Oxidation Of SiC-Based Materials At High Water-Vapor Pressure

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CFCC

CONTINUOUS FIBER CERAMIC COMPOSITE MATERIALS

UT Materials Science & Engineering Seminar

October 17, 2000

Water-Vapor Effects On Oxidation Comprise An Important Area Of Study

- For many years, it has been known that H_2O can accelerate oxidation of Si-based materials (for example, cf. Deal and Grove, 1965)

$$k_p = \frac{2 D_{eff} C^*}{N}$$

For SiO_2 growth, k_p (H_2O) ≈ 10 k_p (O_2)

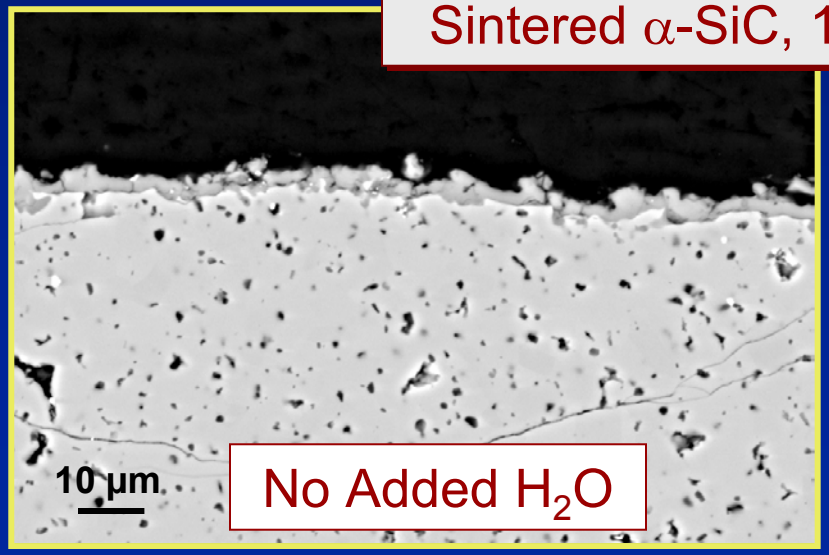
- H_2O found in many high-temperature environments
- Effects of H_2O of increasing concern as gas turbine technology moves toward higher temperatures, higher pressure ratios, and NO_x control

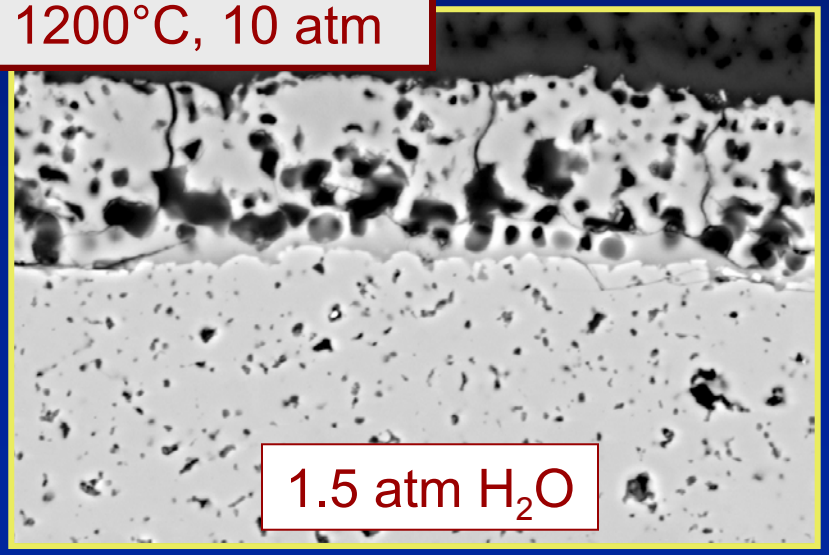
At Higher Pressures Of Water Vapor, Oxidative Degradation is Much Worse

Recent work on monolithic SiC, Si_3N_4:

- Effects on parabolic rate constant (Opila, J. Am. Ceram. Soc.,1999)
- SiO_2 volatility (Opila & Jacobson, ECS Proc.1997; Opila & Hann, J. Am. Ceram. Soc., 1997; Robinson & Smialek, J. Am. Ceram. Soc.,1999; Opila et al., J. Am. Ceram. Soc.,1999)
- Accelerated oxidation with nonprotective SiO_2 formation (More et al., J. Am. Ceram. Soc., 2000)

Sintered α-SiC, 100 h, 1200°C, 10 atm





Little effort on Si-based composites (More et al., IGTI Proc., 1999)

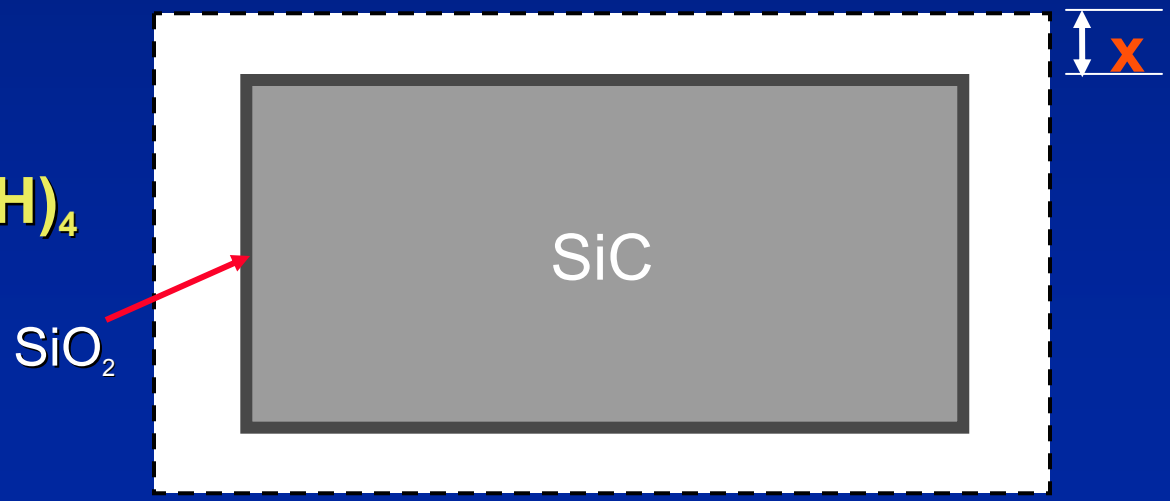
Water Vapor Effects On Oxidation Of SiC

- **Increases k_p**

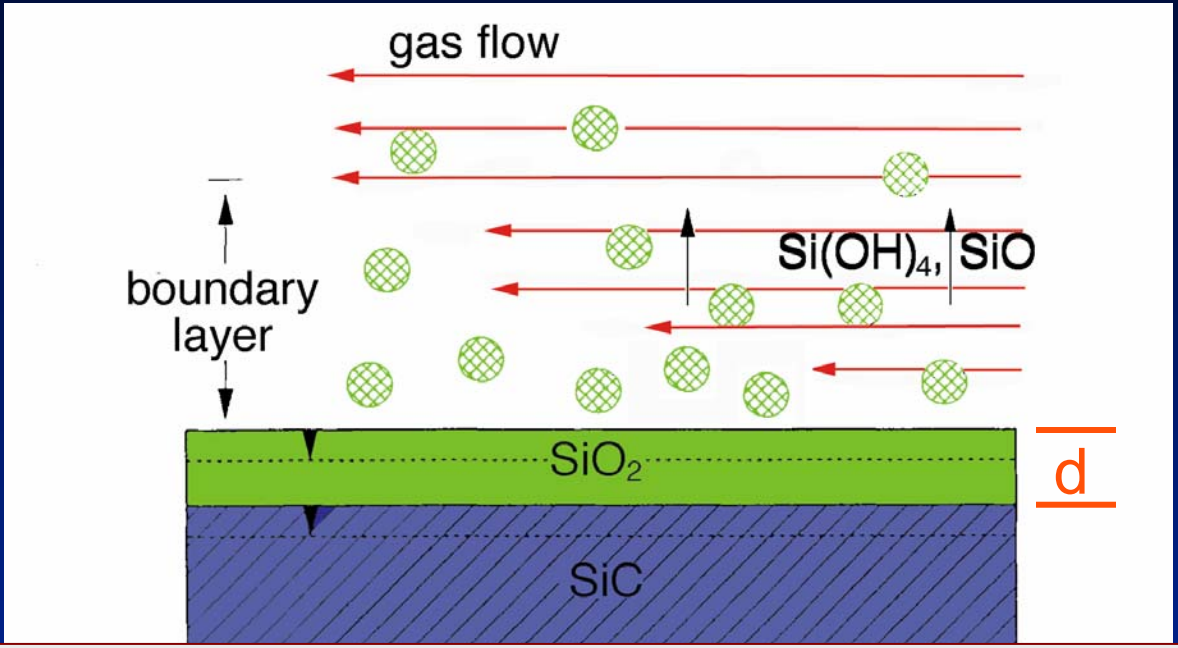
$$x = \sqrt{(k_p \cdot t)}$$

- **Facilitates volatilization of SiO_2**

$$SiO_2 + 2H_2O = Si(OH)_4$$



Volatility Of SiO_2 Can Lead To Substantial Recession Of Si-Based Materials



SiO_2 Recession Rate = k_l = const.• $\underline{v}^{1/2}\{\exp(-\Delta G_o/RT)\}\underline{P}^{3/2}$

Robinson & Smialek, 1999; Opila et al., 1999

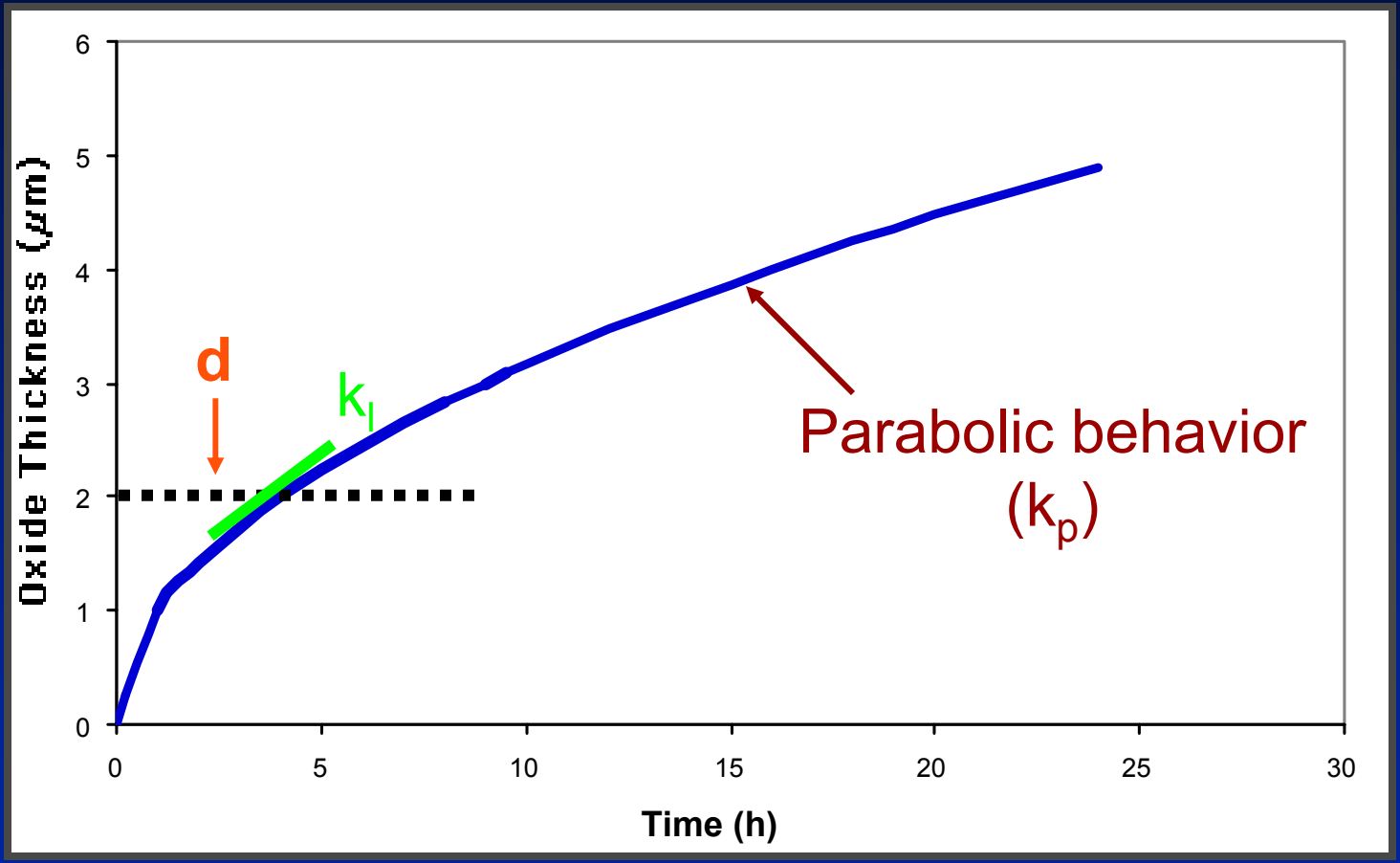
<u>Paralinear kinetics (moving boundary):</u>

SiO_2 volatilization controls SiC recession: $k_l t$

d = constant with time = $k_p/2k_l$

Opila & Hann, 1997

Limiting Product Thickness Sets High Rate

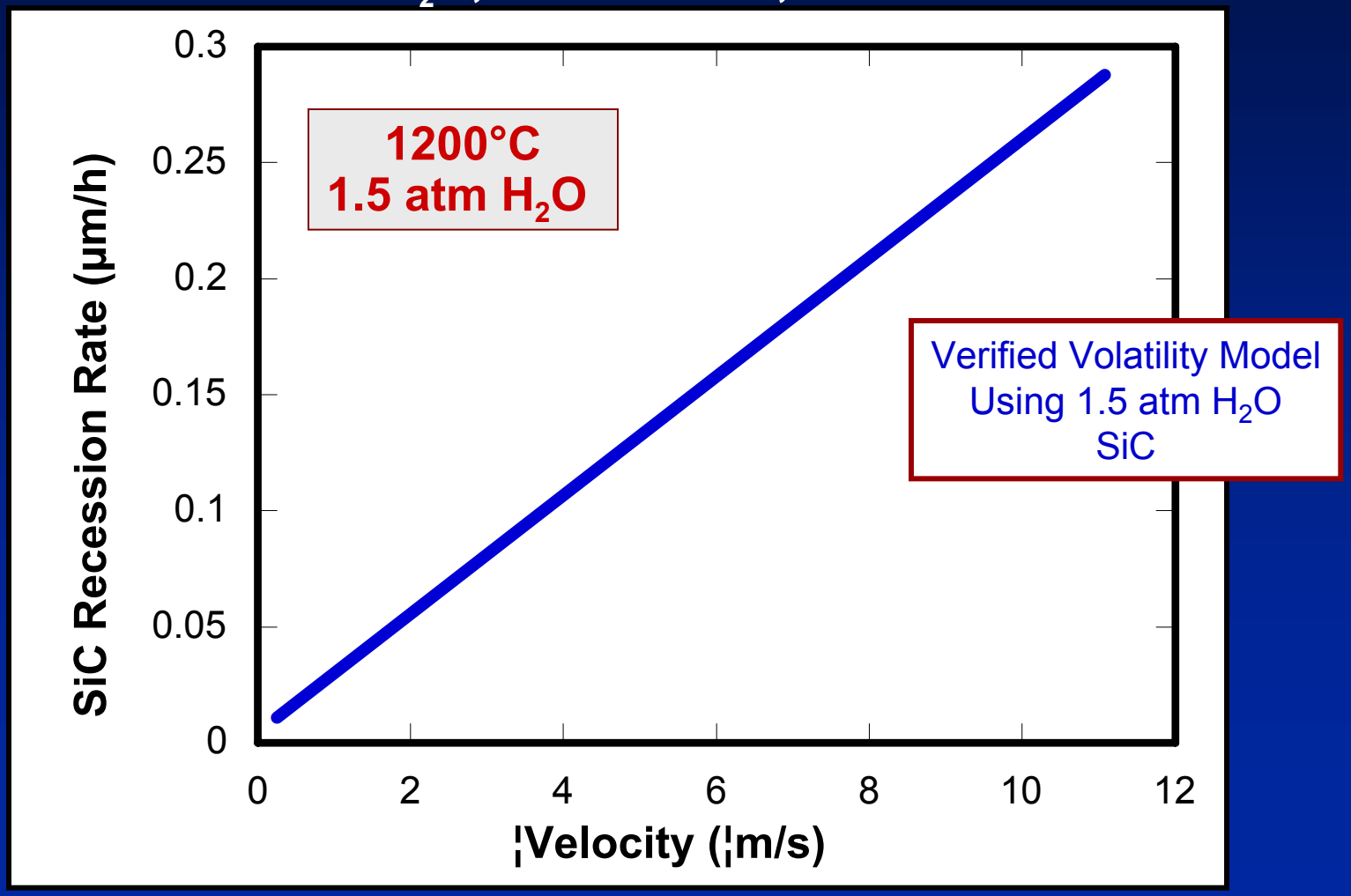


$$d = k_p/2k_l$$

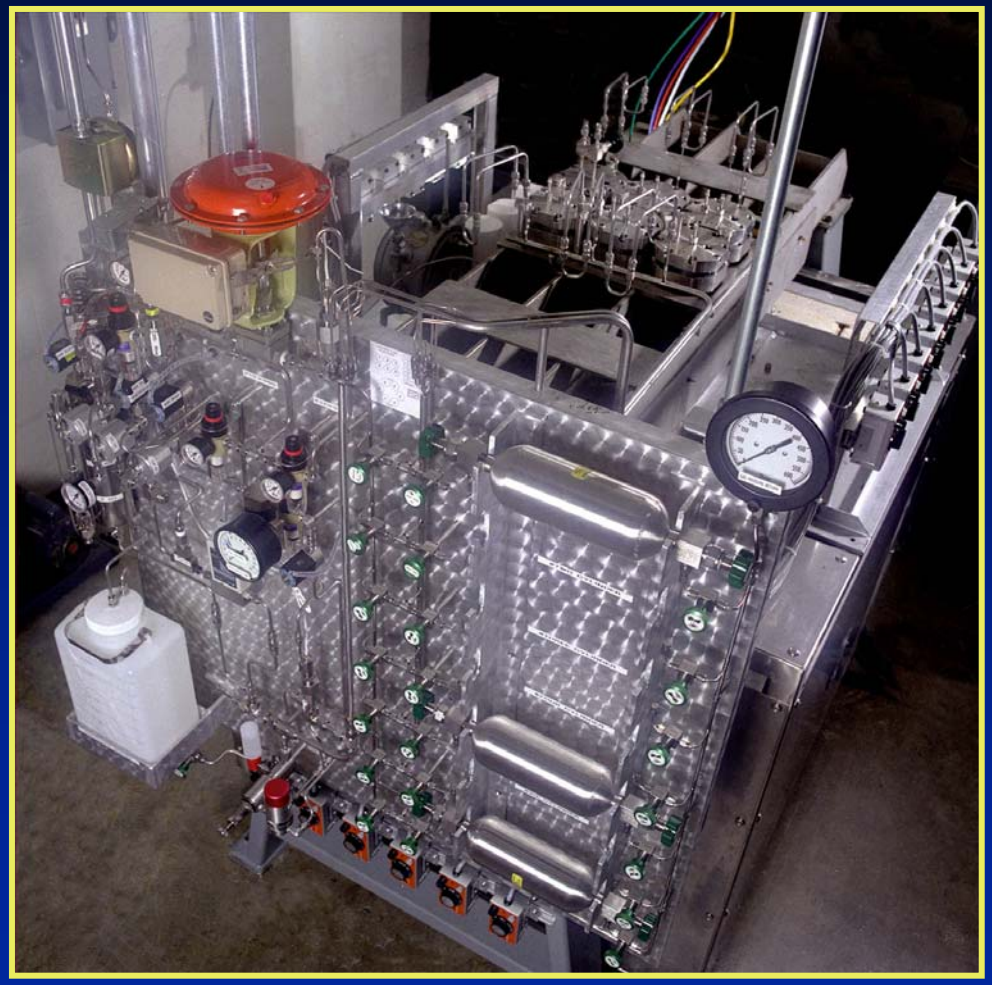
Volatility Model Effectively Describes Recession Of SiC Over Appreciable Range Of v, P, And T

SiO_2 Recession Rate = k_l = const.• $\underline{v}^{1/2}\{\exp(-\Delta G_o/RT)\}\underline{P}^{3/2}$

