Oxidation of Advanced Environmental Barrier Coatings

Rebekah Webster

NASA Glenn Research Center, Cleveland, OH
University of Virginia, Charlottesville, VA

High Temperature Corrosion Gordon Research Conference
July 19, 2023

Acknowledgements

- Elizabeth Opila at the University of Virginia
- Rolls-Royce and program manager Dr. Robert Golden
- Analytical Instrumentation Facility (AIF), NC State University

- Kang Lee, Bernadette Puleo, and Bryan Harder of the Environmental Effects and Coatings Branch at NASA Glenn Research Center
- Transformational Tools & Technologies (TTT) Project
- Hybrid Thermally Efficient Core (HyTEC) Project

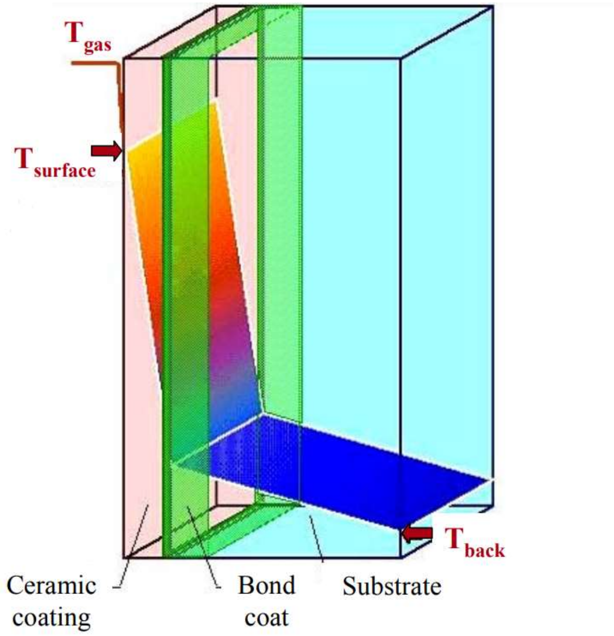
Outline

1. Background
2. Current-generation environmental barrier coatings (EBCs)
    - Oxygen diffusion pathways
        - As-sprayed $Y_2Si_2O_7$
        - As-sprayed vs. annealed $Yb_2Si_2O_7$
3. Next-generation EBCs
    - Oxide bond coat
    - Topcoat development

Background

The growing demand for improved engine efficiency and performance has resulted in significant increases in aircraft turbine operating temperatures.

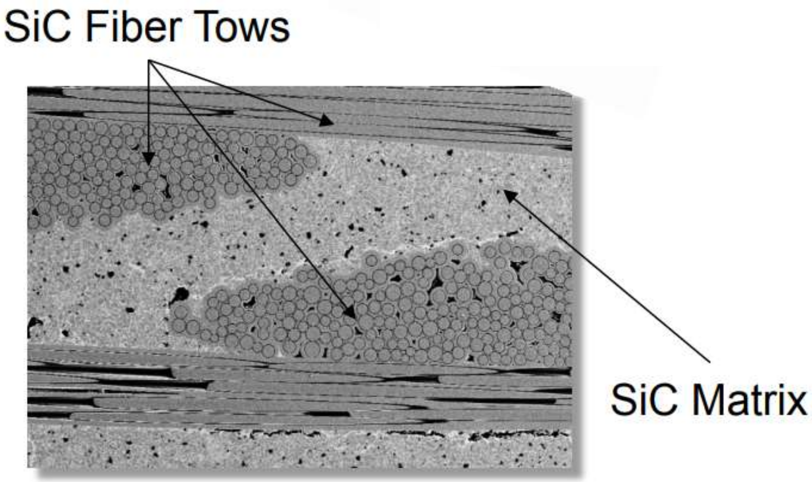
- Metallic hot-section materials (Ni-base superalloys) are reaching their temperature limit
  - Thermal barrier coatings (TBCs) and cooling technologies allow Ni-base superalloys to operate at gas temperatures that exceed their melting point



Background

The growing demand for improved engine efficiency and performance has resulted in significant increases in aircraft turbine operating temperatures.

- SiC/SiC ceramic matrix composites (CMCs) are less dense and can withstand higher operating temperatures without the need for TBC → increased efficiency



Background

- SiC forms a slow-growing, protective SiO_2 scale in dry oxygen

$$SiC + \frac{3}{2} O_2(g) \rightarrow SiO_2 + CO(g)$$

Oxidation

Background

- SiC forms a slow-growing, protective SiO_2 scale in dry oxygen

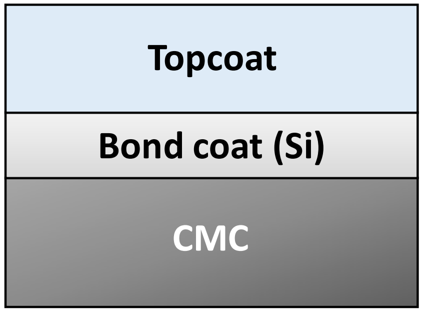
$$SiC + \frac{3}{2}O_2(g) \rightarrow SiO_2 + CO(g)$$ **Oxidation**

- However, in presence of water vapor (combustion environment), SiO_2 volatilizes to form a gaseous hydroxide, resulting in material recession

$$SiO_2 + H_2O(g) \rightarrow Si(OH)_4(g)$$ **Recession**

Background

- Environmental barrier coatings (EBCs) are necessary to prevent environmental degradation of SiC/SiC CMCs
  - Topcoat provides barrier to turbine environment
  - Bond coat provides bonding adhesion and acts as sacrificial layer for oxidation control

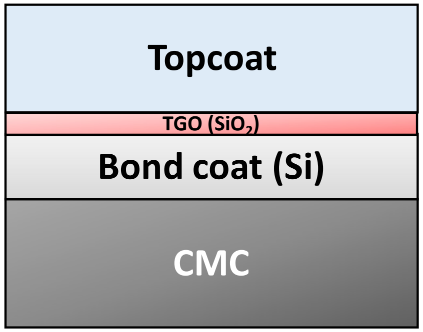


Intrinsic Material Selection Criteria

- Coefficient of thermal expansion (CTE) match
- Sintering resistance
- Low H_2O/O_2 diffusivity/solubility
- Phase stability
- Low modulus
- Limited coating interaction

Background

- Environmental barrier coatings (EBCs) are necessary to prevent environmental degradation of SiC/SiC CMCs
  - Topcoat provides barrier to turbine environment
  - Bond coat provides bonding adhesion and acts as sacrificial layer for oxidation control
  - Oxidation of bond coat (Si) results in formation of SiO_2 thermally grown oxide (TGO)

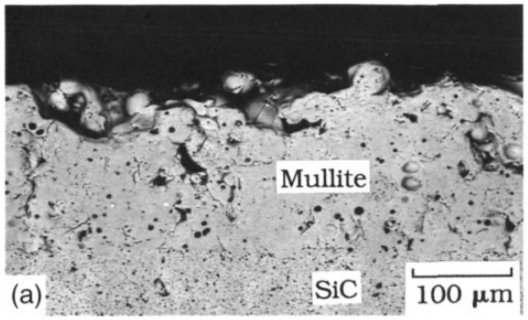


Intrinsic Material Selection Criteria

- Coefficient of thermal expansion (CTE) match
- Sintering resistance
- Low H_2O/O_2 diffusivity/solubility
- Phase stability
- Low modulus
- Limited coating interaction

Background

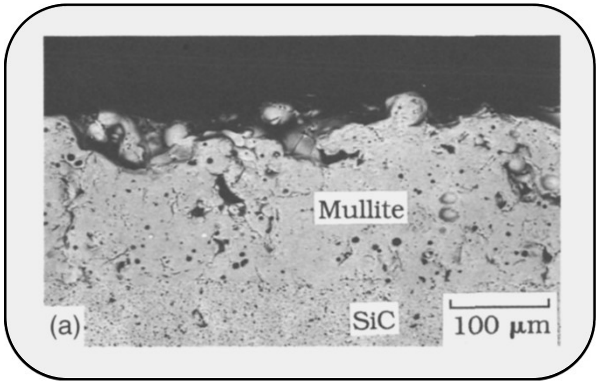
Mullite coating
NASA 1993



Lee et al. , *J. Am. Ceram. Soc.* (1995).

