect of testing conditions in steam cycling:

Cycle length [hrs]	1, 5, 35
Hanging type	Sapphire rod or Pt basket
Seal after each cycle	Unbroken or Broken

CVD to 35 hrs



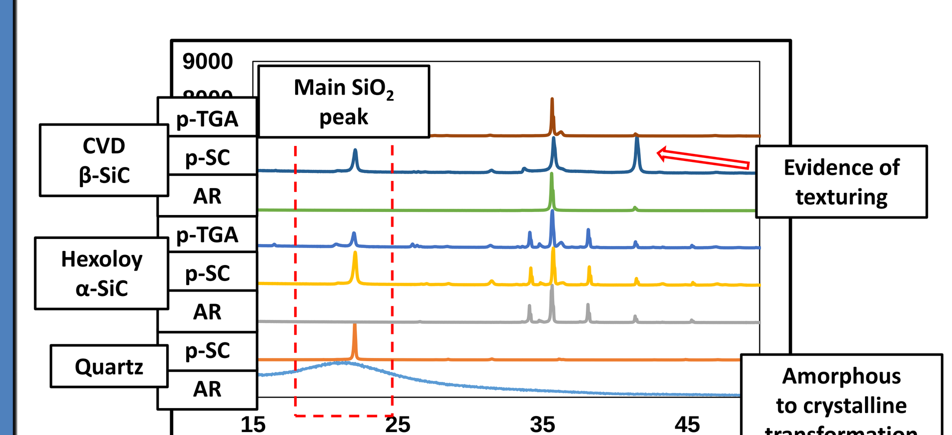
Hexoloy to 35 hrs

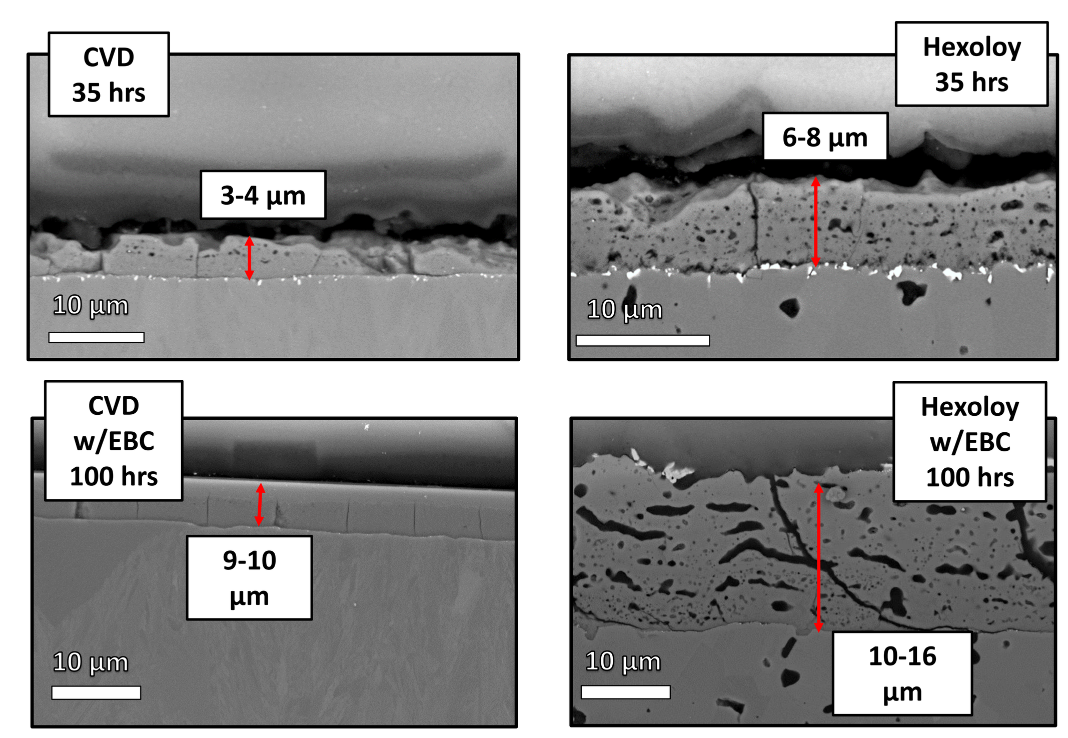


- Cycle time, holder type, and environment are controlled to understand the effects on oxidation and recession
- Dash lines are expected values from missing data
- Holder has largest effect on recession