0.3-0.9 atm H_2O, 0.05-150 m/s, 1150 - 1500°C



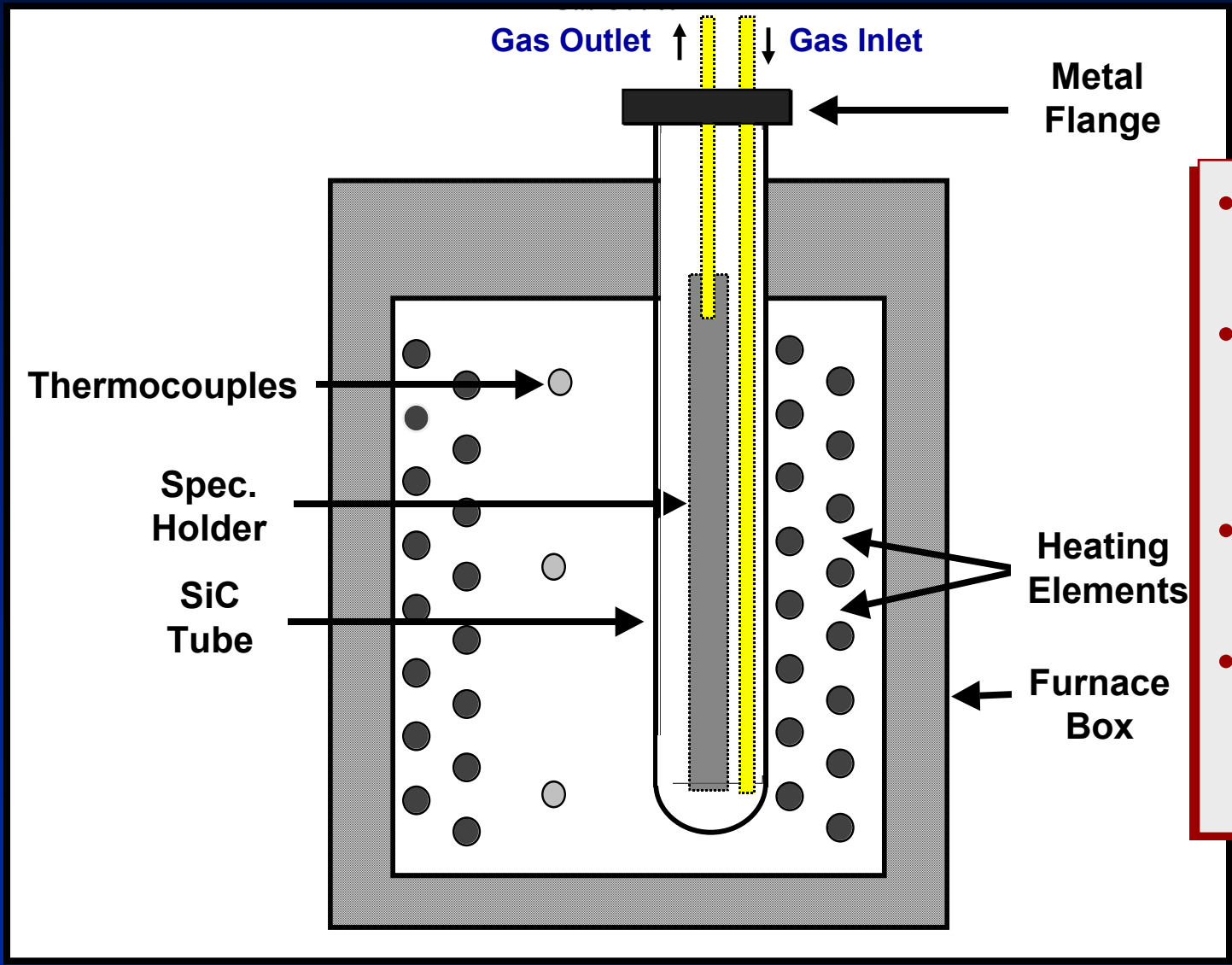
We Conduct High-Pressure Exposures In Specialized High-Temperature Rigs



"Keiser Rig"

- temperatures up to 1550°C
- pressures to 500 psi
- 0.05-0.3 cm/s
- mixed-gas supply system

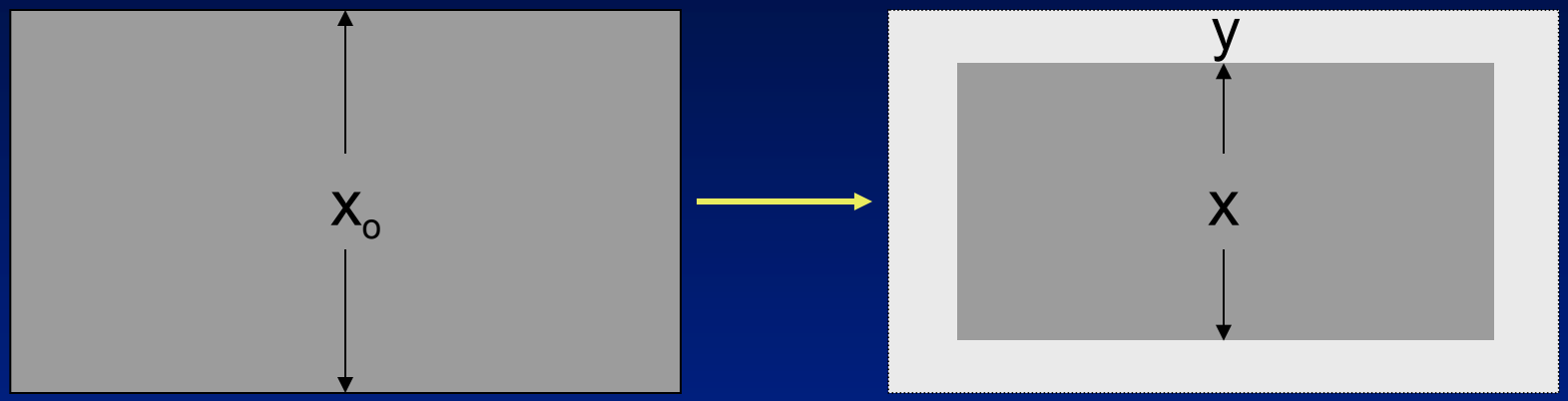
Experimental Conditions



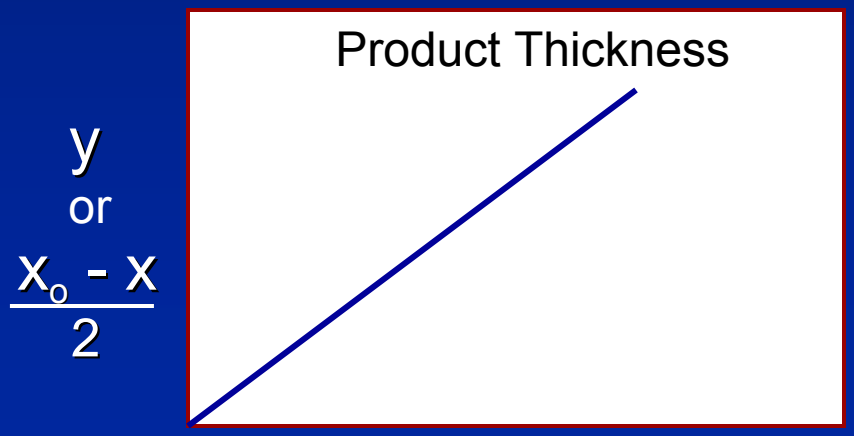
- 1200°C
- 10 atm total pressure
- Air-15%H_2O
- SiC, Si_3N_4, SiC/SiC, oxide/oxide

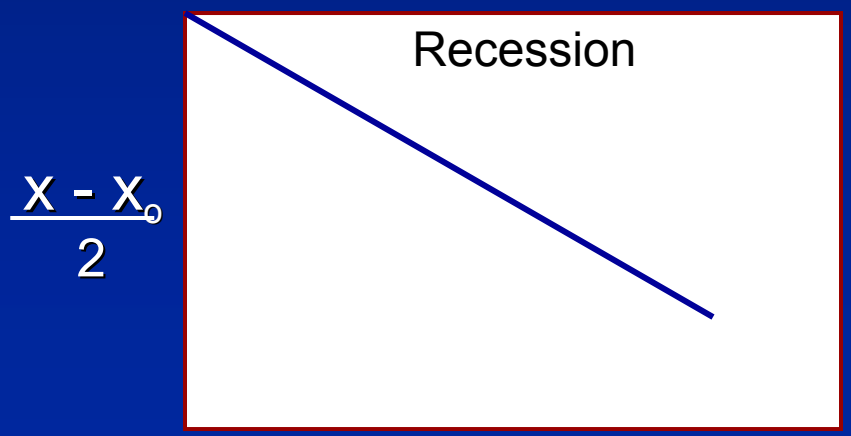
Extent Of Oxidation Is Determined By Microstructural Analysis

Oxidation Damage Is Measured From Cross Sections

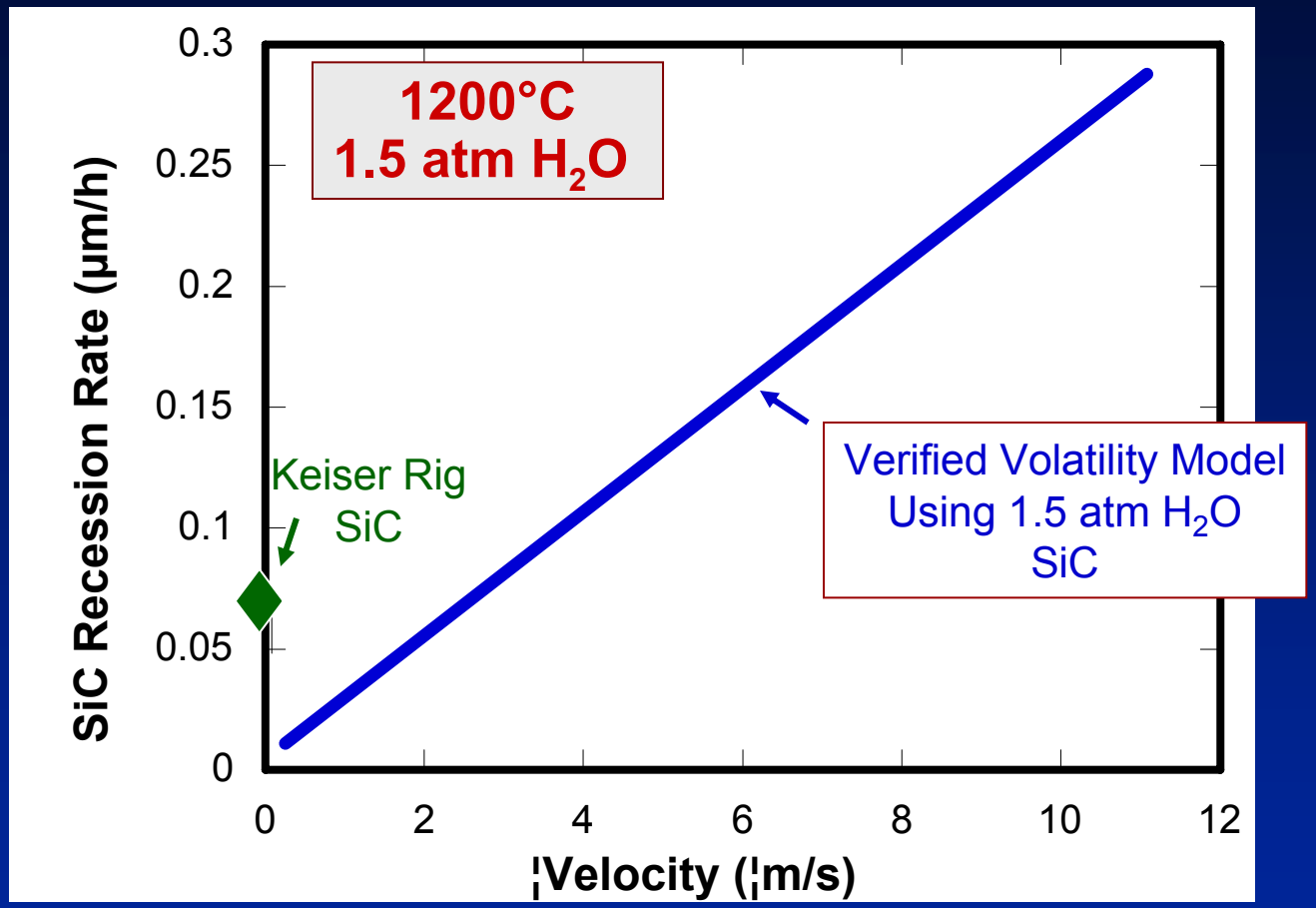


Before Exposure **After Exposure**



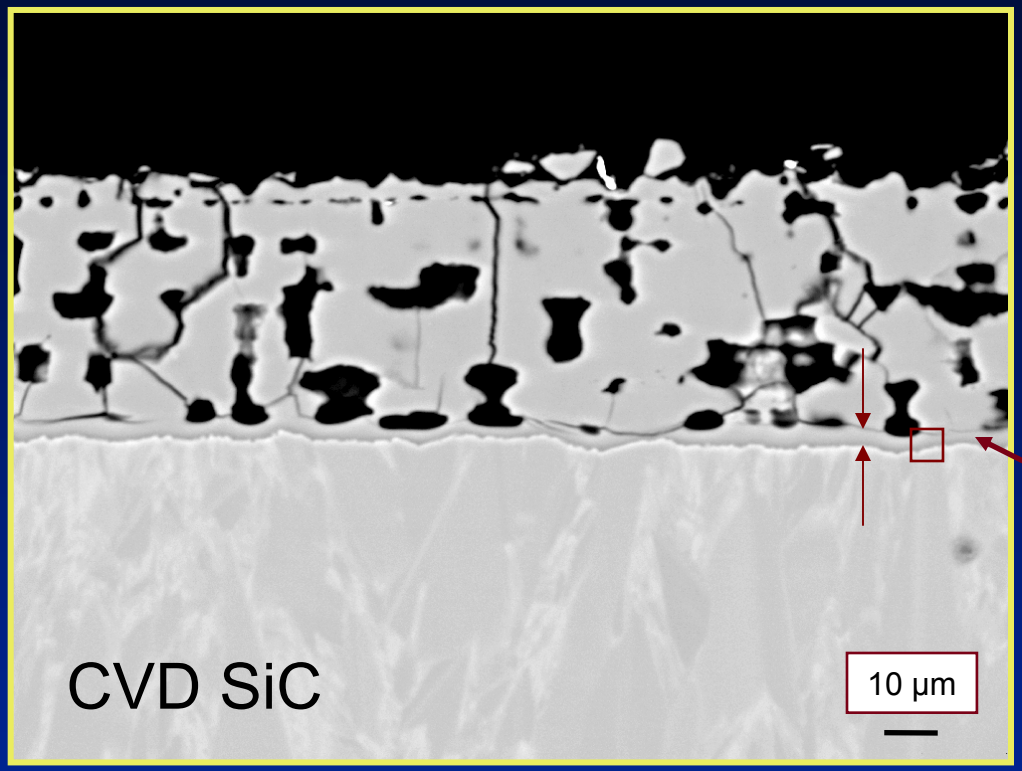


Despite Slow Flow In Keiser Rig, Substantial Oxidation-Induced SiC Recession Is Observed



At Sufficiently High H_2O Pressures, Rapid Oxidation Can Also Occur At Very Low Gas Flow Rates

Typical Surface Features Observed After Exposure To High Water-Vapor Pressure And Low Gas Velocities

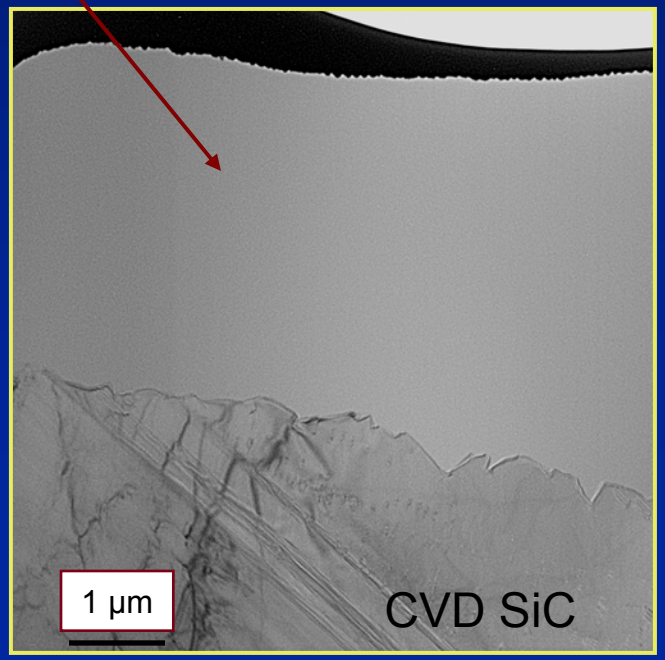


Cristobalite

SiO_2 (total)

d

Vitreous SiO_2



500 h, 1200°C, 1.5 atm H_2O

Vitreous (~ amorphous) layer is dense and thickness (d) is constant with time!

Constancy Of Thickness Of Dense (Vitreous) SiO_2 Layer Suggests A Moving Boundary Phenomenon

For SiC:

- Form Silica By Solid-State Oxidation
- Convert Dense Vitreous Silica To Porous, Nonprotective Cristobalite

From paralinear kinetics:

$$d = k_p/2k_l$$

Measurements Of d and k_l (Recession Rate) For CVD SiC Yield Correct k_p

$$d = k_p/2k_l$$

For CVD SiC, 1200°C, 1.5 atm H_2O

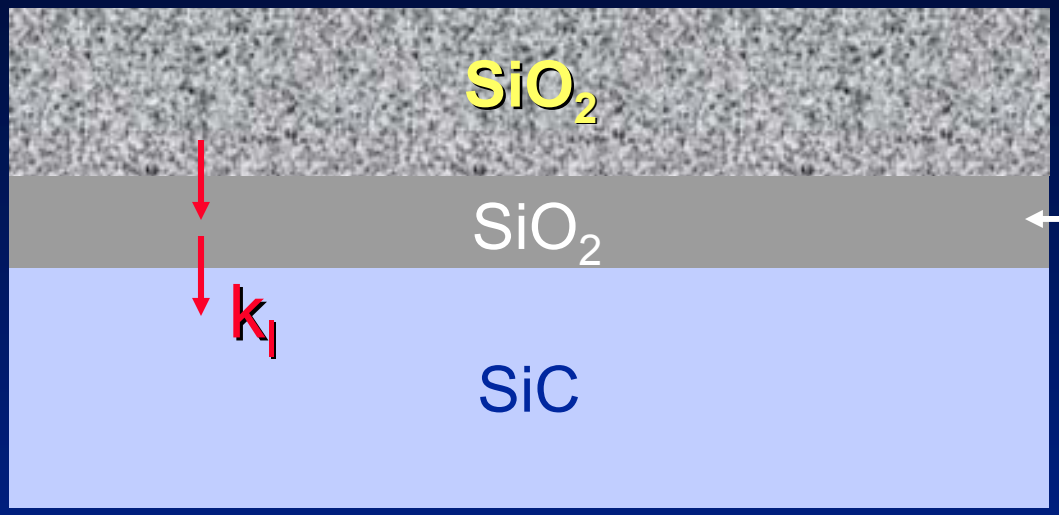
d = 4 µm

k_l (from slope of SiC recession curves) = 0.06 µm/h

$k_p = d \cdot 2\, k_l = 0.48\ \mu m^2/h$

k_p (Opila, 1999) = 0.49 $\mu m^2/h$!!!

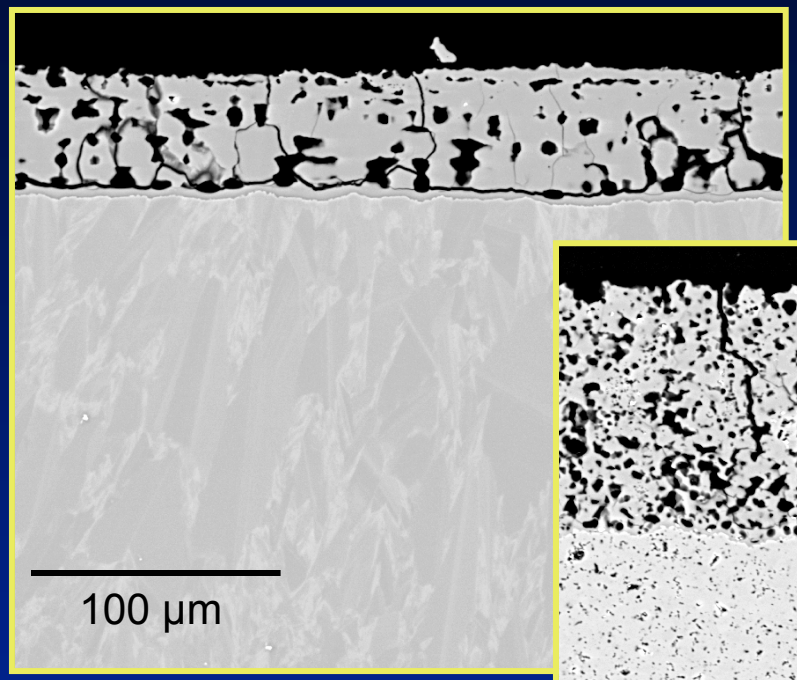
What Controls The Conversion Of Dense To Nonprotective Silica?