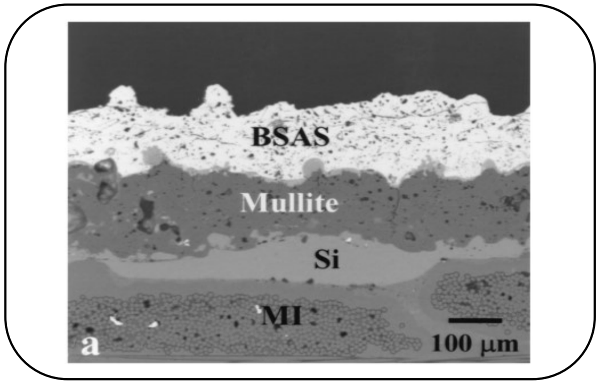
Background

Mullite coating
NASA 1993



Lee et al. , *J. Am. Ceram. Soc.* (1995).

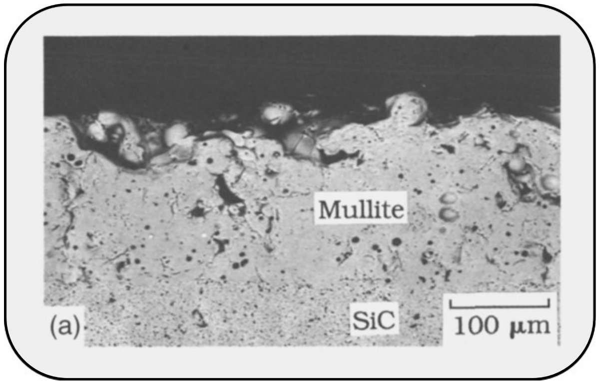
Gen I EBC
NASA, GE, PW 1997



Lee et al., *J. Am. Ceram. Soc.* (2003).

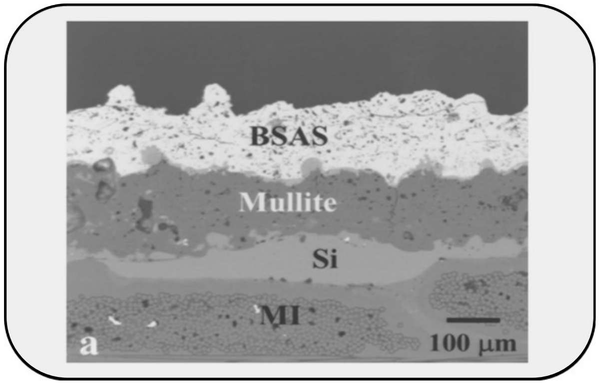
Background

Mullite coating
NASA 1993



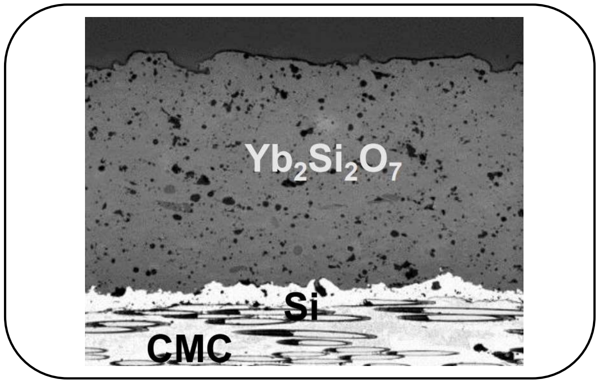
Lee et al. , *J. Am. Ceram. Soc.* (1995).

Gen I EBC
NASA, GE, PW 1997



Lee et al., *J. Am. Ceram. Soc.* (2003).

Gen II EBC
NASA 2003



Lee et al., *J. Eur. Ceram. Soc.* (2005).

Gen II EBCs are current-generation, consist of rare earth (RE) silicate topcoat and Si bond coat. Operating temperature limited by melting point of Si (~1410°C).

Current-generation EBCs

- Low oxygen diffusivity is requirement of topcoat layer ($RE_2Si_2O_7$)
  - Benchmark of 1.1 x 10^{-11} cm^2/s

$$D = \frac{x^2}{t} = \frac{(200\ \mu m)^2}{10{,}000\ h} = 1.1 \times 10^{-11}\,\frac{cm^2}{s}$$

Current-generation EBCs

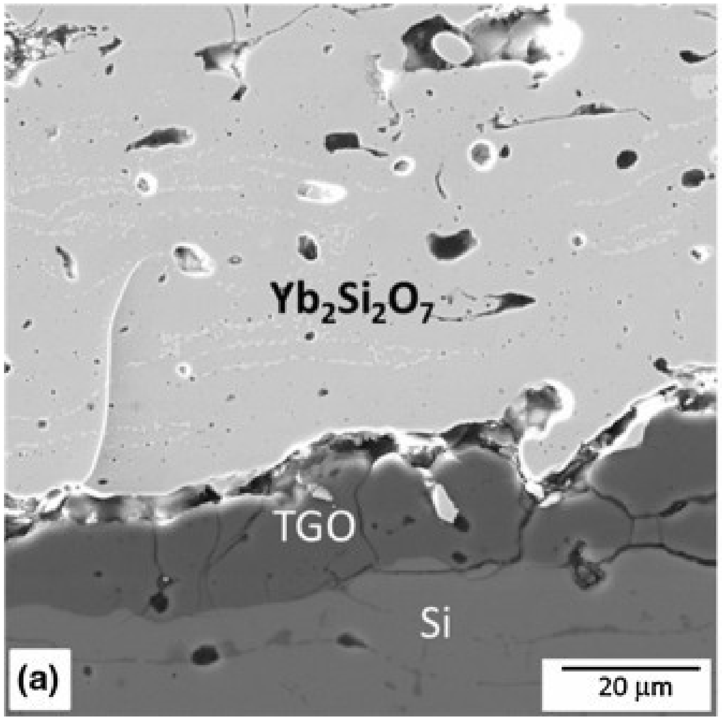
- Diffusion coefficient of oxygen in dense **β-$Yb_2Si_2O_7$** has been previously determined
  - ~10^{-14} cm^2/s at 1400°C (Wada et al.)

- Golden reported oxygen diffusion coefficient of ~10^{-12}-10^{-13} cm^2/s for dense **β/γ-$Y_2Si_2O_7$** at 1100-1300°C

Wada et al., *Acta Materialia* (2017).
Golden, Ph.D. Dissertation (2016).