Structural analysis (X-ray diffraction and Scanning Electron Microscopy):

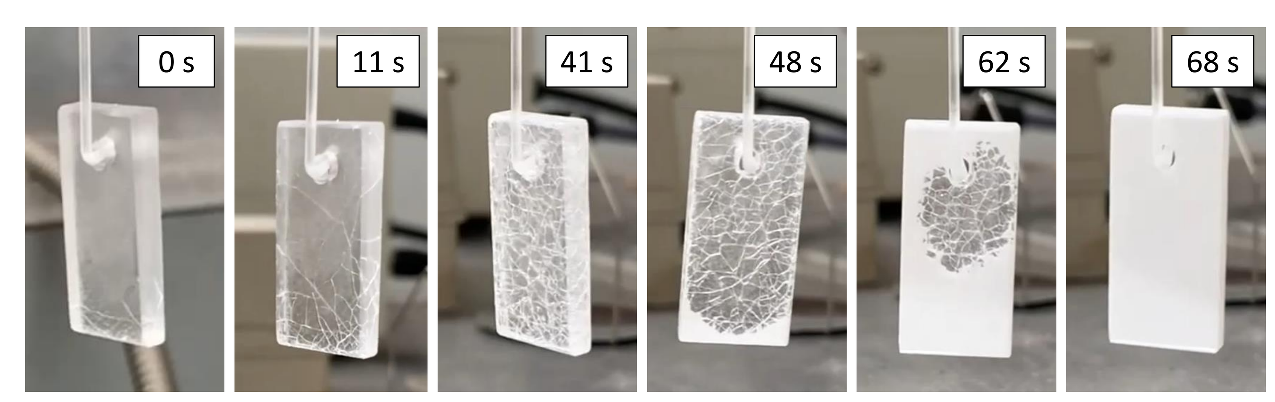
- XRD and SEM confirm the presence of the SiO_2 grown on the SiC surface.
- As expected, Hexoloy has a thicker TGO layer and a correspondingly higher intensity in XRD

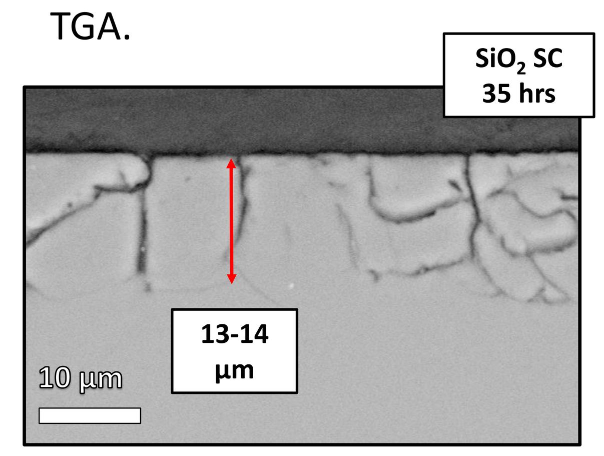




Diffusional effects:

- SiO_2 after 100 hrs at 1426 °C in 50/50 H_2O/O_2 in TGA to the right
- SiO_2 SEM after 35 hrs
- Amorphous until quenched
- Diffusion plays a role in crystallization as can be seen in the comparison between SC and TGA.





Conclusion:

- TGO growth and failure is complex
- Temperature cycling more closely resembles in use characteristics
- The choice of substrate, cycle time, sample holder all strongly affect the TGO growth rate through oxidation and recession; must be accounted for when reporting rates

References:

[1]Deal *et al*. – J. Appl. Phys. – (1965)
[2]Rodriguez-Viejo – J. Eur. Cer. Soc. – (1994)
[3]Song – J. Appl. Phys. – (2004)
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[5]Sibieude – Thin Solid Films – (1991),
[6]Deal *et al*. – ECS – (1965)