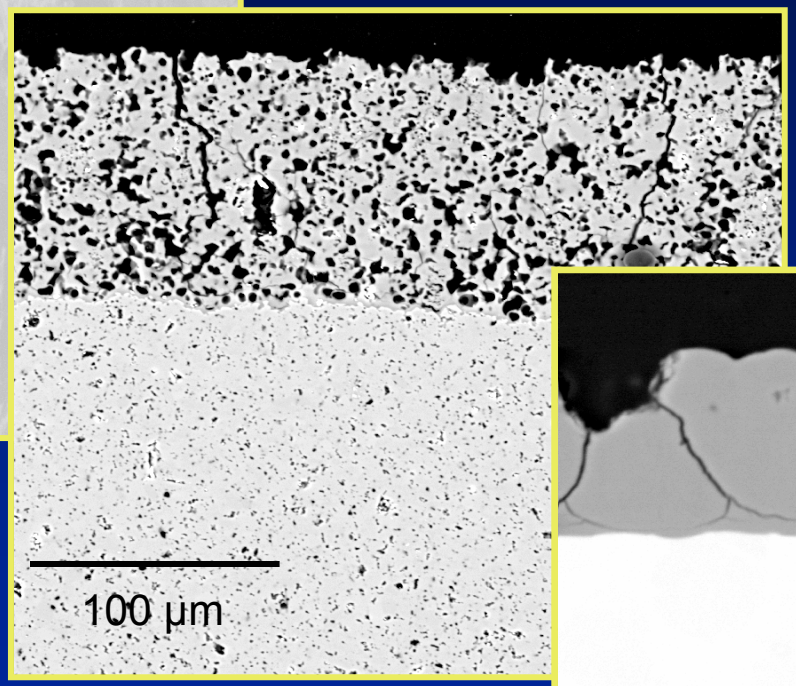
Layer thickness constant with time

Few Pores When Pure Si Oxidized

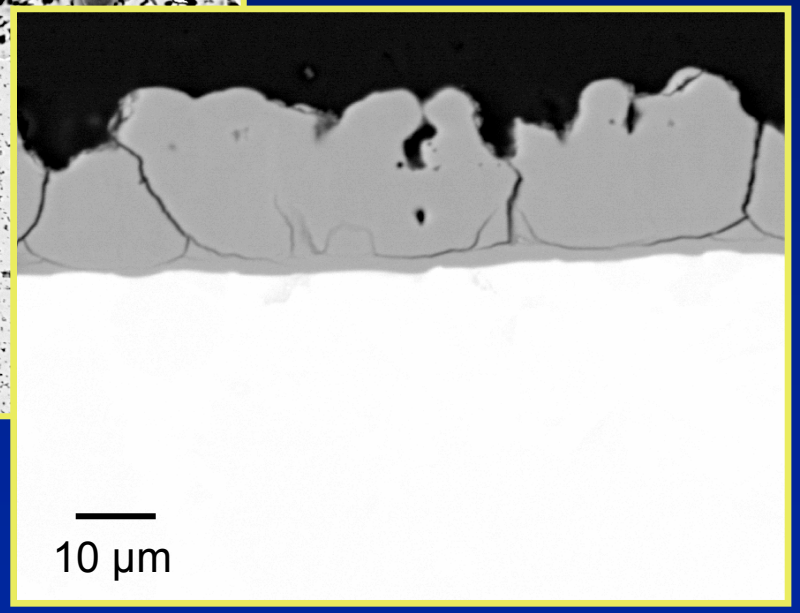
8.5 atm air, 1.5 atm H_2O, 500 h



CVD SiC

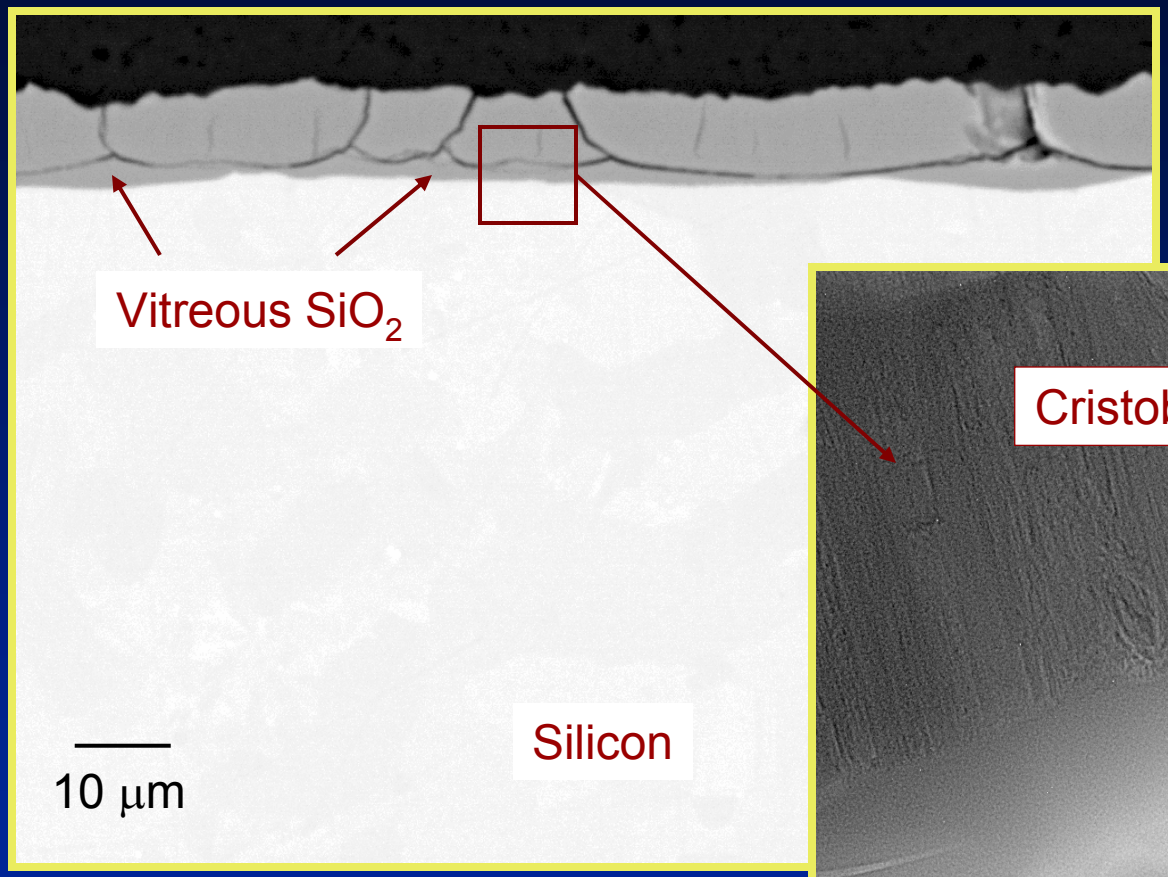


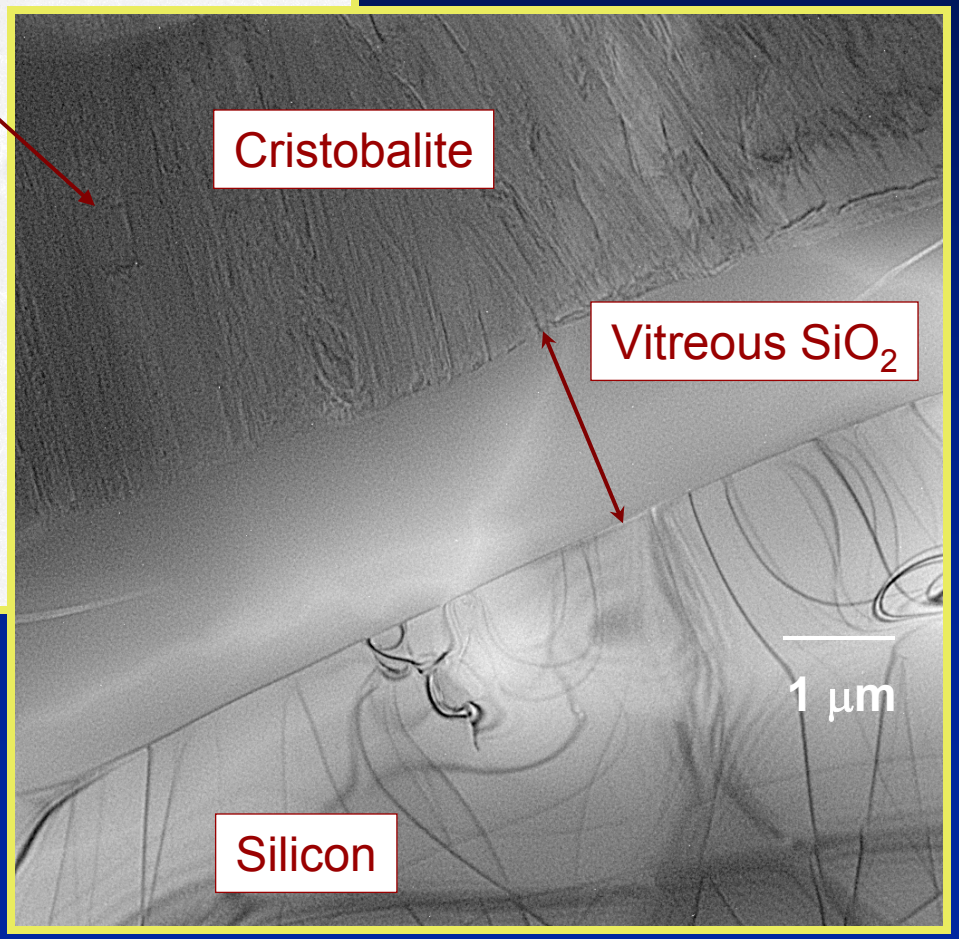
SA



Pure Si

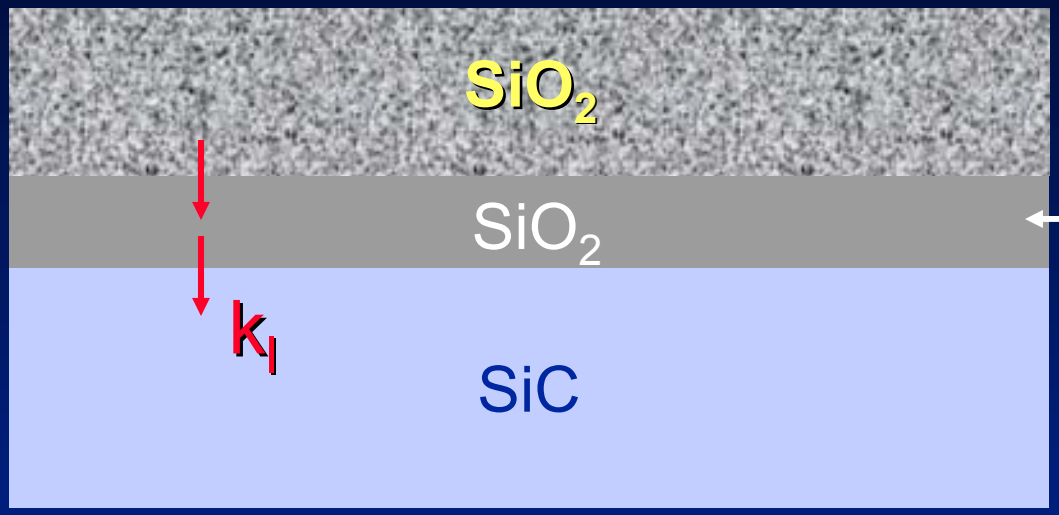
Exposure Of Si Resulted In Similar Two-Layer Scale But Cristobalite Was Dense In This Case





8.5 atm air, 1.5 atm H_2O, 500 h

What Controls The Conversion Of Dense To Nonprotective Silica?



Layer thickness constant with time

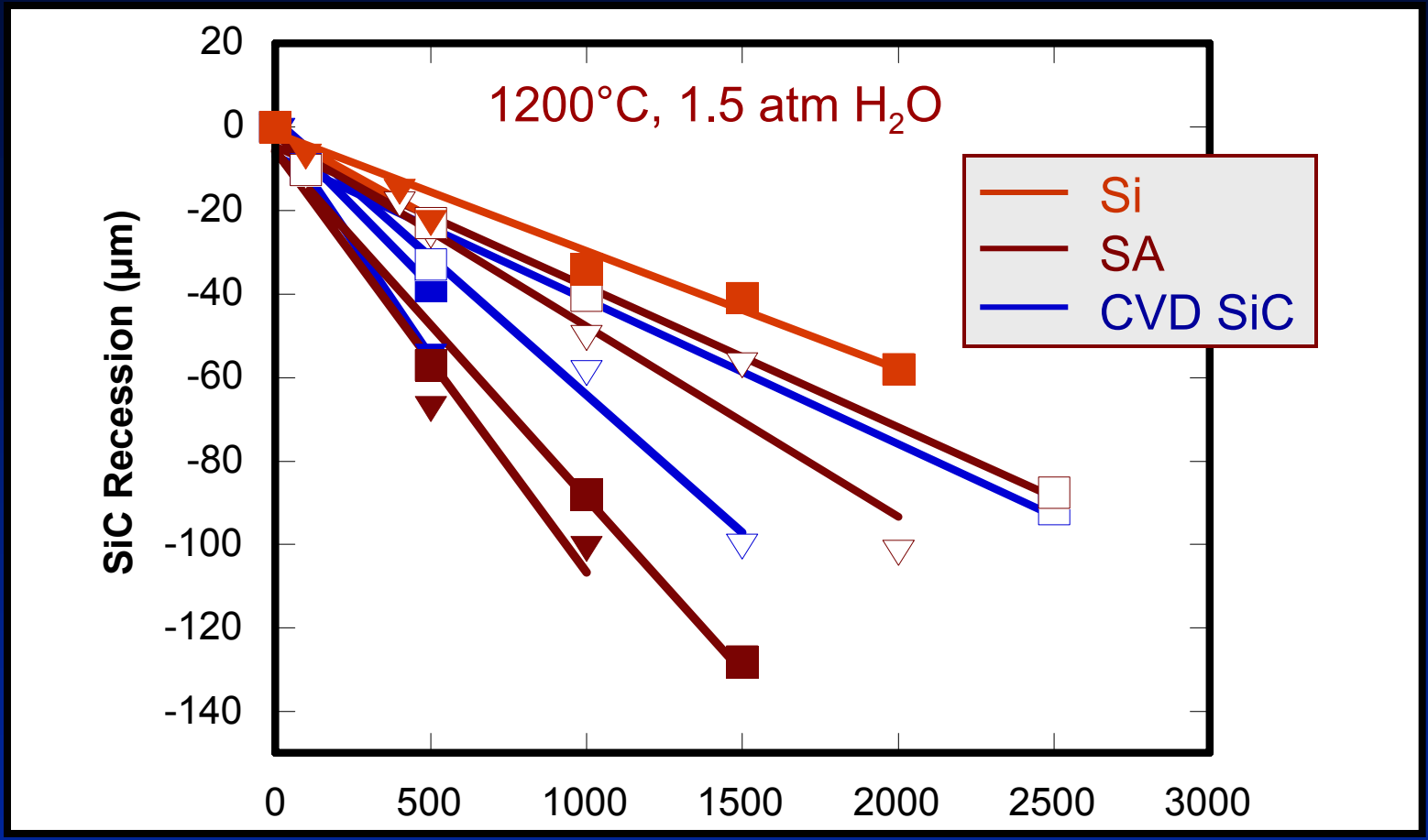
Rapid Defect Creation By Accumulation Of Gaseous Species In Outer Scale

$$Si + 2H_2O\ (g) = SiO_2 + 3H_2\ (g)$$

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

$$SiC + 3H_2O\ (g) = SiO_2 + CO\ (g) + 3H_2\ (g)$$

Recession Rate For Silicon Was High, But Lower Than That Of SiC



Si: 0.03 - 0.04 µm/h

CVD SiC: 0.04 - 0.07 µm/h

SA: 0.04 - 0.10 µm/h

Recession Rates For SiC-Based Composites Are Significantly Higher Than Those Of SiC

~1200°C, 1.5 atm H_2O

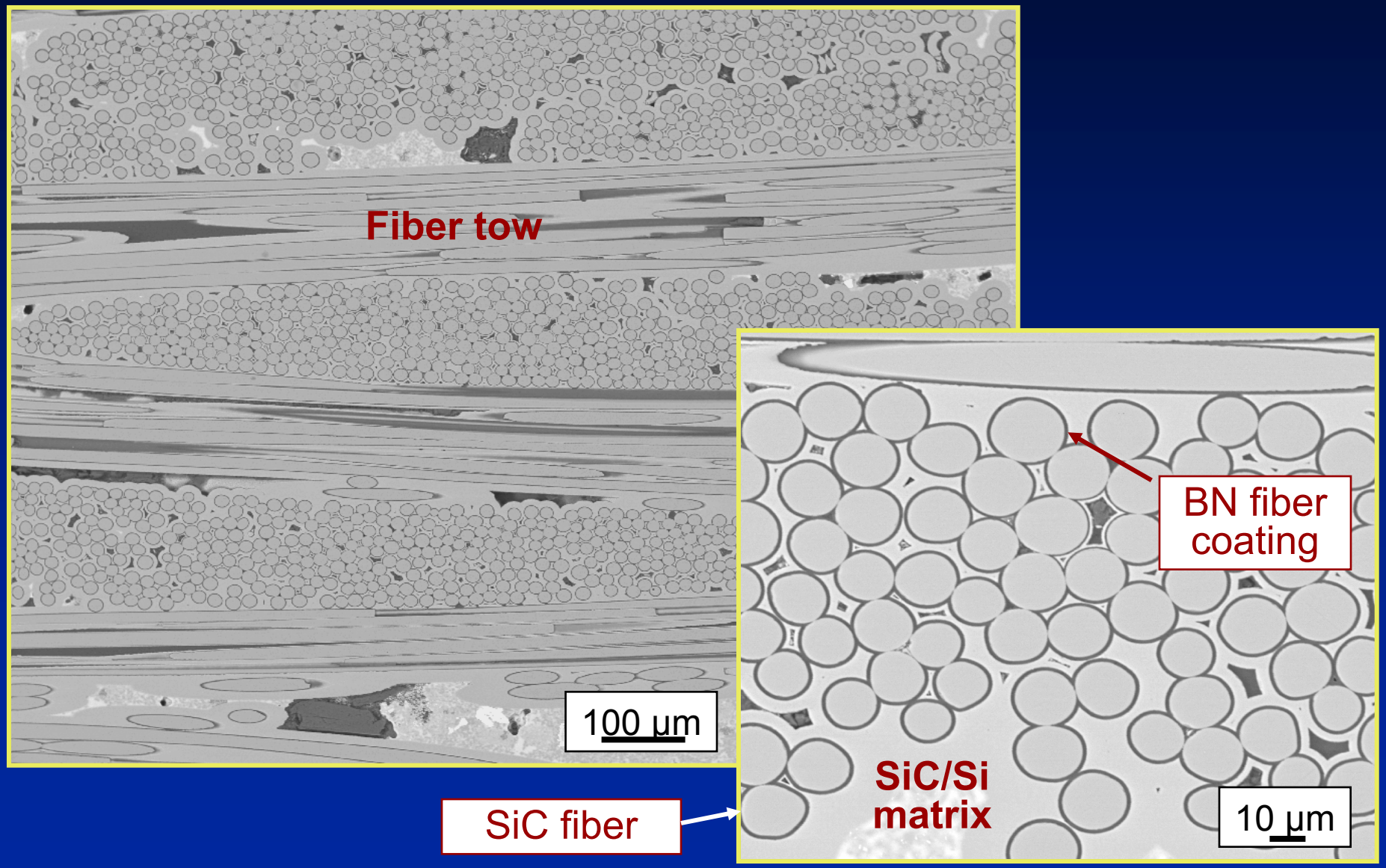
	μm/h
CVD SiC (Keiser Rig):	**0.06**
SiC/SiC (Keiser Rig):	**0.4**

Work At High H_2O Pressures Motivated By Use Of Fiber-Reinforced Ceramic Composites As Combustor Liners