Current-generation EBCs

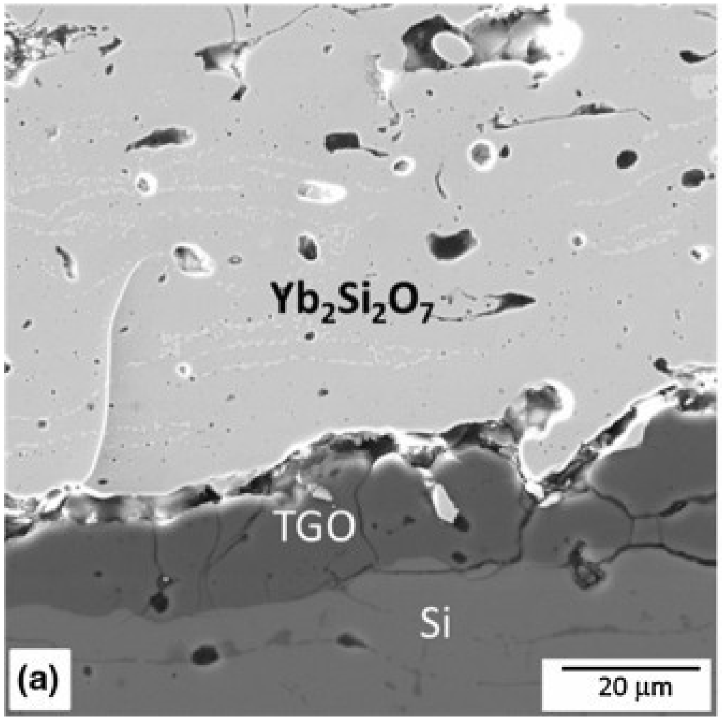
- EBCs typically deposited by thermal spray process (air plasma spray; APS)
  - Results in complex microstructure containing pores, cracks, secondary phases



Lee et al., *J. Therm. Spray Technol.* (2021).
1000 cycles, 1316°C, steam

Current-generation EBCs

- EBCs typically deposited by thermal spray process (air plasma spray; APS)
  - Results in complex microstructure containing pores, cracks, secondary phases
  - Richards et al. estimated diffusion coefficient of oxidizing species in steam-cycled APS $Yb_2Si_2O_7$ to be ~10^{-8} cm^2/s at 1316°C



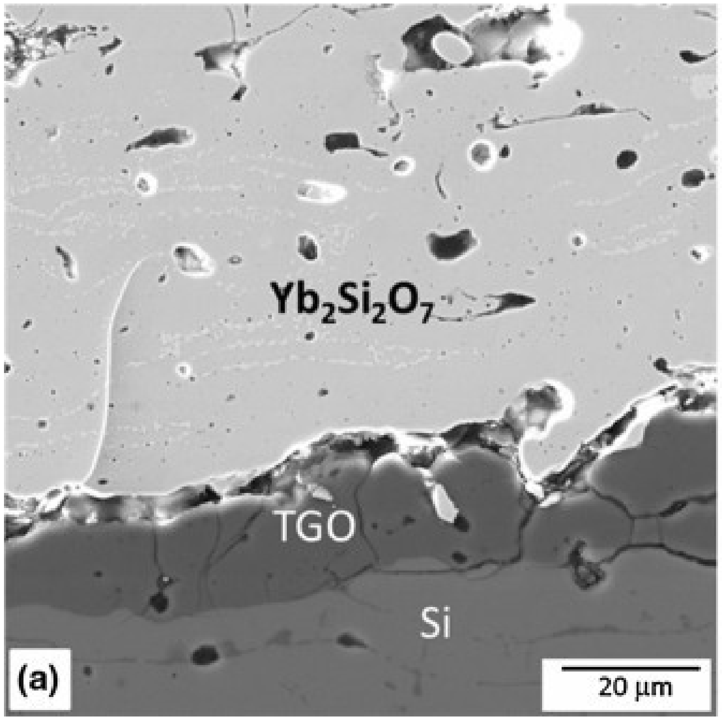
Lee et al., *J. Therm. Spray Technol.* (2021).
1000 cycles, 1316°C, steam

Richards et al., *Acta Materialia* (2016).

Current-generation EBCs

- EBCs typically deposited by thermal spray process (air plasma spray; APS)
  - Results in complex microstructure containing pores, cracks, secondary phases
  - Richards et al. estimated diffusion coefficient of oxidizing species in steam-cycled APS $Yb_2Si_2O_7$ to be ~10^{-8} cm^2/s at 1316°C

Can we monitor oxygen diffusion pathways in APS materials?



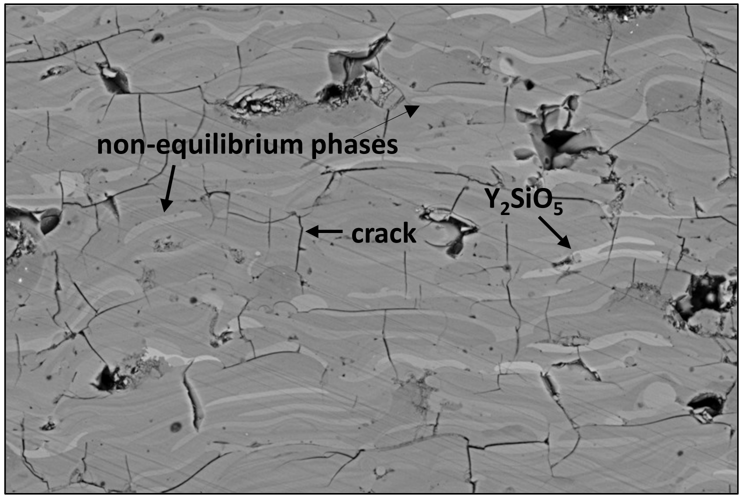
Lee et al., *J. Therm. Spray Technol.* (2021).
1000 cycles, 1316°C, steam

Richards et al., *Acta Materialia* (2016).

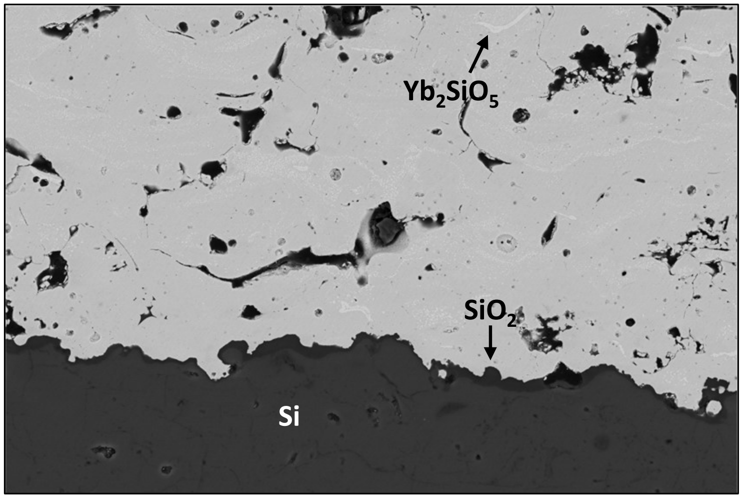
Oxygen diffusion pathways

- APS $Y_2Si_2O_7$ (standalone, as-sprayed) and $Yb_2Si_2O_7$ (on APS Si, pre-annealed and as-sprayed) investigated

as-sprayed APS $Y_2Si_2O_7$



pre-annealed APS $Yb_2Si_2O_7$ on APS Si

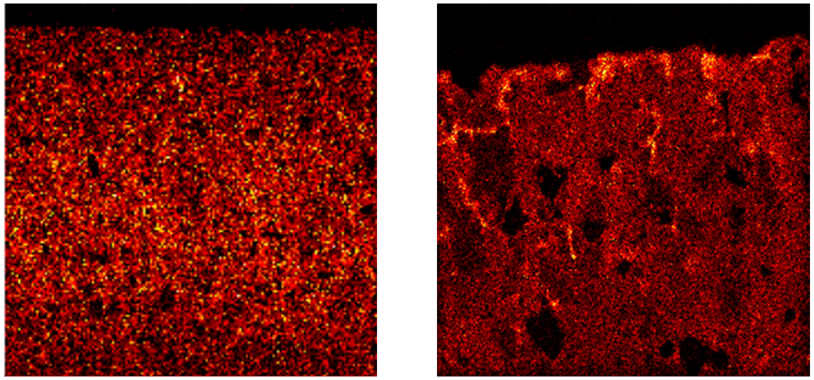


Oxygen diffusion pathways

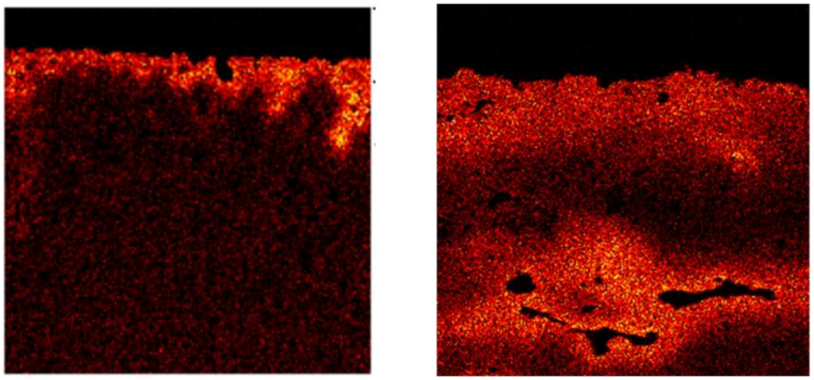
- APS $Y_2Si_2O_7$ (standalone, as-sprayed) and $Yb_2Si_2O_7$ (on APS Si, pre-annealed and as-sprayed) investigated
- Samples encapsulated in fused quartz ampules for $^{18}O_2$ exchange
  - 1100°C for 75 h
  - 1200°C for 25 h
  - 1300°C for 7 h
- Resulting samples analyzed in cross-section by scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS)