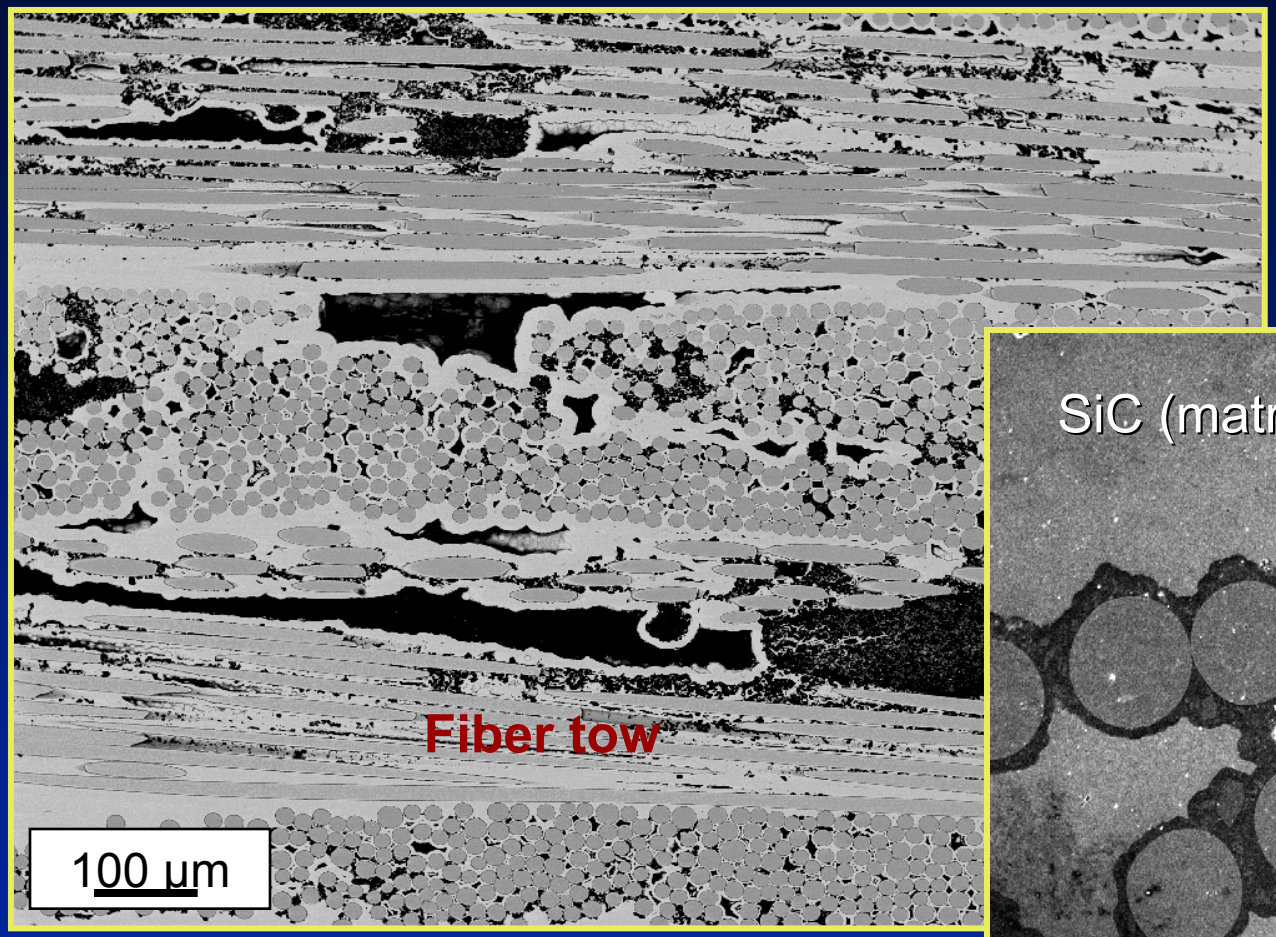
Inner (33 cm diam) and outer (76 cm diam) liners for Solar Turbines Centaur Engines

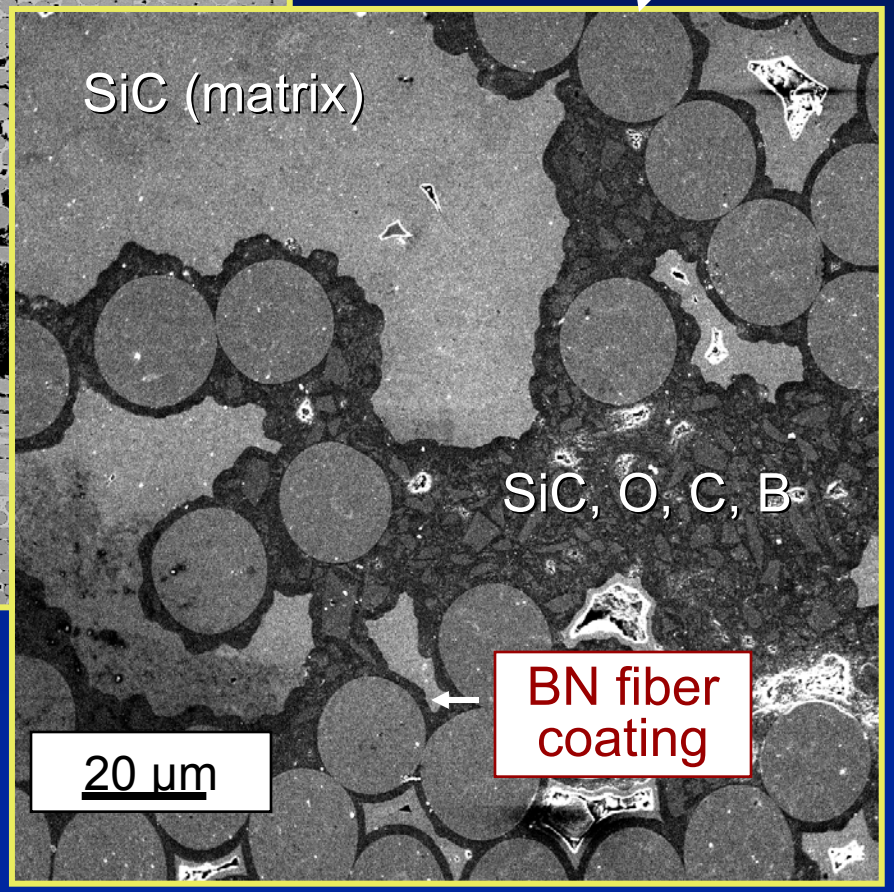
- High-temperature, low NO_x operation
- Graceful failure relative to monolithic ceramics

Melt-Infiltrated (MI) SiC/BN/SiC



Chemical Vapor Infiltrated (CVI) SiC/BN/SiC

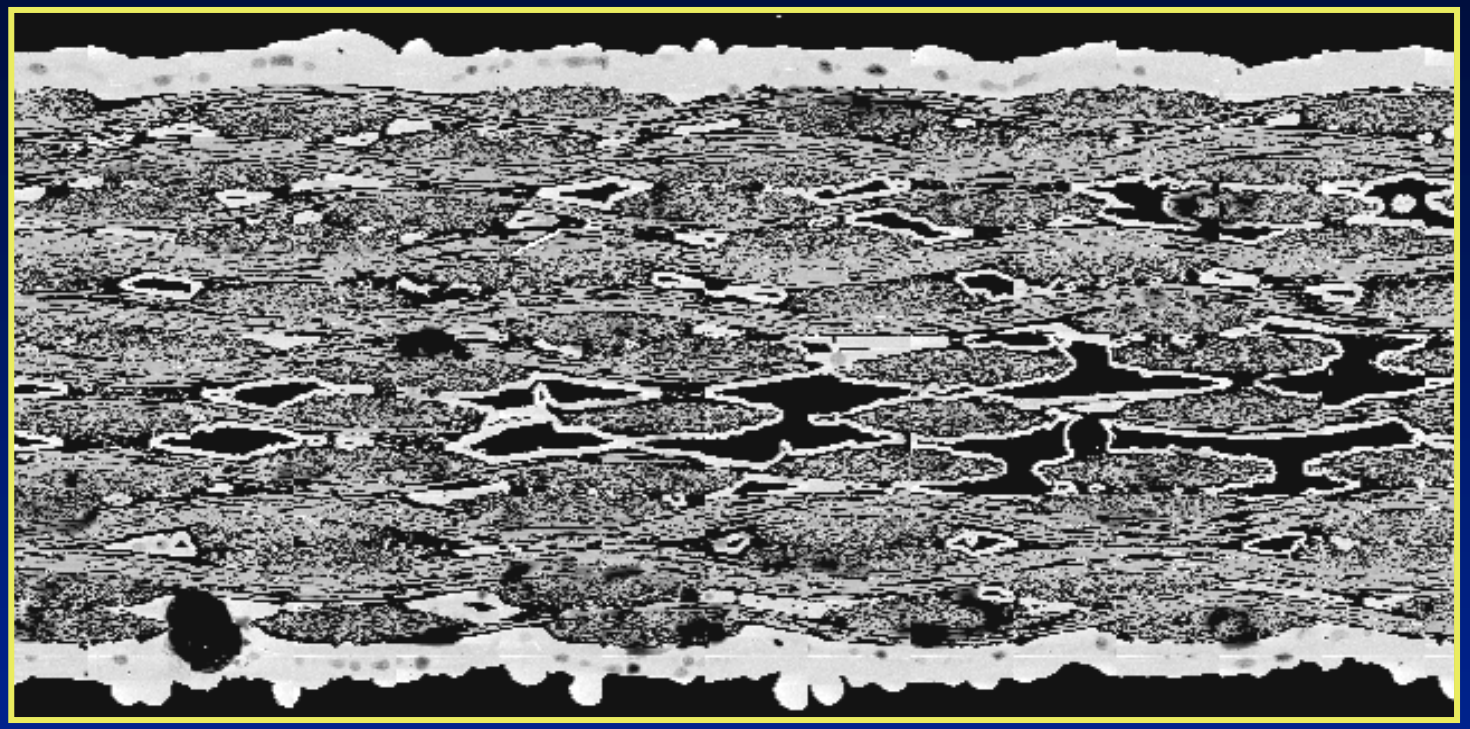




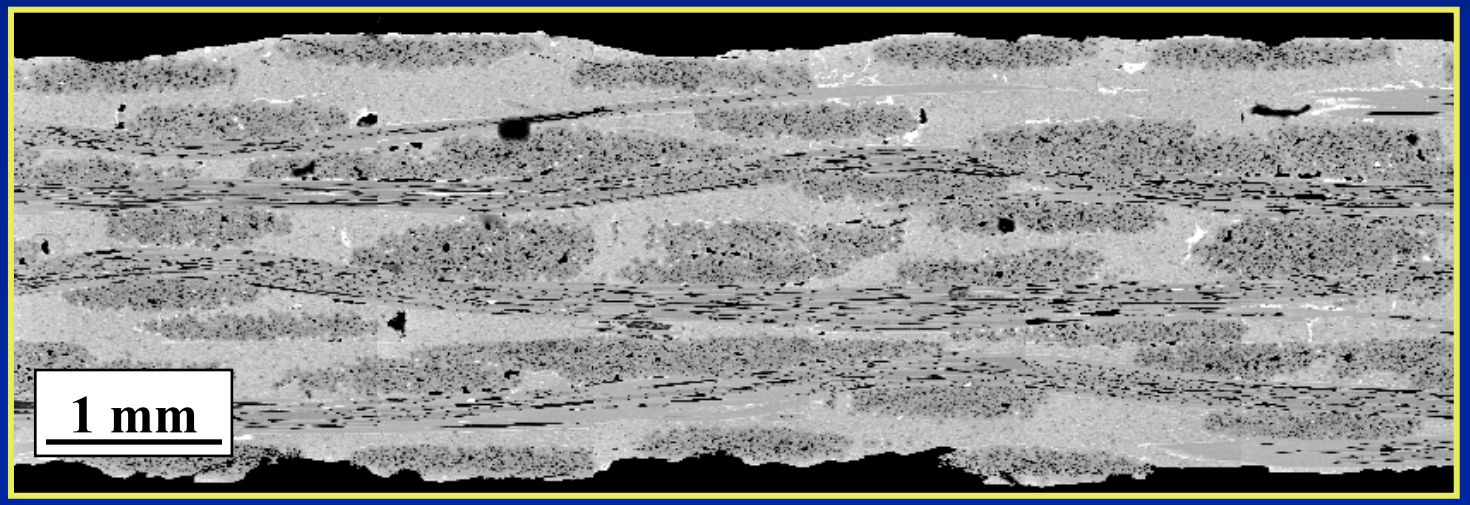
- B-containing filler
- no free Si in matrix

There Was A Substantial Difference In Density Between CVI And MI SiC/BN/SiC

CVI

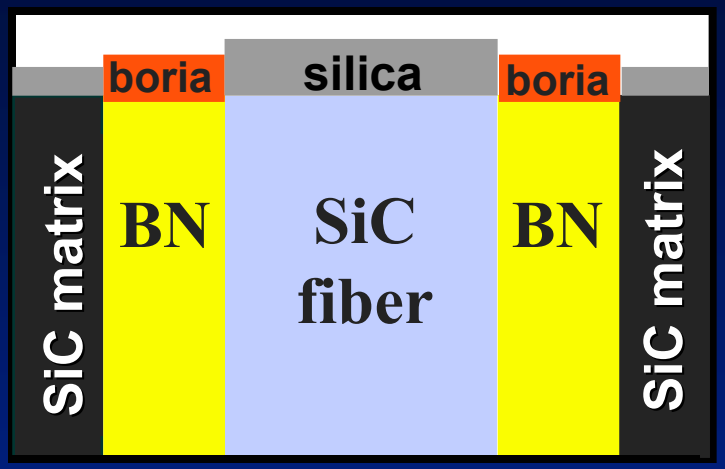


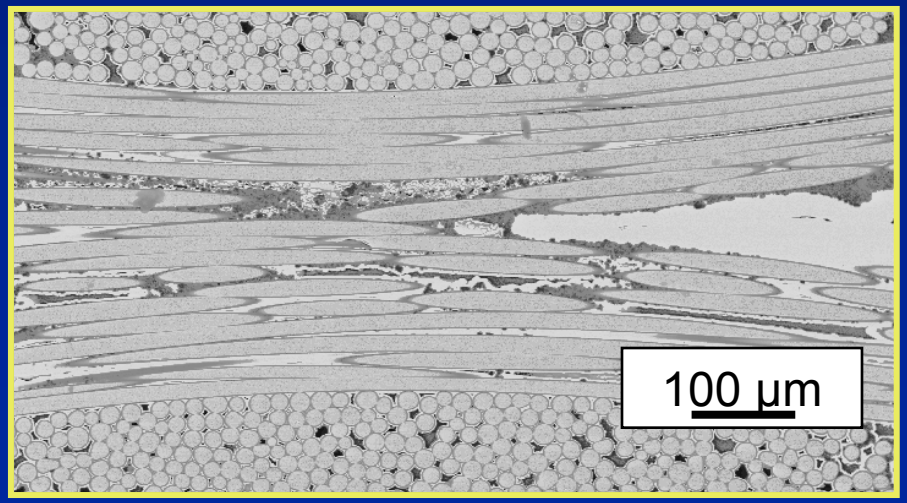
MI



Composite Characteristics

- SiC of various purities (matrix, fiber)
- Si (MI matrix)
- BN fiber coating
- B-containing constituents in matrix
- Other additives
- Interconnected porosity
- Extended interfaces





There Are Multiple Oxidation Reactions

With Oxygen

$$Si + O_2\ (g) = SiO_2$$
$$SiC + 3/2O_2\ (g) = SiO_2 + CO\ (g)$$
$$2BN + 3/2O_2\ (g) = B_2O_3\ (l) + N_2\ (g)$$

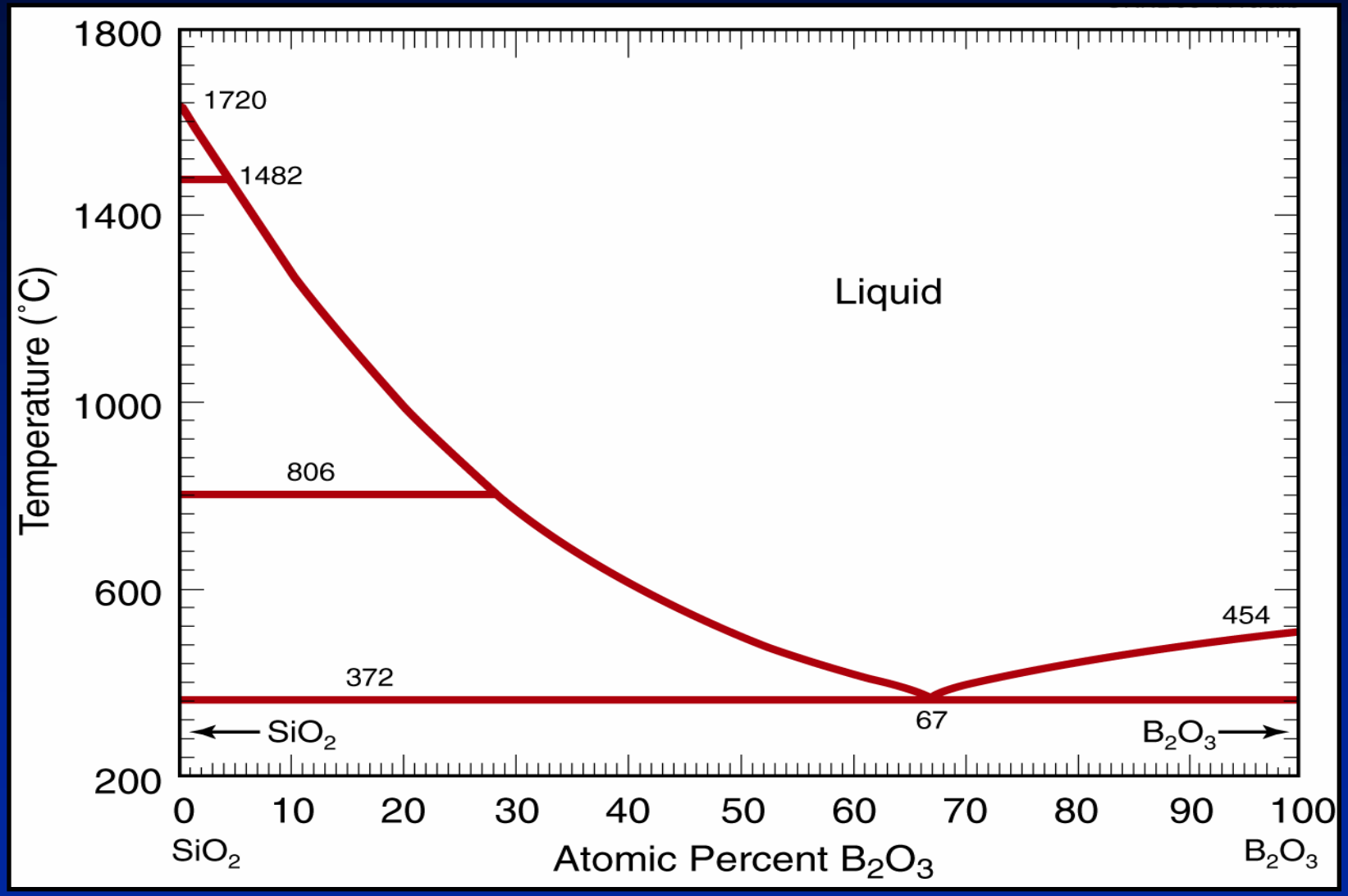
With Water Vapor

$$Si + 2H_2O\ (g) = SiO_2 + 3H_2\ (g)$$
$$SiC + 3H_2O\ (g) = SiO_2 + CO\ (g) + 3H_2\ (g)$$

Between Oxides and Water Vapor

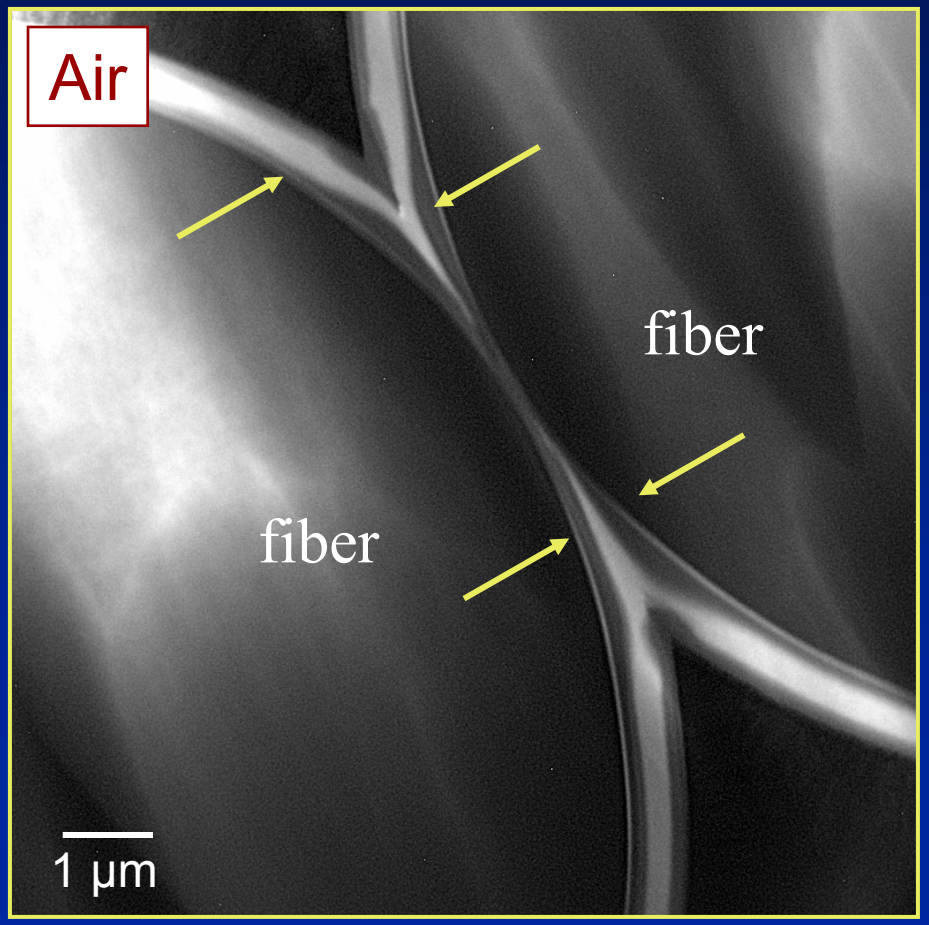
$$SiO_2 + 2H_2O = Si(OH)_4\ (g)$$
$$B_2O_3\ (l) + H_2O\ (g) = 2HBO_2\ (g)$$