Oxygen diffusion pathways – $Y_2Si_2O_7$

1100°C



1200°C

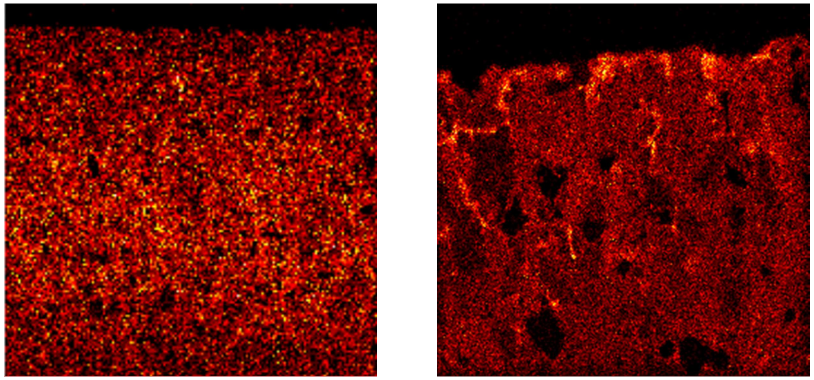


- Deep $^{18}O_2$ penetration
- Some bright areas suggesting fast paths

- Less $^{18}O_2$ penetration
- Oxygen concentrated around pores

Oxygen diffusion pathways – $Y_2Si_2O_7$

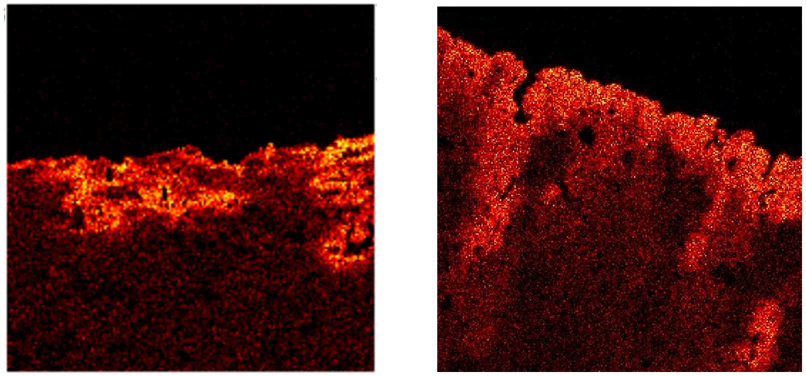
1100°C



scale A

scale B

1300°C



scale A

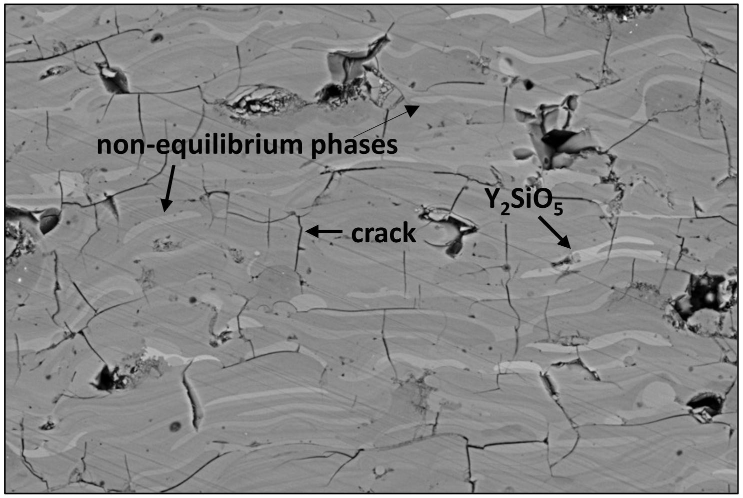
scale B

- Deep $^{18}O_2$ penetration
- Some bright areas suggesting fast paths

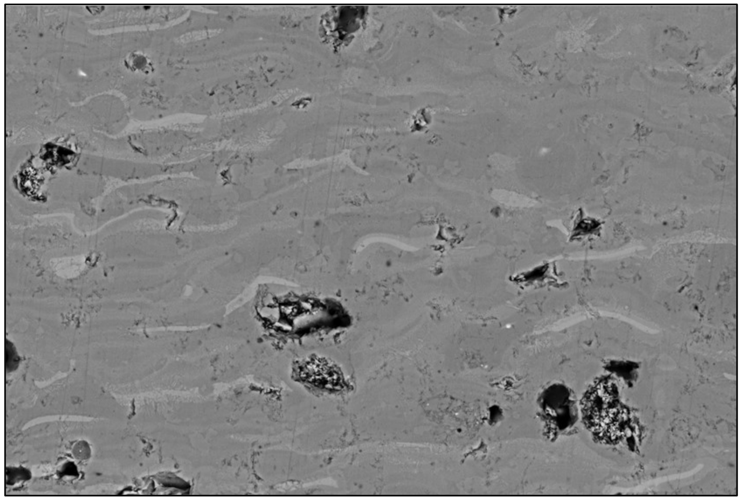
- Less $^{18}O_2$ penetration
- Oxygen concentrated around pores

Oxygen diffusion pathways – $Y_2Si_2O_7$

as-sprayed APS $Y_2Si_2O_7$



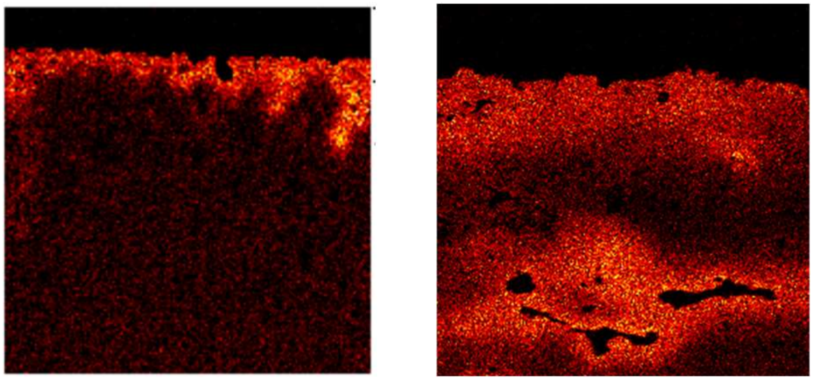
after 1200°C exchange



Hypothesized that $^{18}O_2$ penetration greater at 1100°C due to delayed phase equilibrium, delayed “healing” of splat boundary cracks.

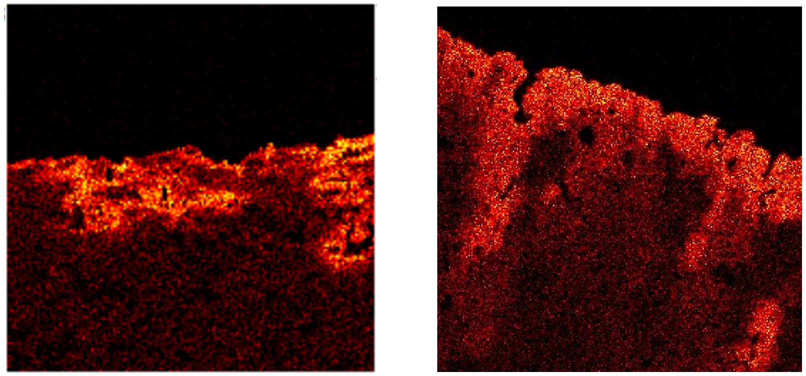
Oxygen diffusion pathways – $Y_2Si_2O_7$

1200°C


scale A

scale B

1300°C


scale A

scale B

Bulk diffusion coefficient estimated as ~10^{-10}-10^{-11} (1200-1300°C) using $D = \frac{x^2}{t}$.

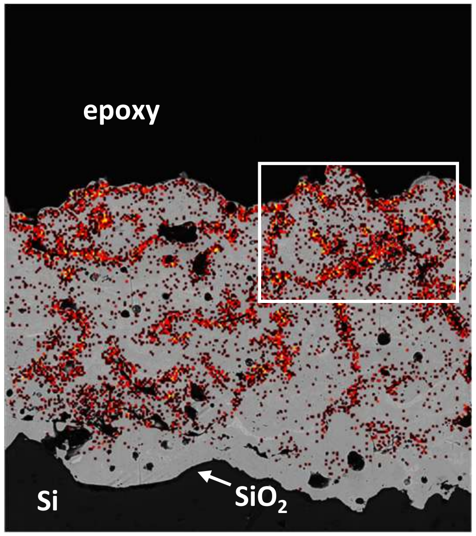
Higher than previously reported (10^{-12}-10^{-13}), but analysis not robust.

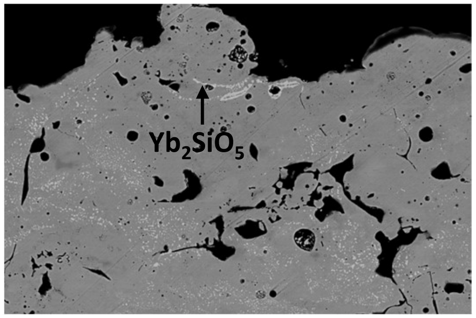
Oxygen diffusion pathways – $Yb_2Si_2O_7$

pre-annealed

1100°C

- Oxygen has not reached bond coat by 75 hours
- ^{18}O concentrated at pores and cracks in the coating
- No discernable correlation between phase ($Yb_2Si_2O_7$, Yb_2SiO_5) and oxygen diffusion



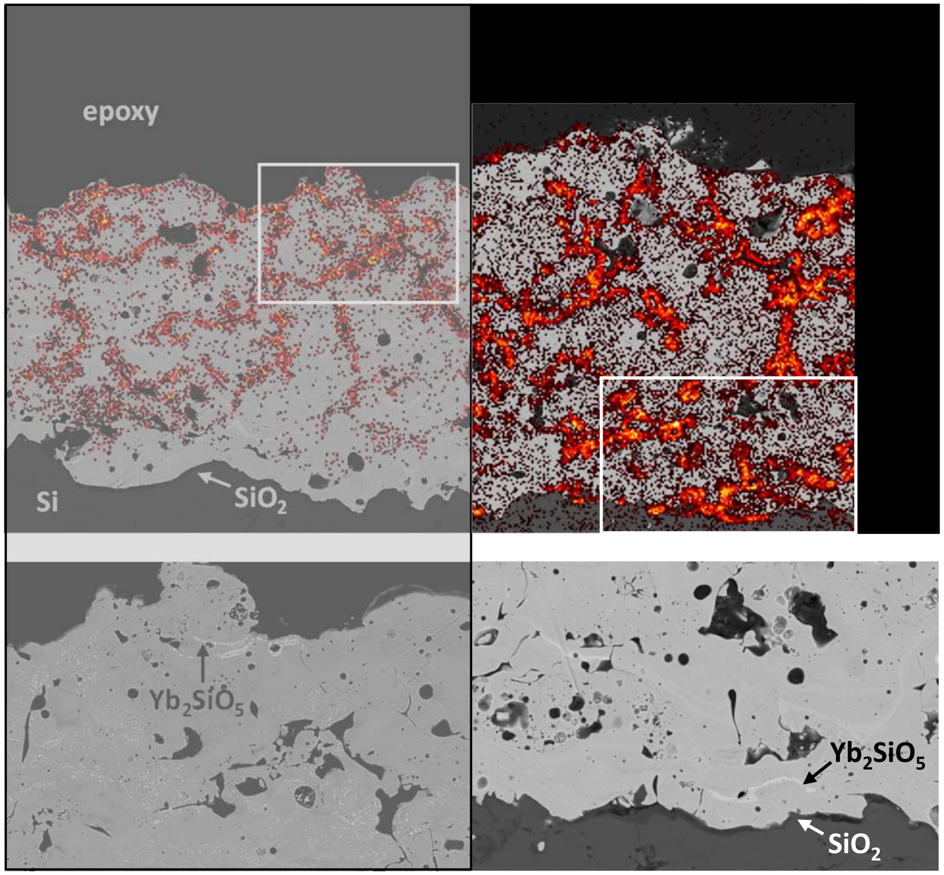


Oxygen diffusion pathways – $Yb_2Si_2O_7$

pre-annealed

1100°C

- Oxygen has not reached bond coat by 75 hours
- ^{18}O concentrated at pores and cracks in the coating
- No discernable correlation between phase ($Yb_2Si_2O_7$, Yb_2SiO_5) and oxygen diffusion



as-sprayed

1100°C

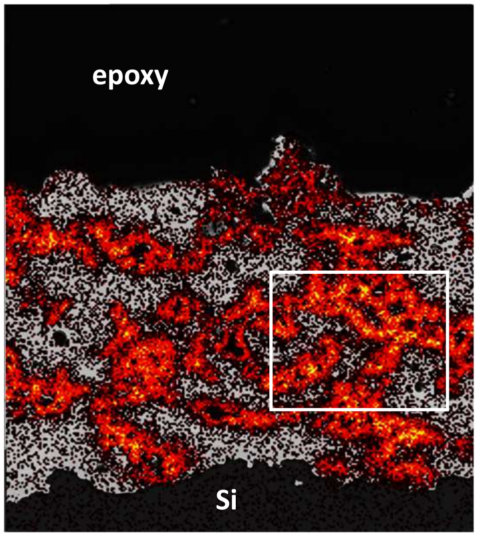
- Oxygen reaches and reacts with bond coat to form SiO_2
- Thick ^{18}O regions concentrated around pores and cracks
- No discernable correlation between phase ($Yb_2Si_2O_7$, Yb_2SiO_5) and oxygen diffusion

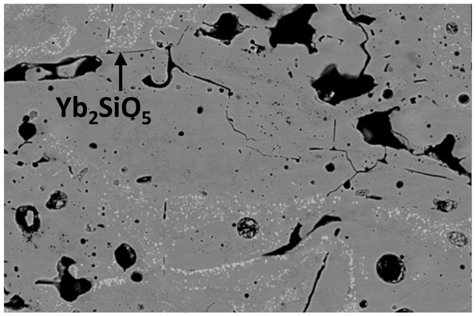
Oxygen diffusion pathways – $Yb_2Si_2O_7$

pre-annealed

1300°C

- **Oxygen reaches bond coat but no clear additional TGO formation**
- Thick regions of concentrated ^{18}O near coating defects
- No discernable correlation between phase ($Yb_2Si_2O_7$, Yb_2SiO_5) and oxygen diffusion