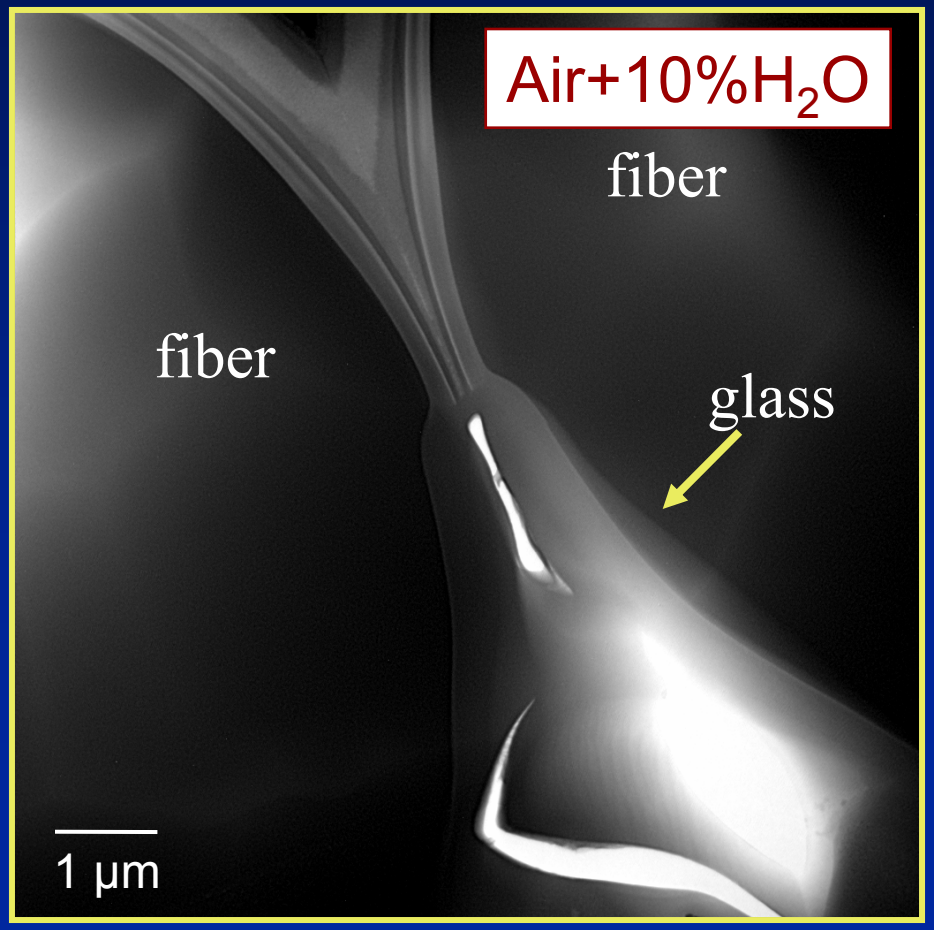
Reaction Of Oxidation Products Leads To Glass Formation



Many Of These Reactions Can Be Observed Even At Low H_2O Pressures And Short Times

CVI SiC/BN/SiC, 950°C, 8 h

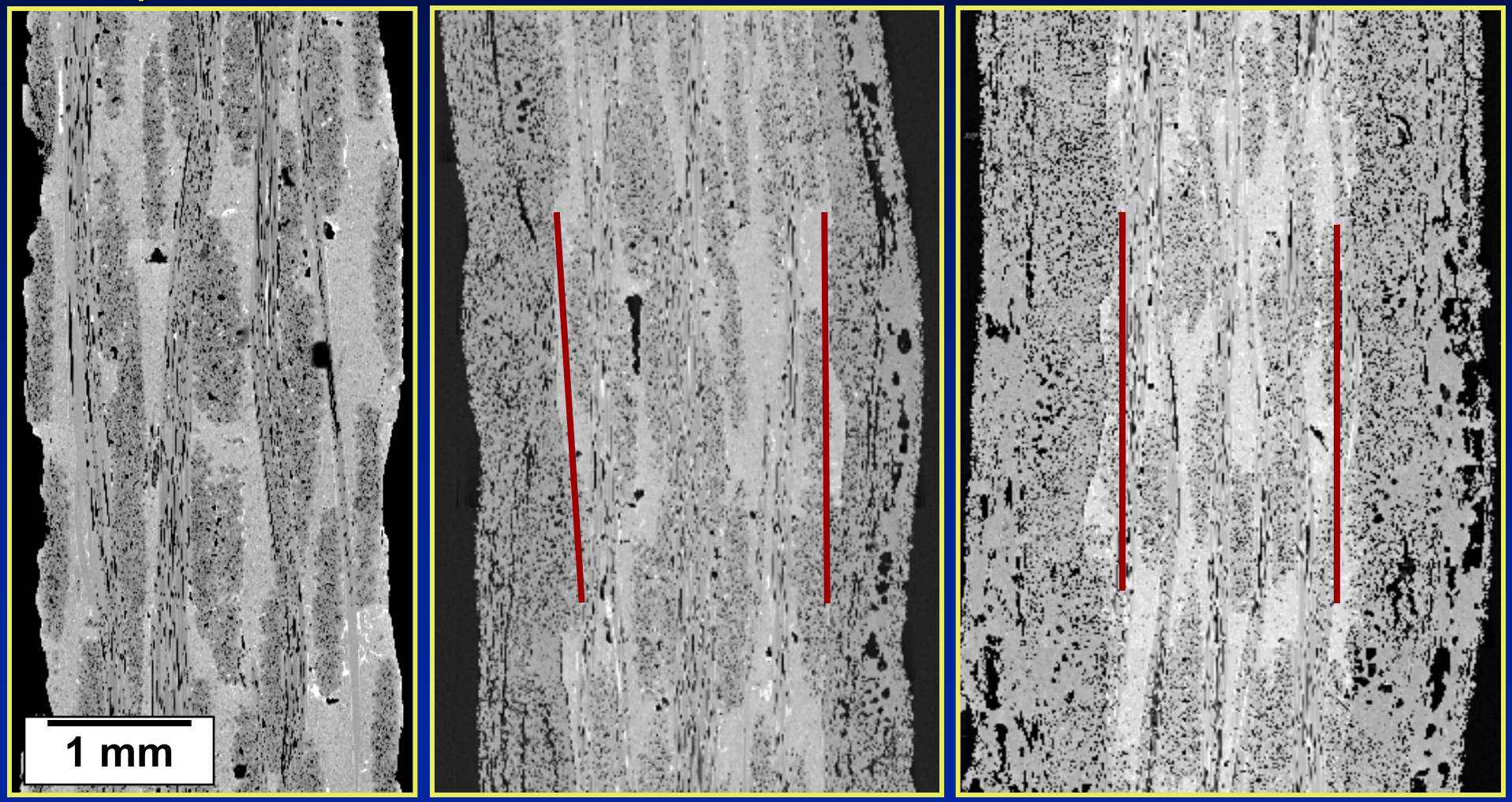




At High H_2O Pressure, Accelerated Composite Recession/Damage Was Observed

MI SiC/BN/SiC, 1200°C, 1.5 atm H_2O

As-processed | 1500 h | 2500 h



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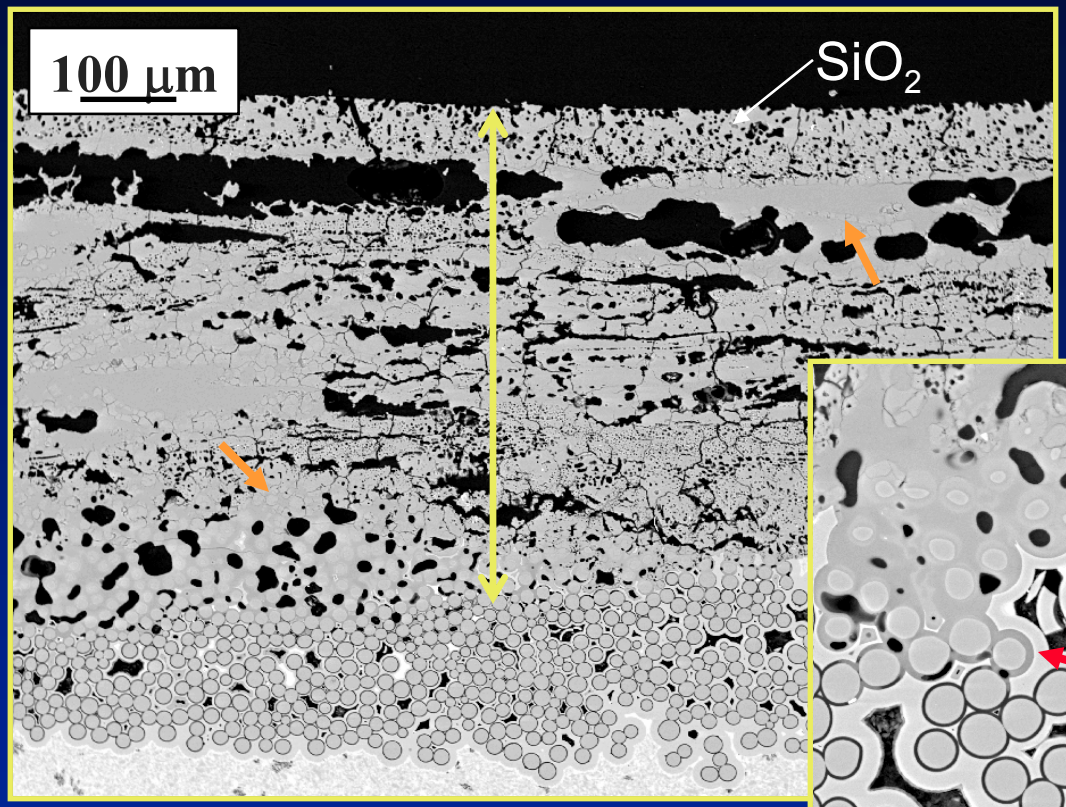
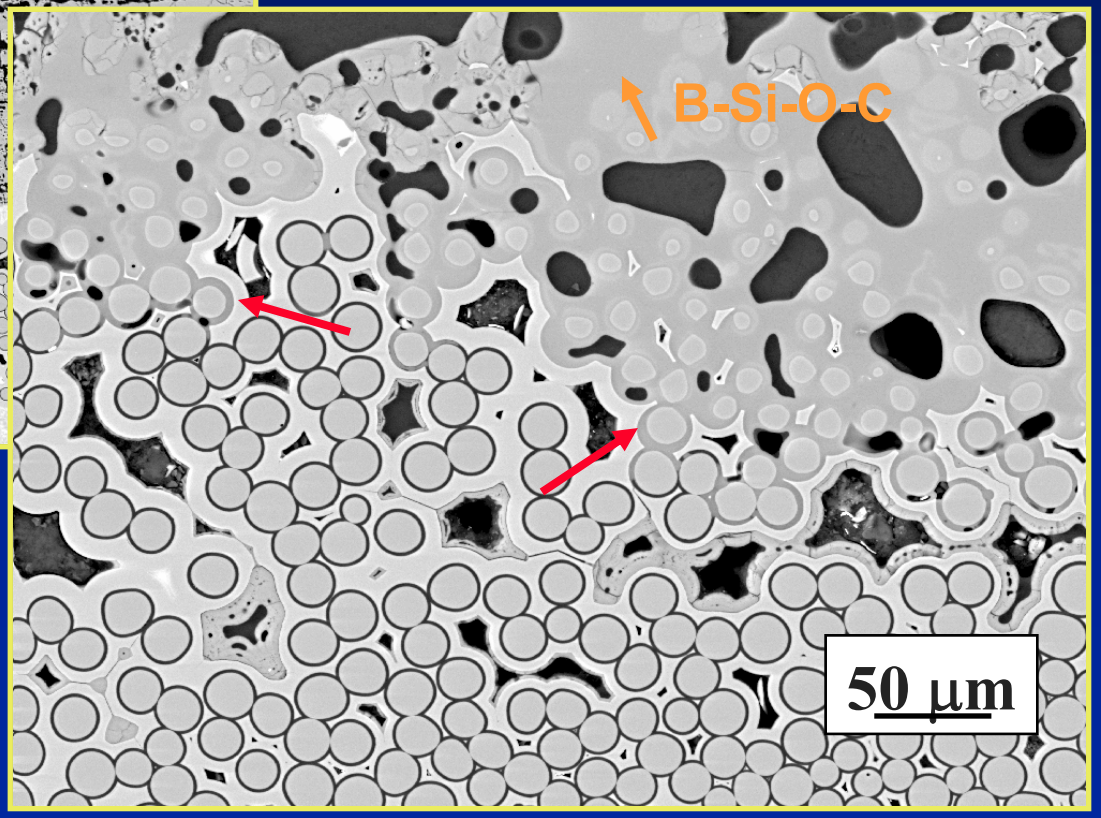
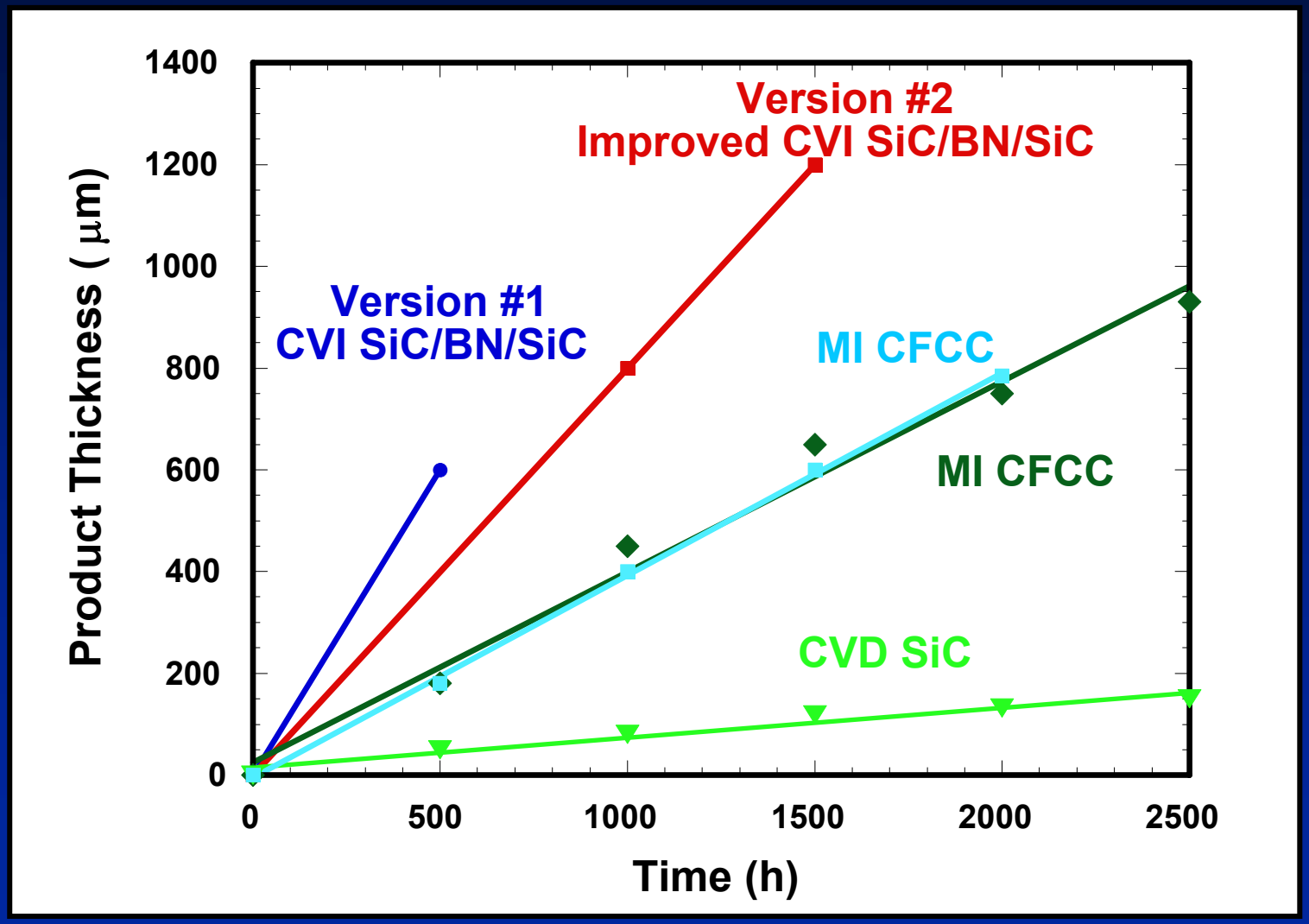


MI SiC/BN/SiC
1200°C, 1000 h
1.5 atm H_2O

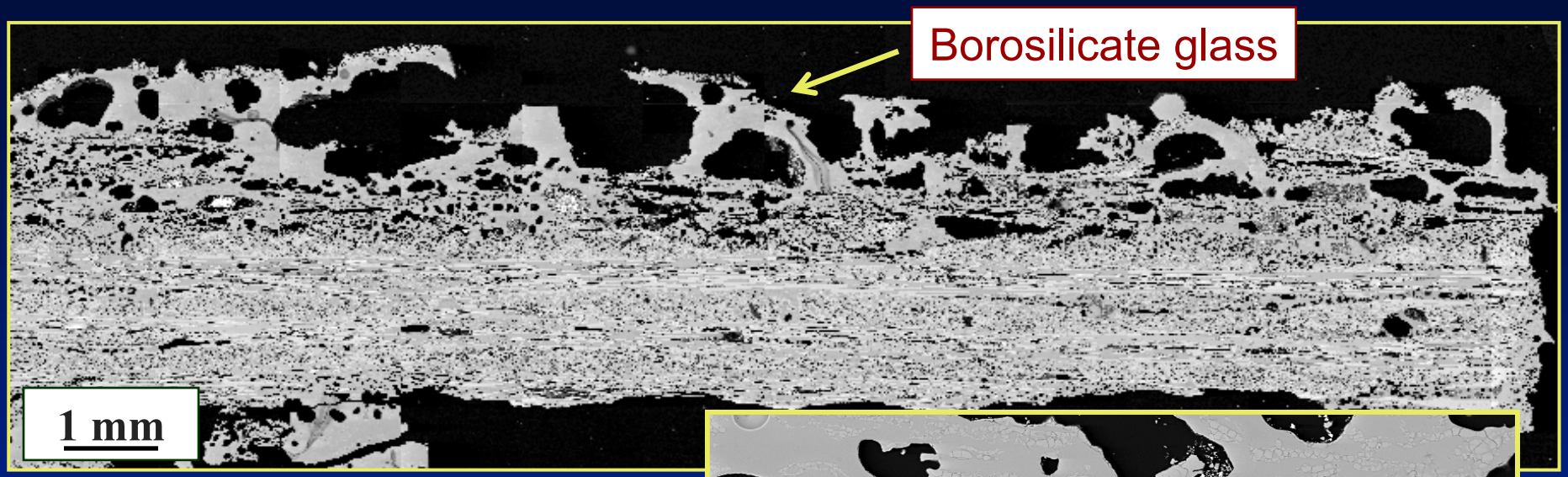


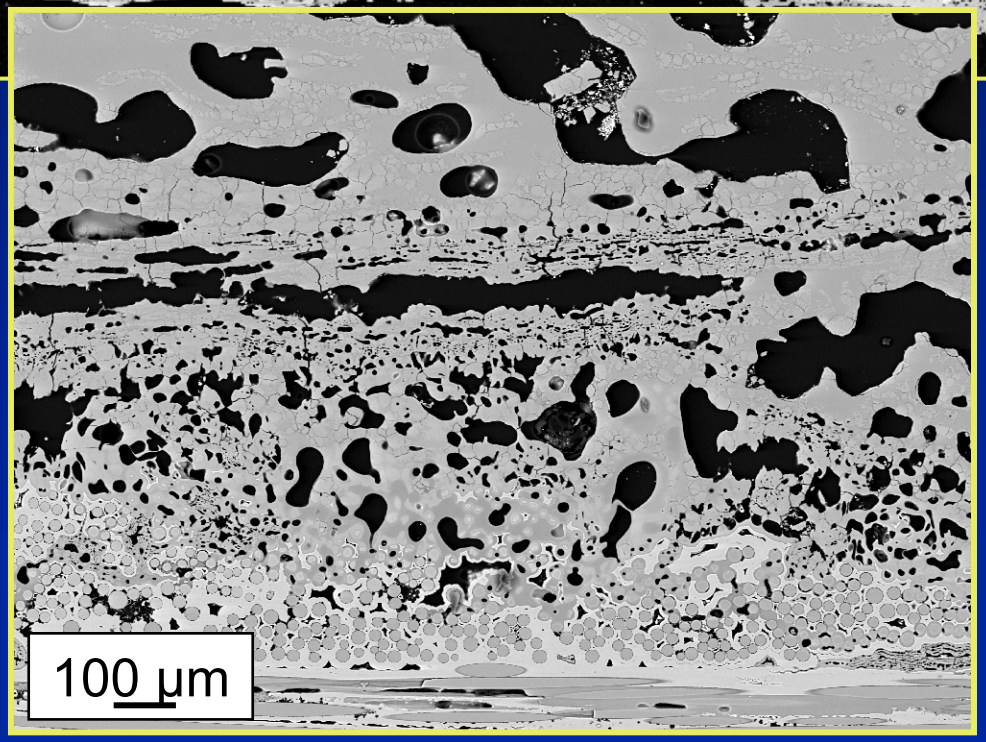
High Rates Of Oxidative Degradation Were Measured