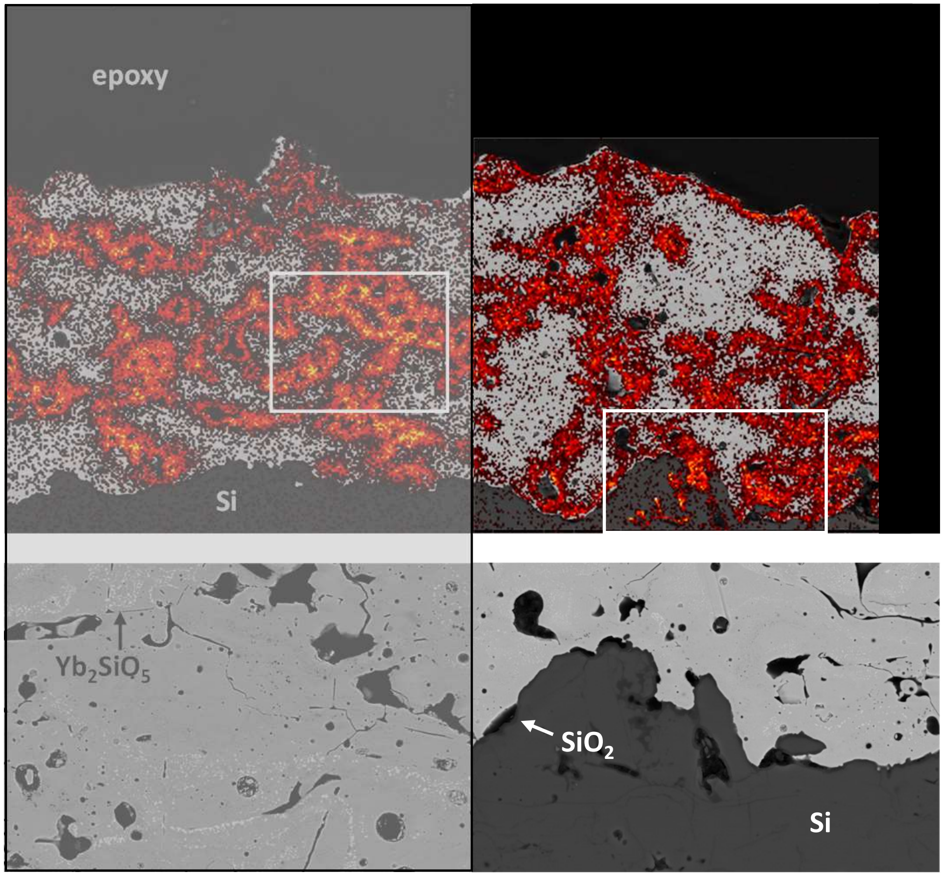


Oxygen diffusion pathways – $Yb_2Si_2O_7$

pre-annealed

1300°C

- Oxygen reaches bond coat but no clear additional TGO formation
- Thick regions of concentrated ^{18}O near coating defects
- No discernable correlation between phase ($Yb_2Si_2O_7$, Yb_2SiO_5) and oxygen diffusion



as-sprayed

1300°C

- **Oxygen reaches and reacts with bond coat to form SiO_2**
- Thick regions of concentrated ^{18}O near coating defects
- No discernable correlation between phase ($Yb_2Si_2O_7$, Yb_2SiO_5) and oxygen diffusion

Oxygen diffusion pathways – takeaways

- Oxygen transport is extremely sensitive to initial condition of APS coating
  - As-sprayed EBCs contain cracks, non-equilibrium phases that can act as fast diffusion paths
  - Even after pre-anneal, defects in coating remain
- No observed effect of $RE_2Si_2O_7$ vs. RE_2SiO_5
  - Expected based on similar oxygen diffusion coefficients for $Y_2Si_2O_7$/Y_2SiO_5 and for $Yb_2Si_2O_7$/Yb_2SiO_5
- Uncertain why diffusion regions appear thicker at defects than at surface of material
  - Overlap in signal?

Next-generation EBCs

EBCs with surface temperatures ≥~1480°C are desired as new technology.

- Temperature capability of current-generation EBCs limited by melting point of silicon (~1410°C)

Next-generation EBCs

EBCs with surface temperatures ≥~1480°C are desired as new technology.

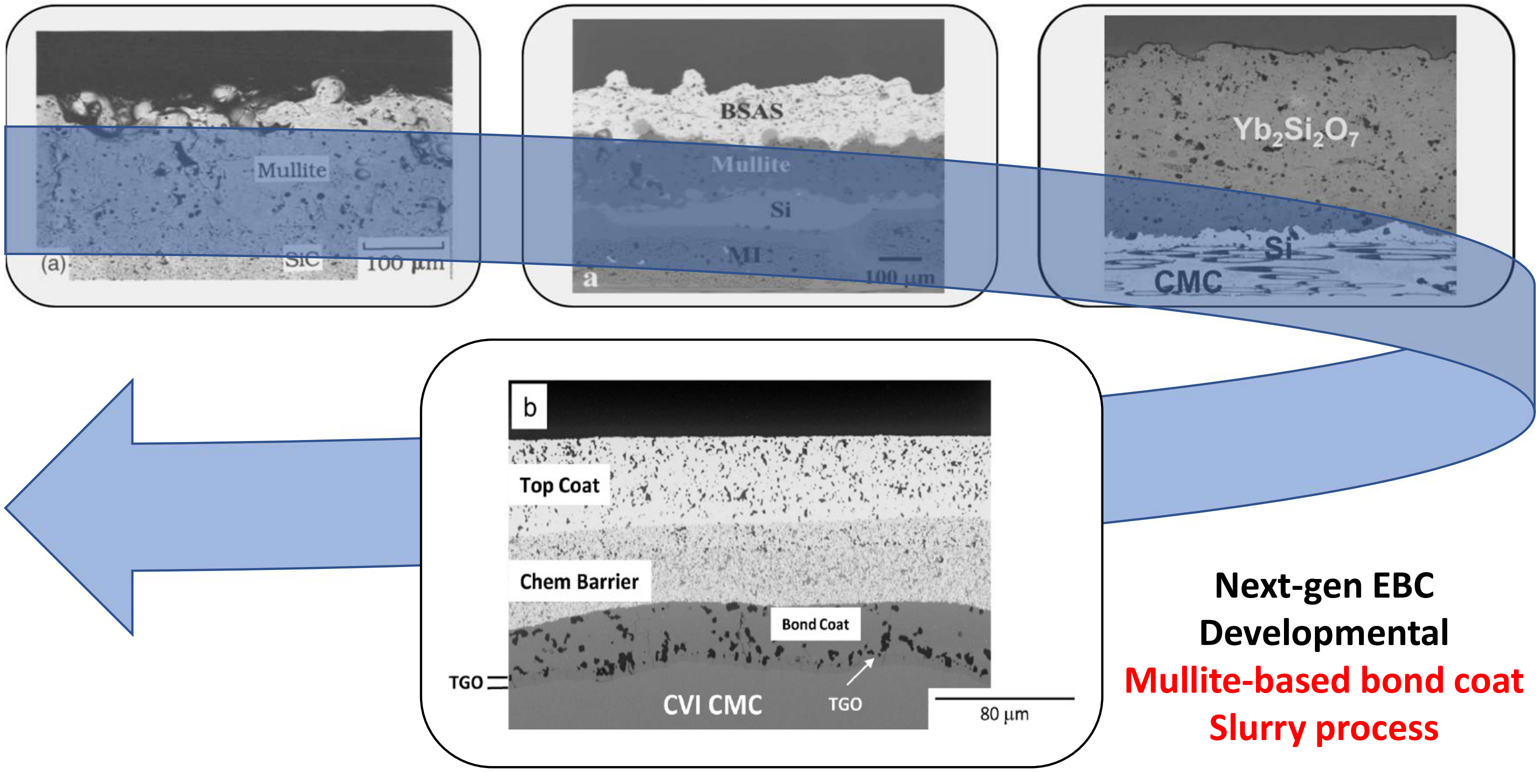
- Temperature capability of current-generation EBCs limited by melting point of silicon (~1410°C)
- Development of oxide bond coat (mullite-based) with higher temperature capability underway at NASA Glenn