1200°C, 1.5 atm H_2O



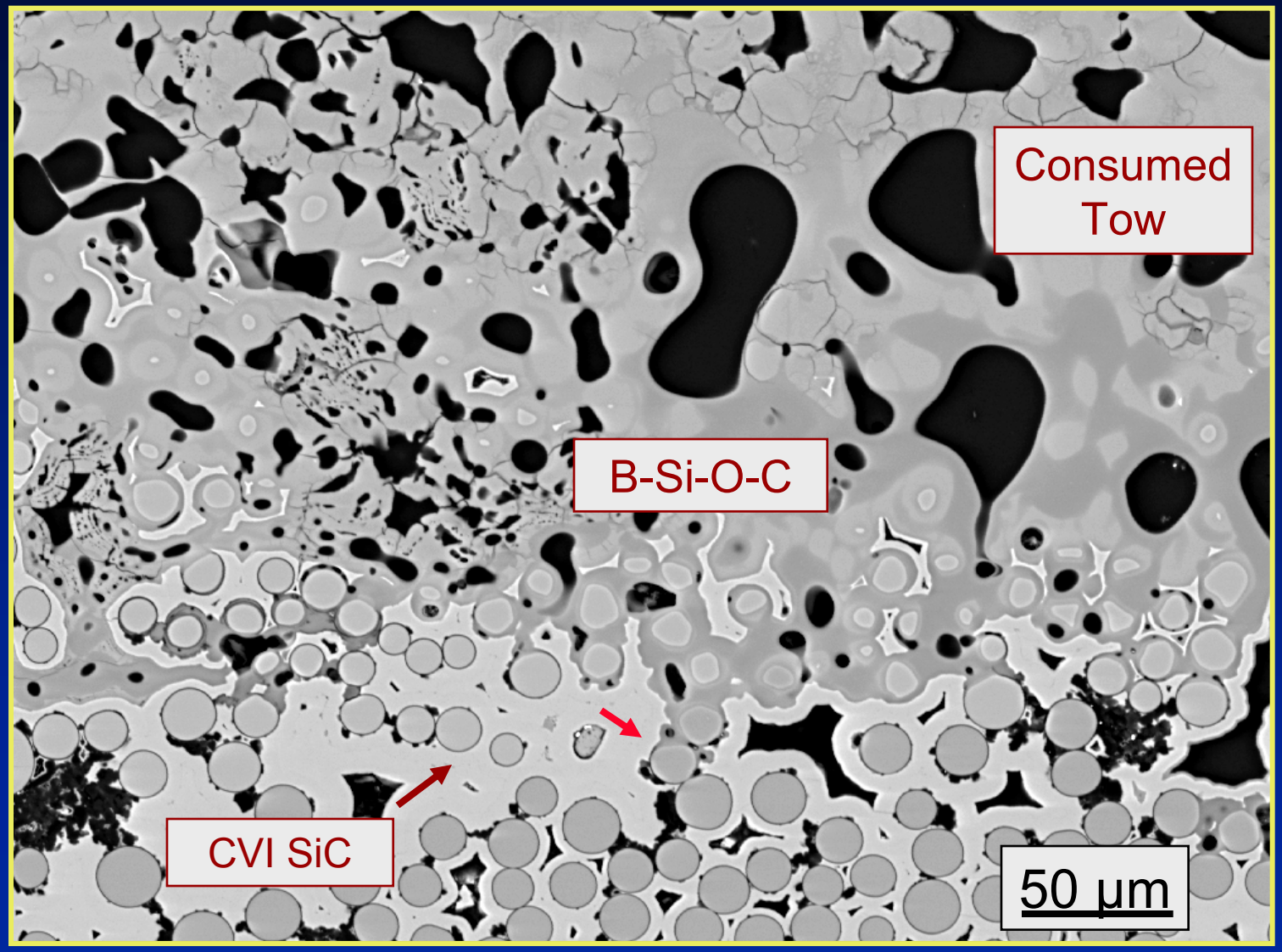
CVI SiC/BN/SiC Showed Greater Degradation





1200°C,1500 h
1.5 atm H_2O

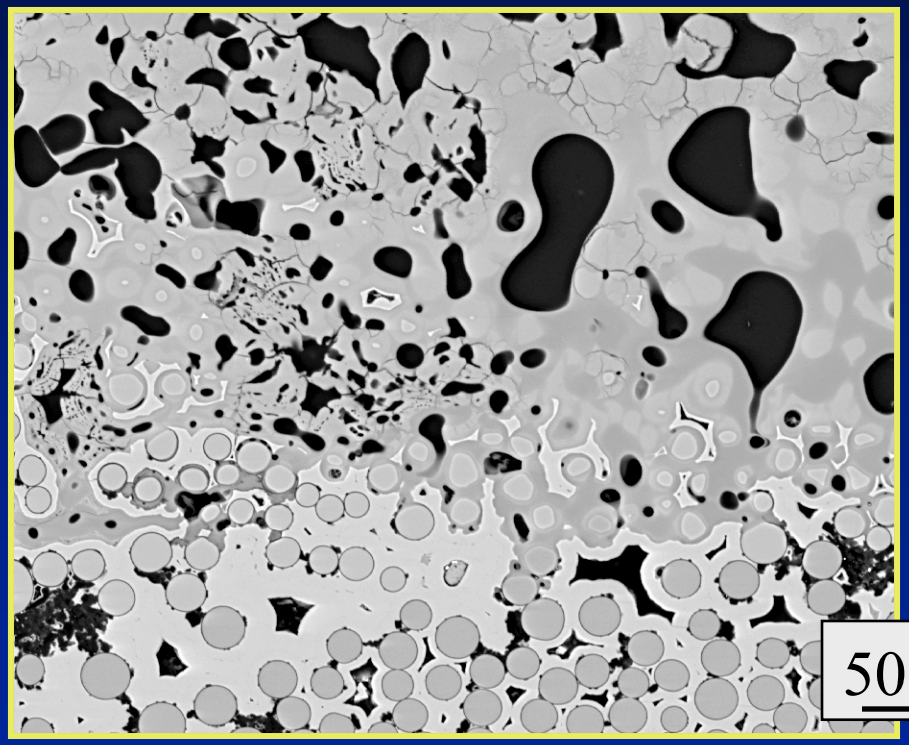
CVI SiC/BN/SiC Showed Greater Degradation, But Same Type Of Reactions As MI Composite



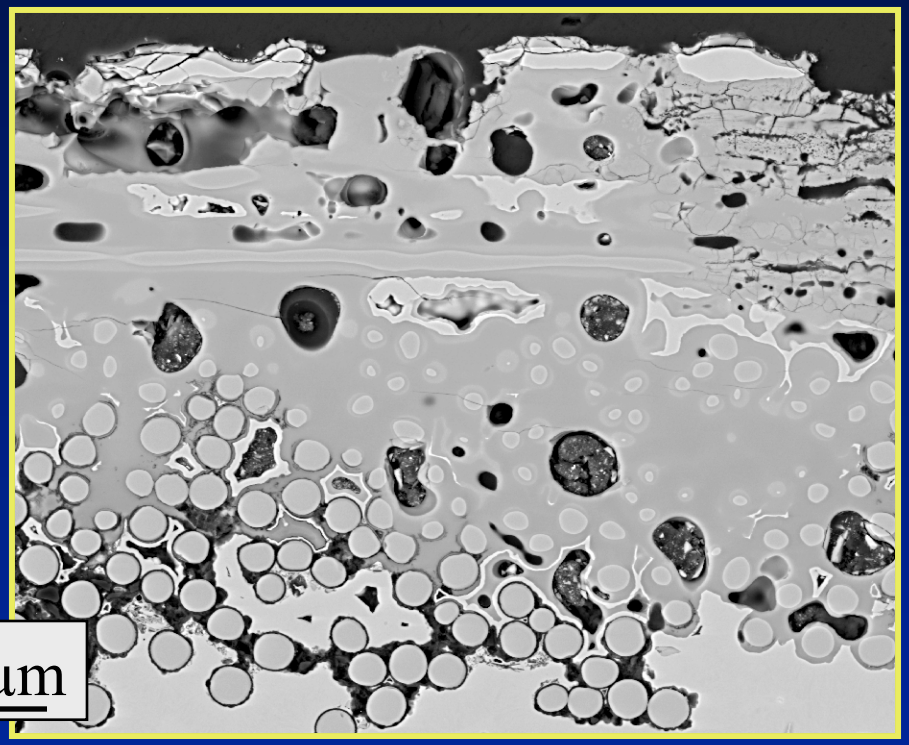
1200°C, 1500 h, 1.5 atm H_2O

Composite Damage Observed In Lab Exposures Was Very Much Like That Of Actual Combustor Liners

Lab Exposure



Engine Test

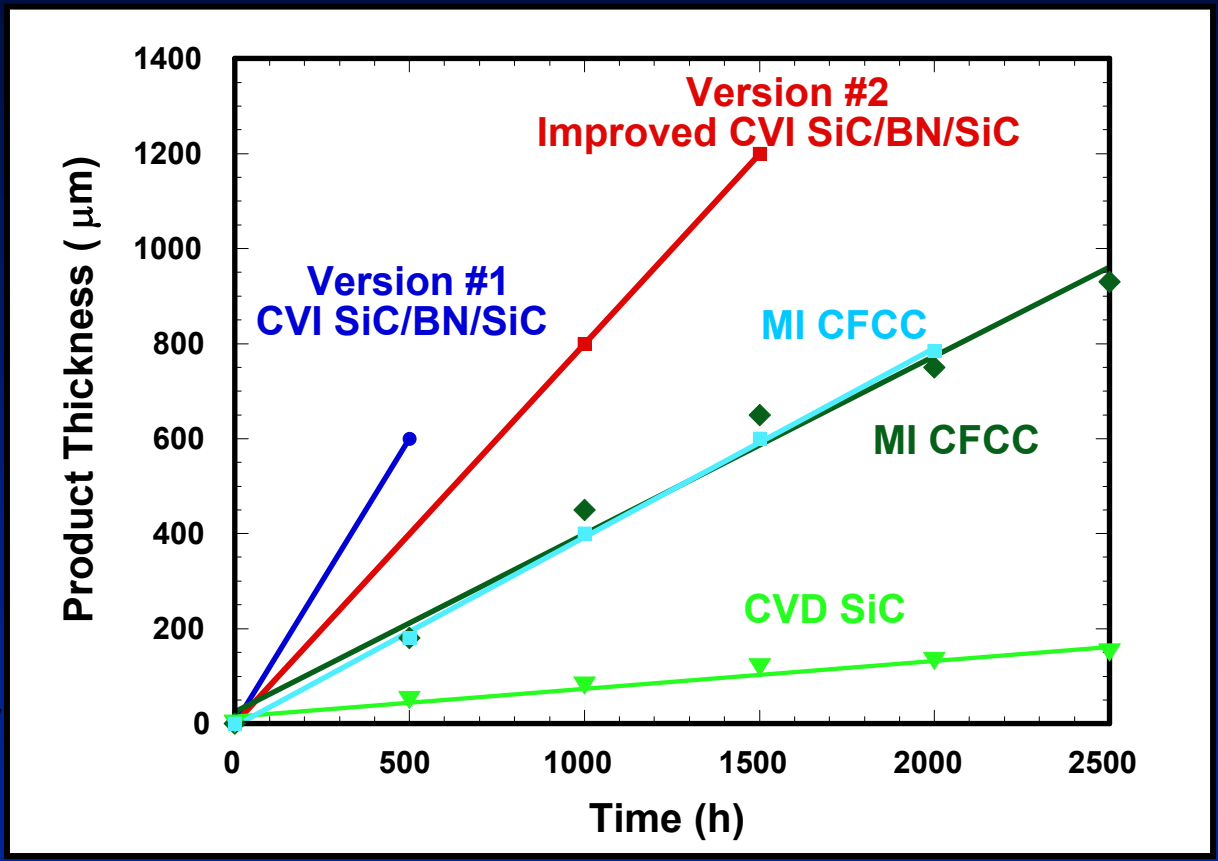


CVI SiC/BN/SiC, 1200°C, 1.5 atm H_2O

Why?

? Do composites degrade more rapidly than monolithics

Multiple constituents leading to multiple reactions with greater degradation rates



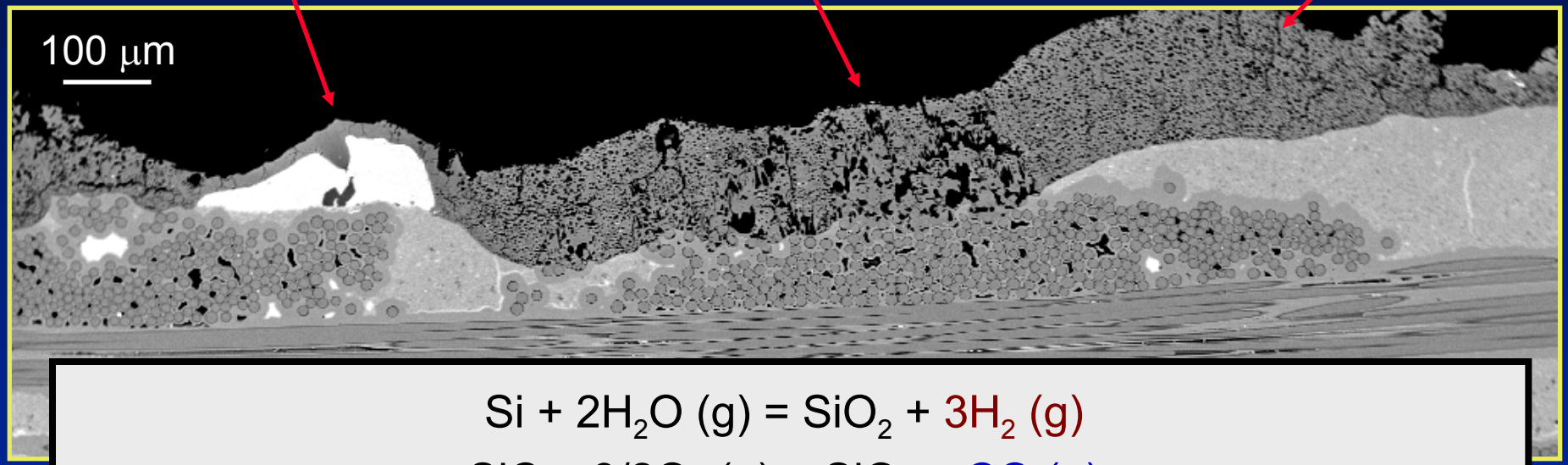
1200°C, 1.5 atm H_2O

Effects Of Various Constituents On Oxidation Rate And Mode Of Degradation

Modest Oxidation
Silicon

Rapid Attack
fiber + CVI SiC + BN

Greater Reaction
Si + SiC + impurities



$$Si + 2H_2O\ (g) = SiO_2 + 3H_2\ (g)$$

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

$$SiC + 3H_2O\ (g) = SiO_2 + CO\ (g) + 3H_2\ (g)$$

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

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

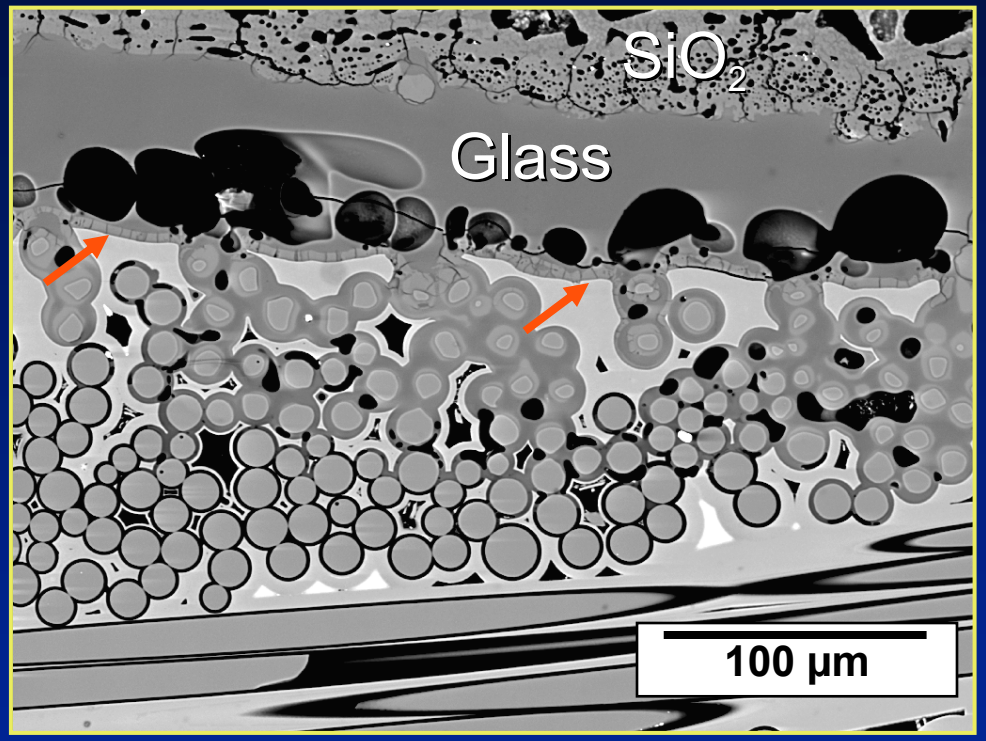
$B_2O_3 + SiO_2$ = borosilicate glass

MI SiC/BN/SiC, 1200°C, 500 h, 1.5 atm H_2O

Composite Behavior Can Be Understood On Basis Of Multiple Reactions And Composite Constituents

- SiC of various purities (matrix, fiber)
- Si of various purities (MI matrix)
- BN fiber coating
- B-containing constituents in matrix
- Other additives

1200°C, 500 h, Air-1.5 atm H_2O (10 atm)

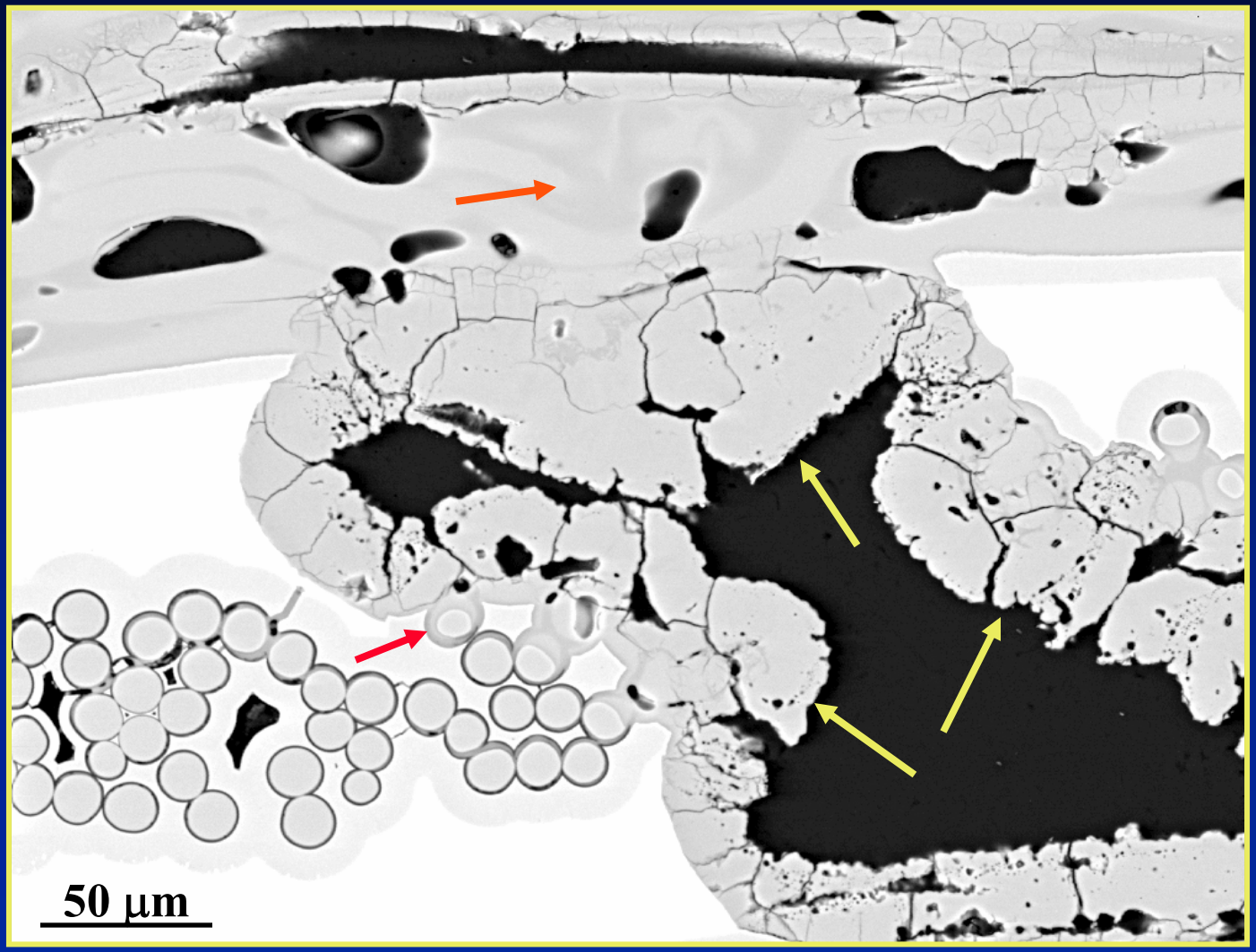


MI SiC/BN/SiC

Degradation Can Be Understood On Basis Of Multiple Reactions And Composite Constituents & Structure

- SiC of various purities (matrix, fiber)
- Si of various purities (matrix)
- B-containing constituents (fiber coatings, matrix)
- Other additives
- Interconnected porosity

Oxidation Within Sub-Surface Porosity

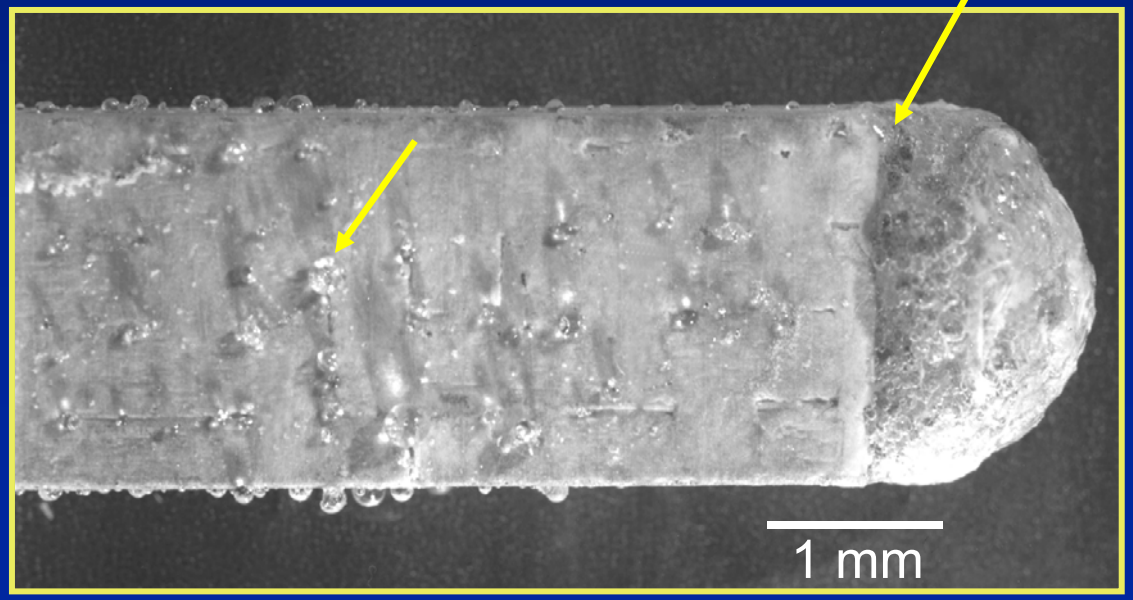


MI SiC/BN/SiC, 1200°C, 1000 h, 1.5 atm H_2O

Degradation Can Be Understood On The Basis Of Multiple Reactions As Well As Composite Structure

- SiC of various purities (matrix, fiber)
- Si of various purities (matrix)
- B-containing constituents (fiber coatings, matrix)
- Other additives
- Interconnected porosity
- Extended interfaces

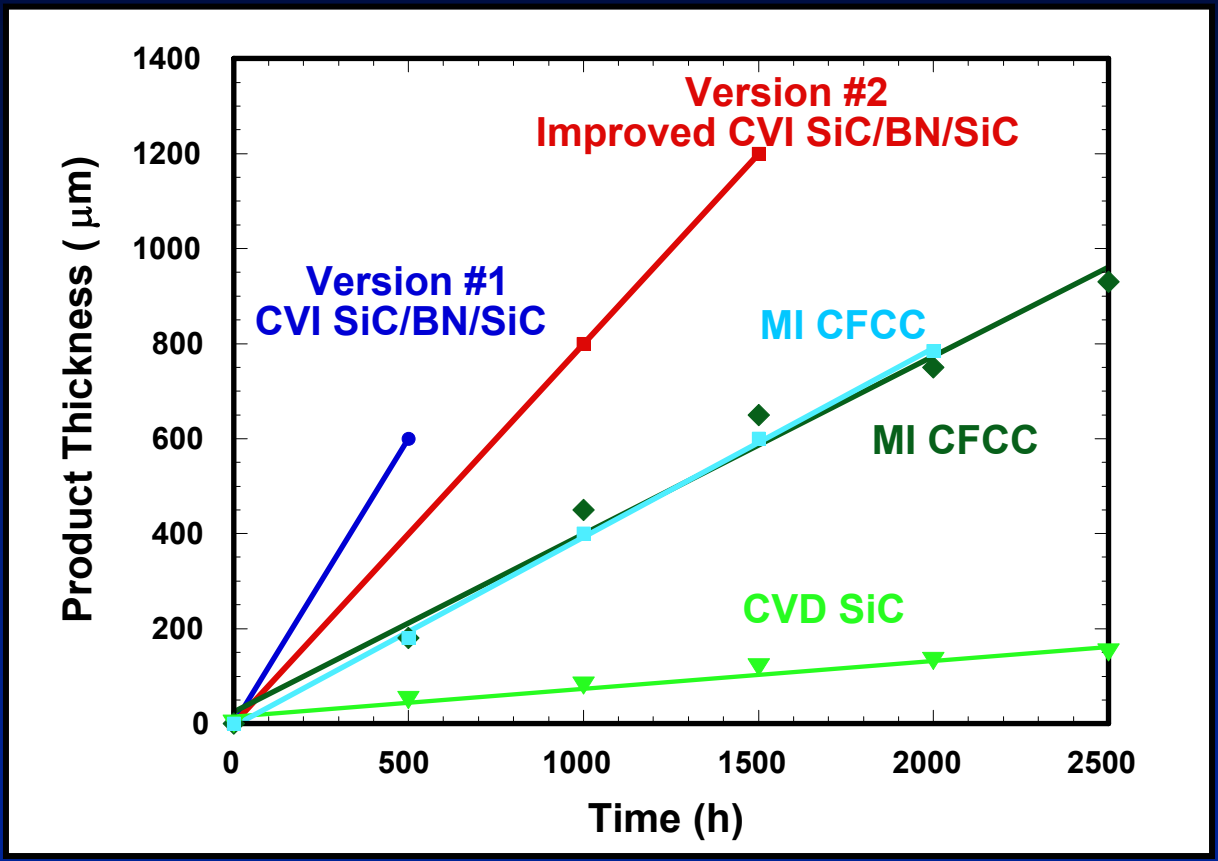
1200°C, 500 h,
Air-1.5 atm H_2O
(10 atm)
CVI SiC/BN/SiC



Why?

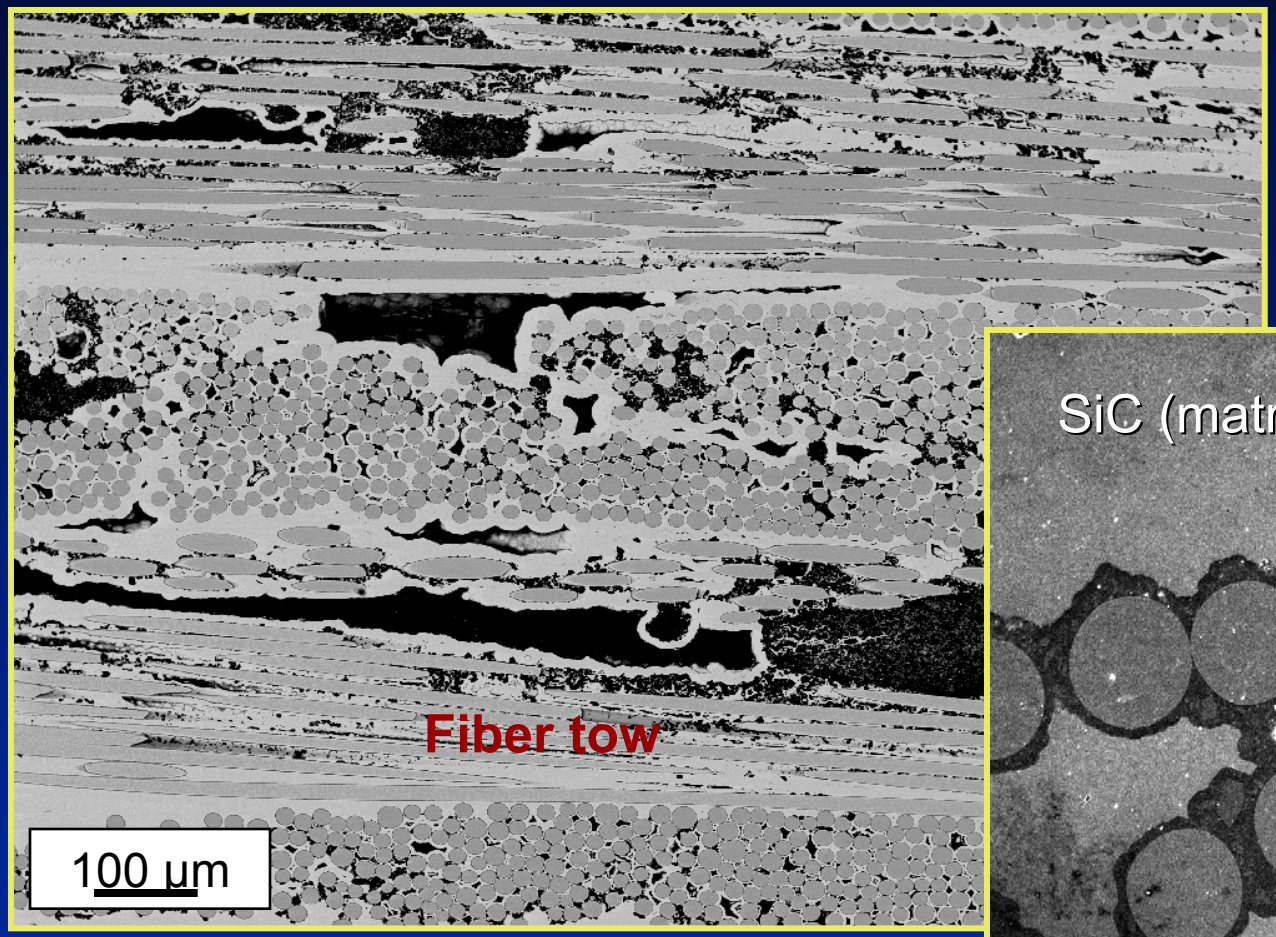
? Do composites degrade more rapidly than monolithics

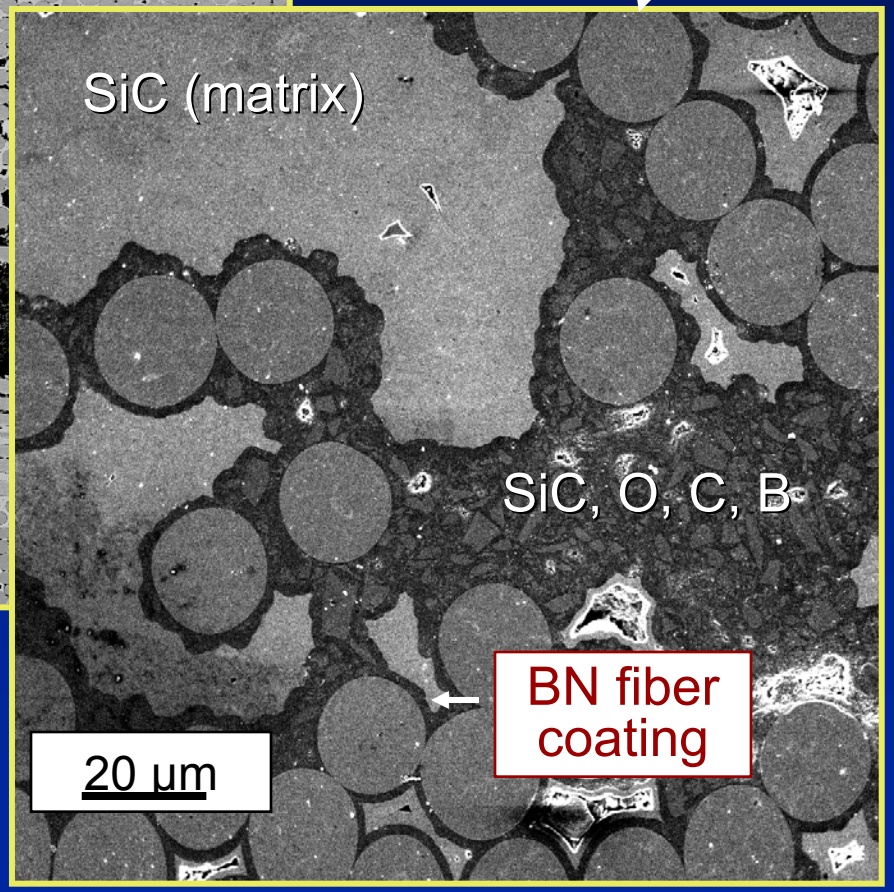
? Is CVI SiC/BN/SiC more susceptible than MI SiC/BN/SiC
- —higher B content
- —lower density



1200°C, 1.5 atm H_2O

Chemical Vapor Infiltrated (CVI) SiC/BN/SiC

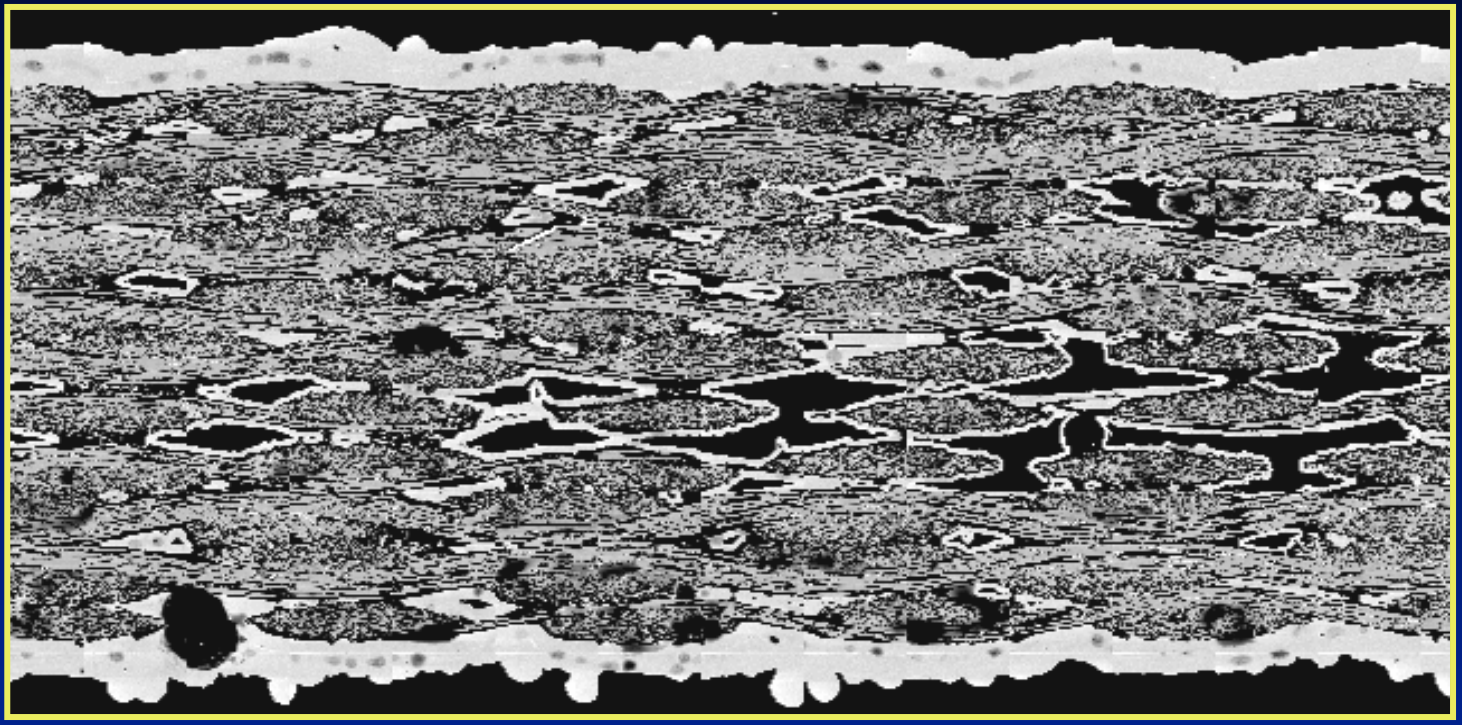




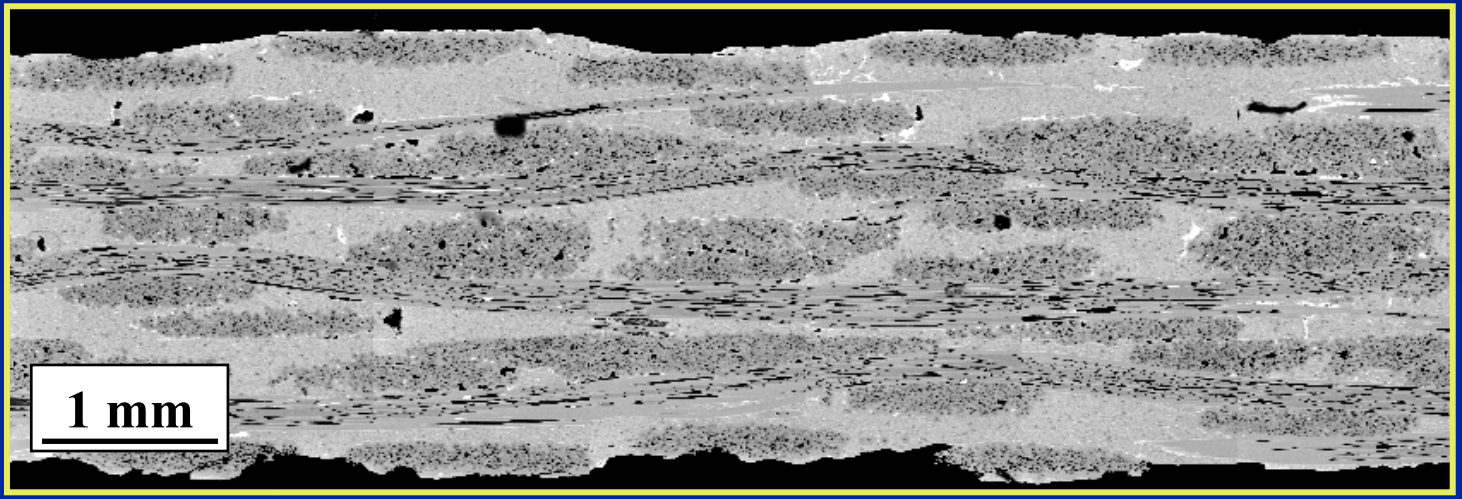
- B-containing filler
- no free Si in matrix

Greater Susceptibility Of CVI SiC/SiC Due To Much Greater Boron Content & More Open Structure

CVI



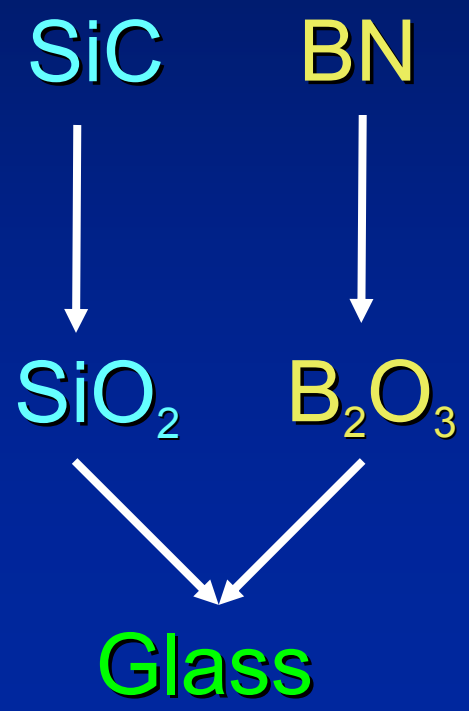
MI



Composite Degradation Not As Sensitive To Gas Velocity Compared To Monolithic Behavior