Background

Mullite coating
NASA 1993

Gen I EBC
NASA, GE, PW 1997

Gen II EBC
NASA 2003

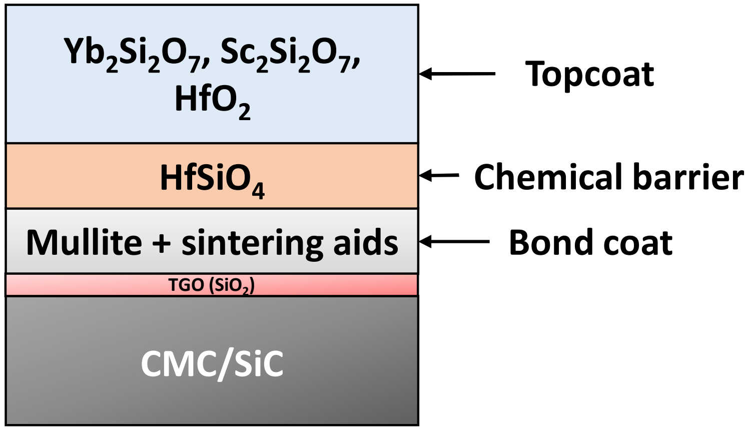


Next-gen EBC
Developmental
Mullite-based bond coat
Slurry process

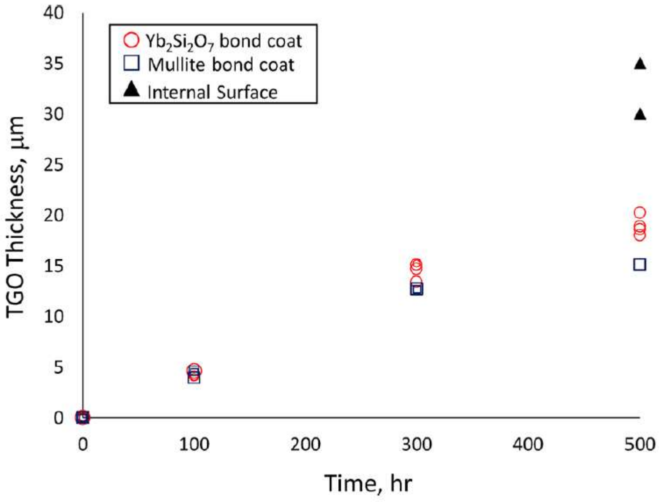
Lee et al., *J. Euro. Ceram. Soc.* (2021).

Oxide bond coat

- Three-layer system with mullite-based bond coat deposited by slurry process
  - Bond coat is not sacrificial, contributes to oxidation protection
  - Slurry process allows for fine control of coating chemistry, relatively easy synthesis



US Patent # 11,325,869 (2022).

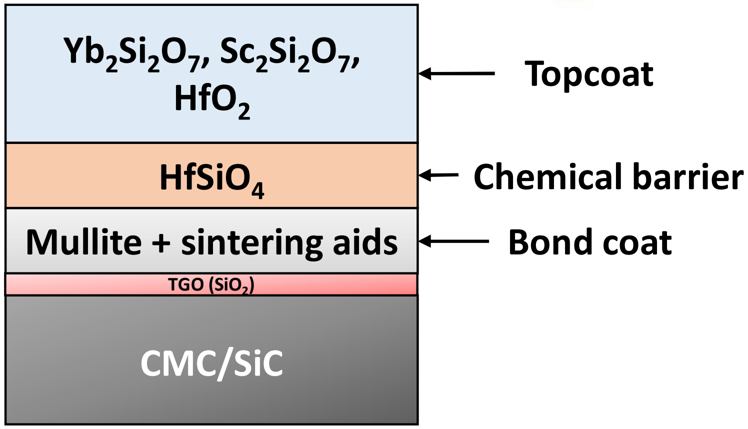


1427°C, steam

Lee et al., *J. Euro. Ceram. Soc.* (2021).

Oxide bond coat

- Three-layer system with mullite-based bond coat deposited by slurry process
  - $Yb_2Si_2O_7$ + (Al_2O_3, mullite) or $Sc_2Si_2O_7$ + (Al_2O_3, mullite) eutectic utilized for sintering at 1525°C



US Patent # 11,325,869 (2022).

	Base Material	Process	Sintering Aids	Amount	
Topcoat	$Yb_2Si_2O_7$	slurry	mullite	< 1 wt%	
	$Sc_2Si_2O_7$	slurry	mullite	< 1 wt%	
	HfO_2	PS-PVD	none	N/A	
	HfO_2	slurry	Si, mullite	TBD	
Chemical barrier	$HfSiO_4$	slurry	Si	< 10 wt%	
Bond coat	mullite	slurry	$Yb_2Si_2O_7$, Al_2O_3, Si, SiC	< 3 wt% (Al, Yb) < 30 wt% (Si, SiC)	baseline
			proprietary oxide, $Sc_2Si_2O_7$	< 3 wt%	improved

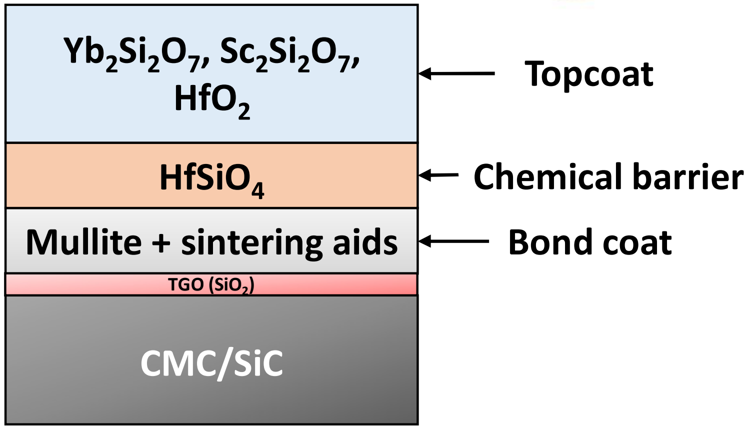
$Yb_2Si_2O_7$ + (Al_2O_3, mullite) = ~**1500°C** eutectic

$Sc_2Si_2O_7$ + (Al_2O_3, mullite) = ~**1525-1550°C** eutectic

PS-PVD = plasma spray-physical vapor deposition

Oxide bond coat

- Three-layer system with mullite-based bond coat deposited by slurry process
  - $Yb_2Si_2O_7$ + (Al_2O_3, mullite) or $Sc_2Si_2O_7$ + (Al_2O_3, mullite) eutectic utilized for sintering at 1525°C



US Patent # 11,325,869 (2022).