~1200°C, 1.5 atm H_2O

	μm/h
SiC/BN/SiC (~ 30 m/s):	**0.5**
SiC/BN/SiC (~0.05 m/s):	**0.4**



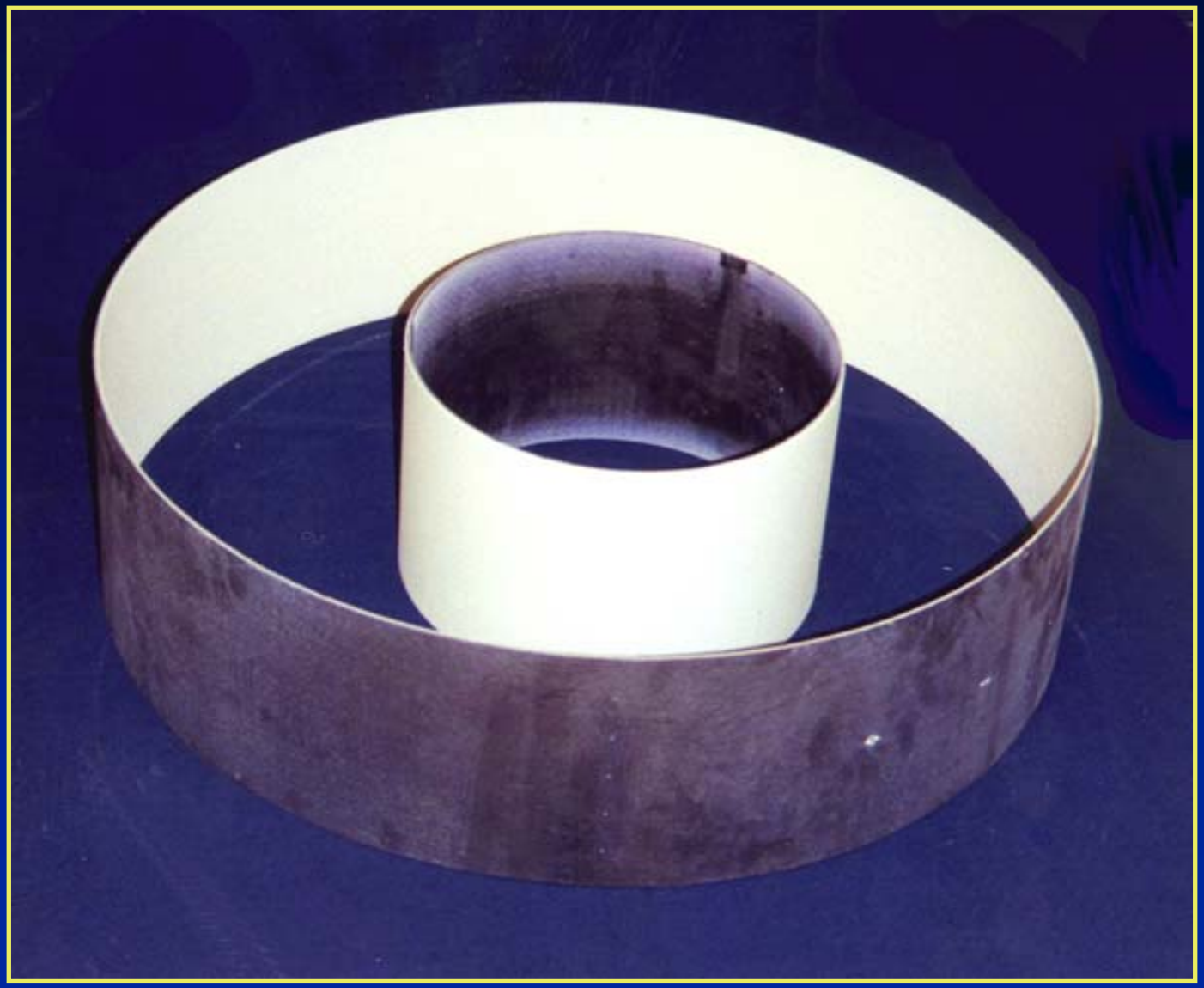
$$SiO_2 + H_2O = Si(OH)_4\ (g)$$
$$B_2O_3\ (l) + H_2O\ (g) = 2HBO_2\ (g)$$

Lack of Velocity Effect Consistent With Multiple Oxidation Reactions And Borosilicate Glass Formation

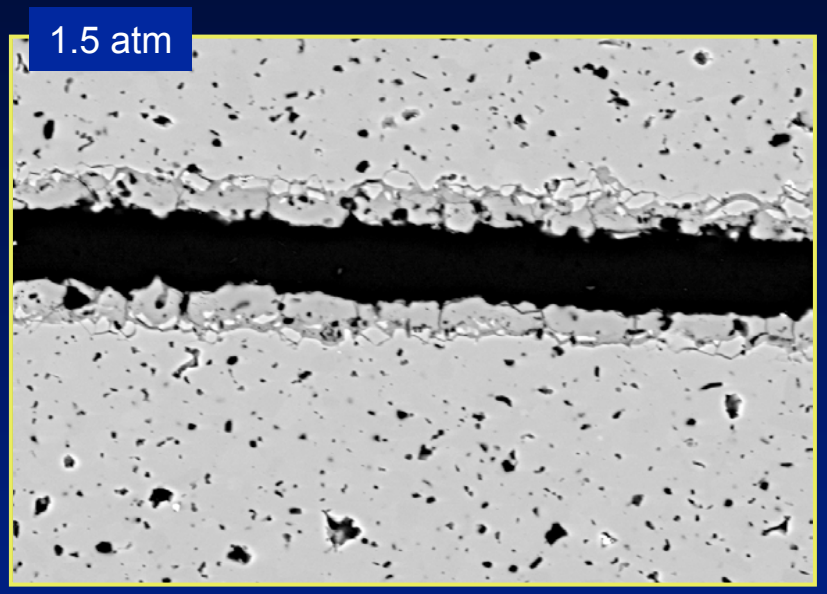
Summary

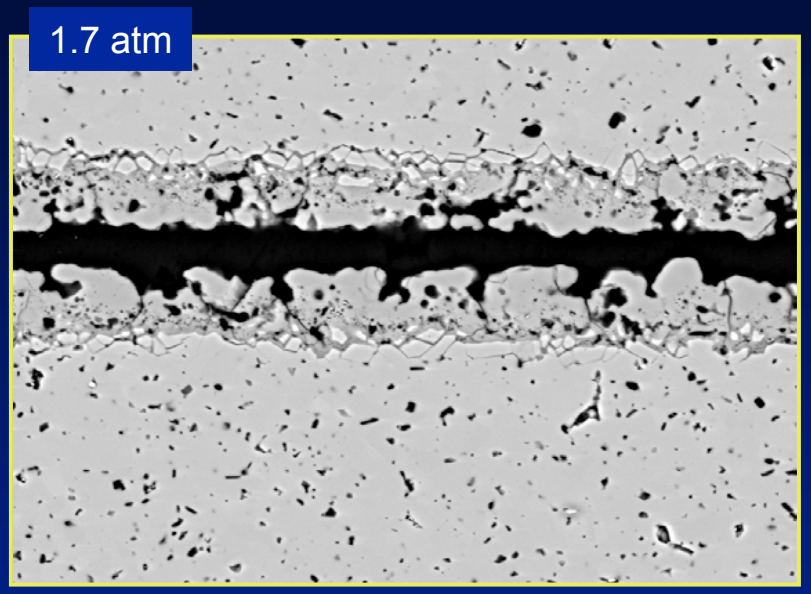
- SiC and SiC-based composites are rapidly attacked in high-temperature environments containing elevated water-vapor pressures (order of 1 atm)
  - Acclerated oxidation of SiC and boron-containing constituents
  - Extensive formation of borosilicate glasses
- Composite degradation will depend on the amounts of the various constituents and how they react with H_2O and interact with each other in this environment
- Protective coatings will be needed for long-term service in high-pressure H_2O environments

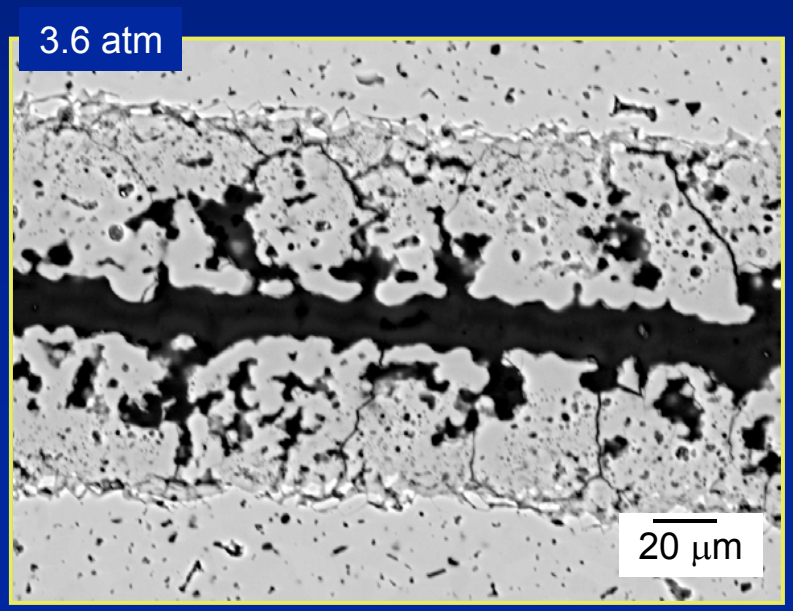
Coated SiC/BN/SiC Combustor Liners Now Have 12,000+ and 6000+ h Of Operation in Turbines



Cristobalite Scale Thickness Increased With Increasing H_2O Pressure

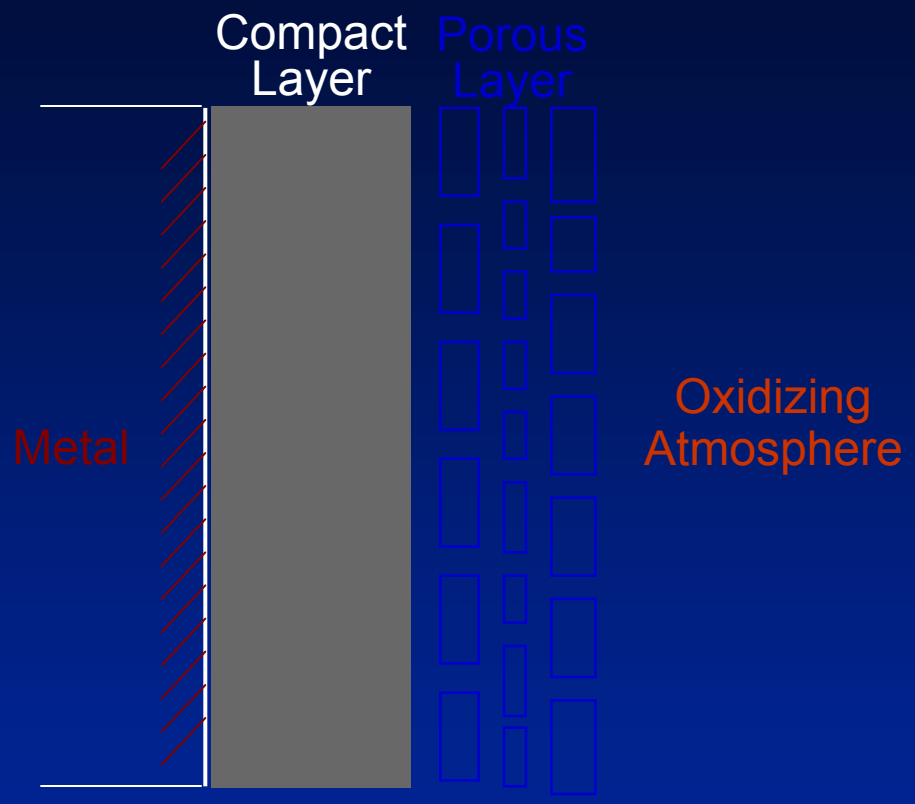






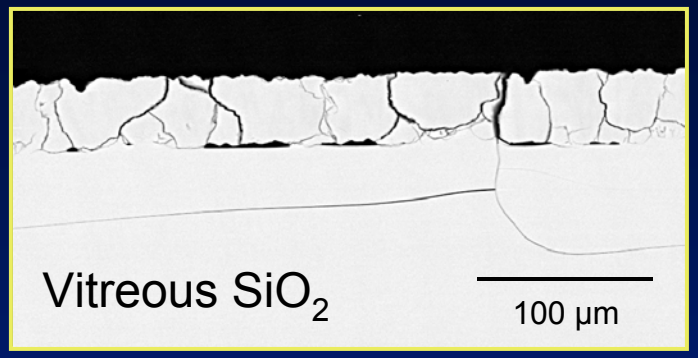
Sintered α-SiC
Exposed at 1260°C
For 100 h

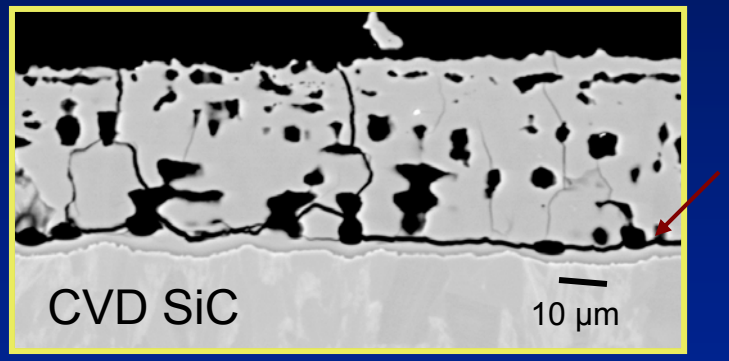
Haycock's Classic Paralinear Treatment Was For Compact Oxide Transforming To Porous Layer

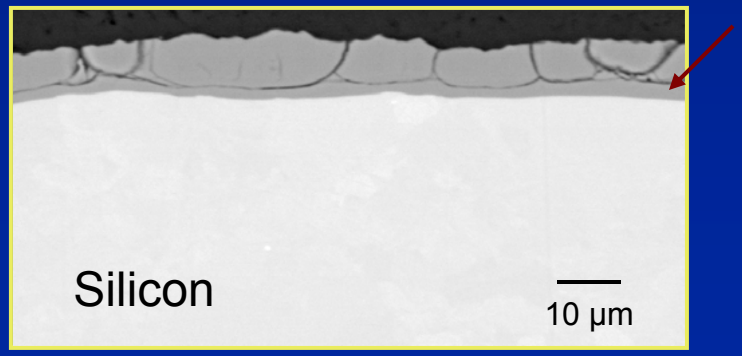


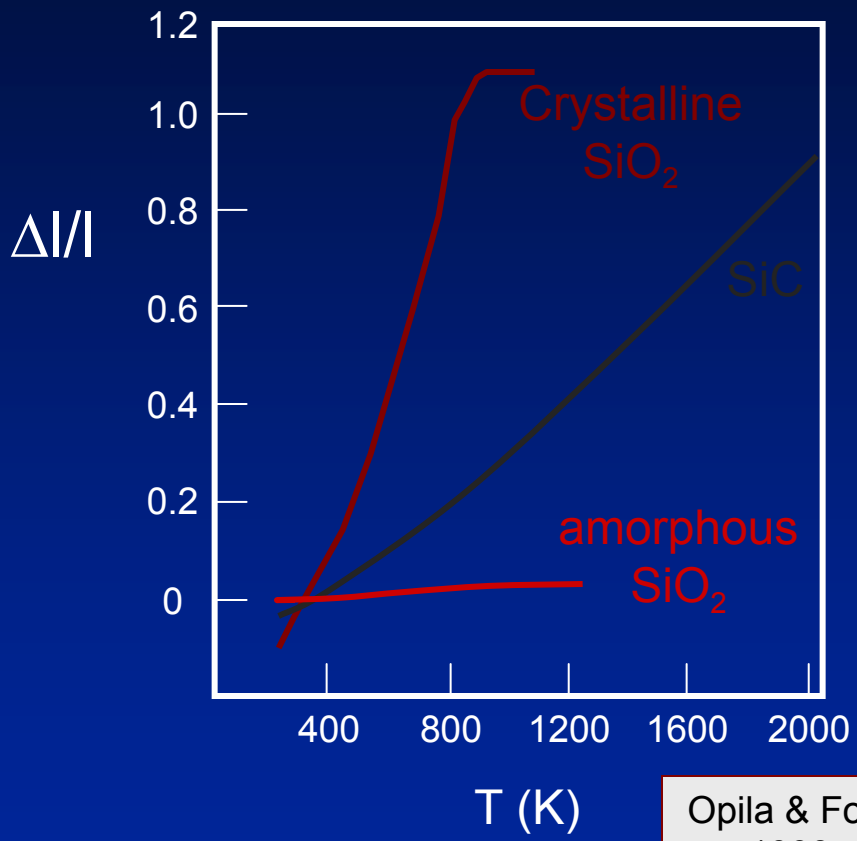
Haycock, 1959

Cracking Of Cristobalite On Vitreous SiO_2 Can Be Explained By CTE Mismatch





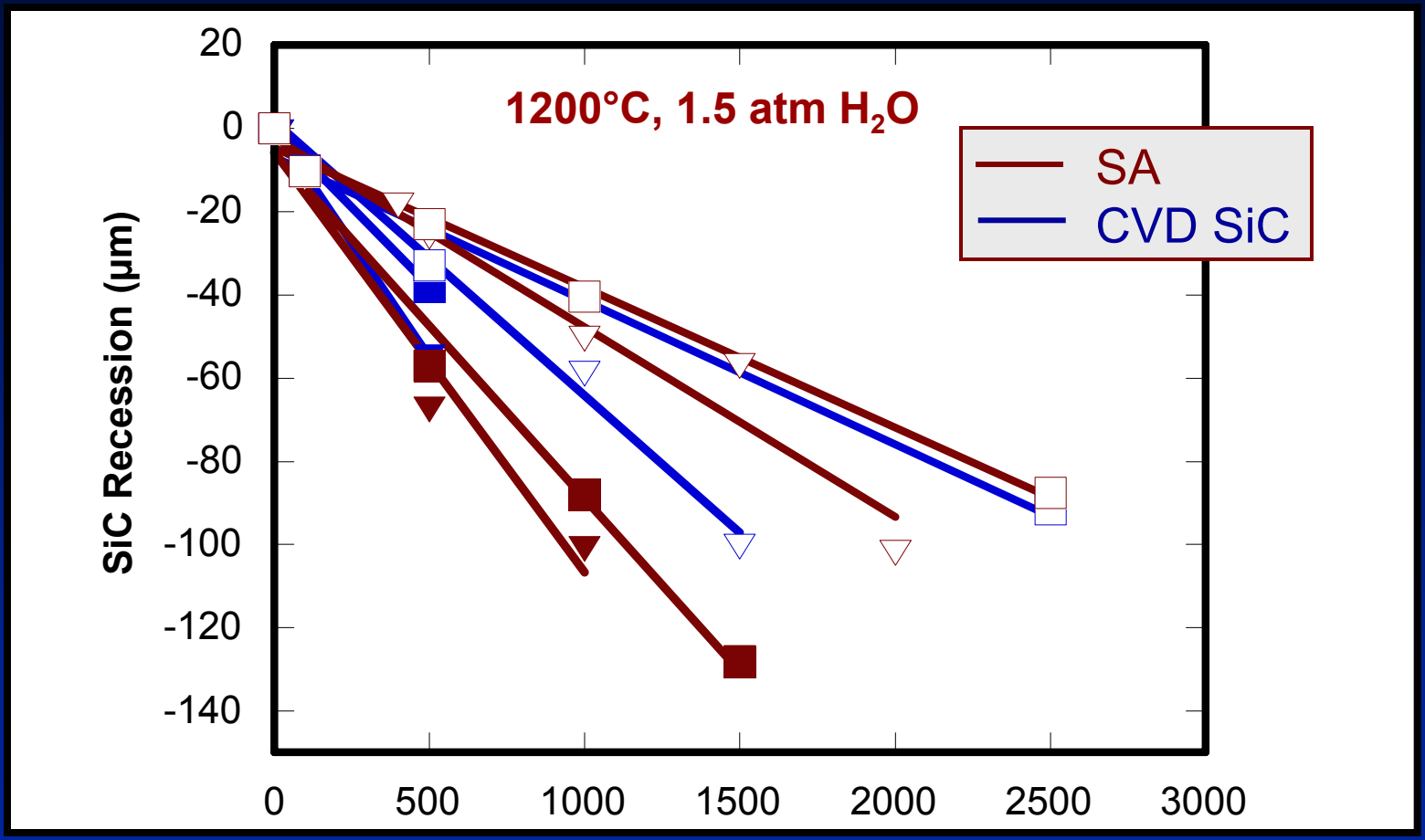




Opila & Fox, 1993

8.5 atm Air, 1.5 atm H_2O, 500 h, 1200°C

We Measured Recession Rates (k_l's)



CVD SiC: 0.04 - 0.07 μm/h

SA: 0.04 - 0.10 μm/h