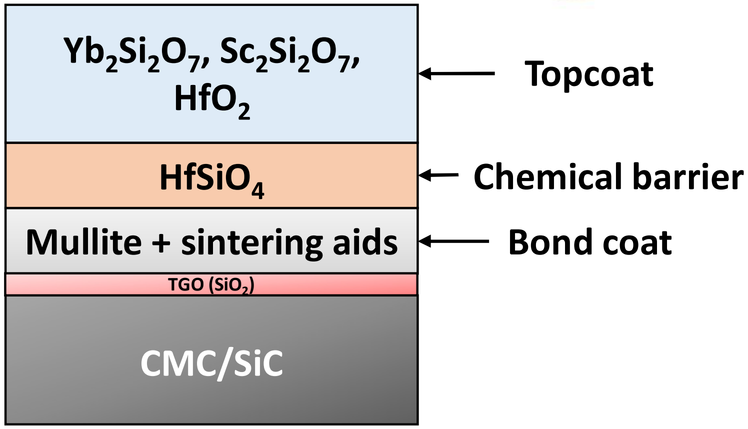
	Base Material	Process	Sintering Aids	Amount	
Topcoat	$Yb_2Si_2O_7$	slurry	mullite	< 1 wt%	
	$Sc_2Si_2O_7$	slurry	mullite	< 1 wt%	
	HfO_2	PS-PVD	none	N/A	
	HfO_2	slurry	Si, mullite	TBD	
Chemical barrier	$HfSiO_4$	slurry	Si	< 10 wt%	
Bond coat	mullite	slurry	$Yb_2Si_2O_7$, Al_2O_3, Si, SiC	< 3 wt% (Al, Yb) < 30 wt% (Si, SiC)	baseline
			proprietary oxide, $Sc_2Si_2O_7$	< 3 wt%	improved

Sintering aid amount/type can be optimized for temperature of interest and topcoat chemistry.

PS-PVD = plasma spray-physical vapor deposition

Oxide bond coat

- Three-layer system with mullite-based bond coat deposited by slurry process
  - $Yb_2Si_2O_7$ + (Al_2O_3, mullite) or $Sc_2Si_2O_7$ + (Al_2O_3, mullite) eutectic utilized for sintering at 1525°C



$Yb_2Si_2O_7$, $Sc_2Si_2O_7$, HfO_2 ← Topcoat

$HfSiO_4$ ← Chemical barrier

Mullite + sintering aids ← Bond coat

TGO (SiO_2)

CMC/SiC

US Patent # 11,325,869 (2022).

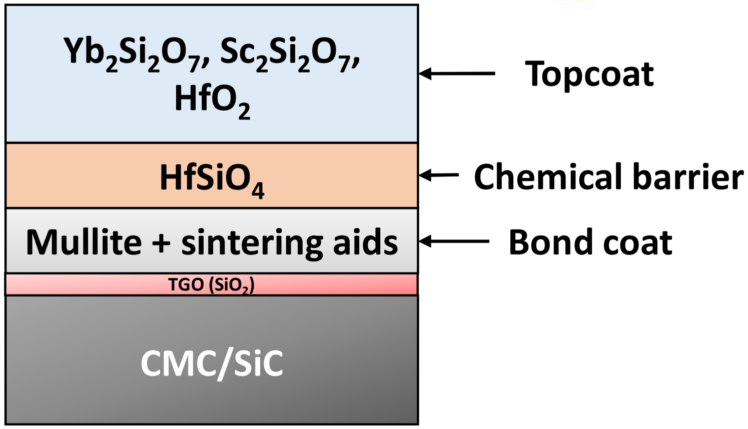
Chemical barrier prevents direct-contact reaction between $Yb_2Si_2O_7$/$Sc_2Si_2O_7$ and mullite.

	Base Material	Process	Sintering Aids	Amount	
Topcoat	$Yb_2Si_2O_7$	slurry	mullite	< 1 wt%	
	$Sc_2Si_2O_7$	slurry	mullite	< 1 wt%	
	HfO_2	PS-PVD	none	N/A	
	HfO_2	slurry	Si, mullite	TBD	
Chemical barrier	$HfSiO_4$	slurry	Si	< 10 wt%	
Bond coat	mullite	slurry	$Yb_2Si_2O_7$, Al_2O_3, Si, SiC	< 3 wt% (Al, Yb) < 30 wt% (Si, SiC)	baseline
			proprietary oxide, $Sc_2Si_2O_7$	< 3 wt%	improved

PS-PVD = plasma spray-physical vapor deposition

Oxide bond coat

- Three-layer system with mullite-based bond coat deposited by slurry process
  - $Yb_2Si_2O_7$ + (Al_2O_3, mullite) or $Sc_2Si_2O_7$ + (Al_2O_3, mullite) eutectic utilized for sintering at 1525°C



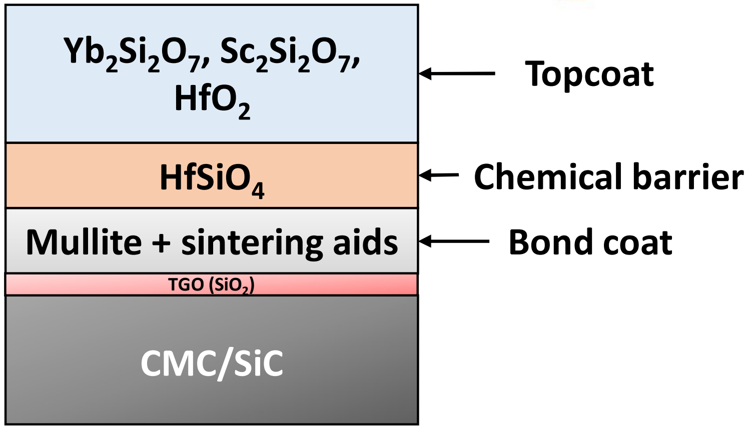
US Patent # 11,325,869 (2022).

	Base Material	Process	Sintering Aids	Amount	
Topcoat	$Yb_2Si_2O_7$	slurry	mullite	< 1 wt%	
	$Sc_2Si_2O_7$	slurry	mullite	< 1 wt%	
	HfO_2	PS-PVD	none	N/A	
	HfO_2	slurry	Si, mullite	TBD	
Chemical barrier	$HfSiO_4$	slurry	Si	< 10 wt%	
Bond coat	mullite	slurry	$Yb_2Si_2O_7$, Al_2O_3, Si, SiC	< 3 wt% (Al, Yb) < 30 wt% (Si, SiC)	baseline
			proprietary oxide, $Sc_2Si_2O_7$	< 3 wt%	improved

PS-PVD = plasma spray-physical vapor deposition

Oxide bond coat

- Three-layer system with mullite-based bond coat deposited by slurry process
  - $Yb_2Si_2O_7$ + (Al_2O_3, mullite) or $Sc_2Si_2O_7$ + (Al_2O_3, mullite) eutectic utilized for sintering at 1525°C



US Patent # 11,325,869 (2022).

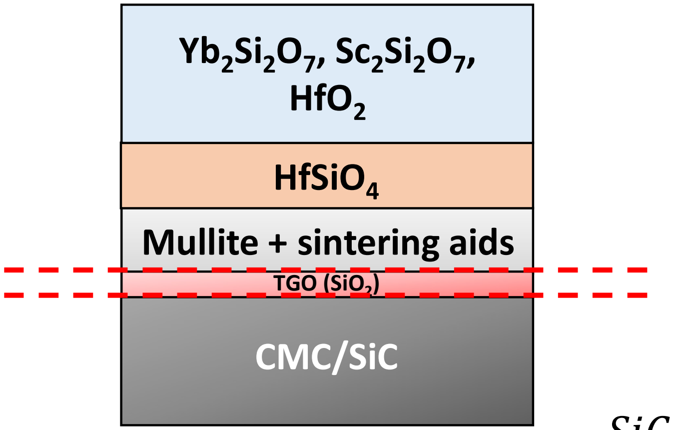
	Base Material	**Process**	**Sintering Aids**	**Amount**	
Topcoat	$Yb_2Si_2O_7$	slurry	mullite	< 1 wt%	
	$Sc_2Si_2O_7$	slurry	mullite	< 1 wt%	
	HfO_2	PS-PVD	none	N/A	
	HfO_2	slurry	Si, mullite	TBD	
Chemical barrier	$HfSiO_4$	slurry	Si	< 10 wt%	
Bond coat	mullite	slurry	$Yb_2Si_2O_7$, Al_2O_3, Si, SiC	< 3 wt% (Al, Yb) < 30 wt% (Si, SiC)	baseline
			proprietary oxide, $Sc_2Si_2O_7$	< 3 wt%	improved

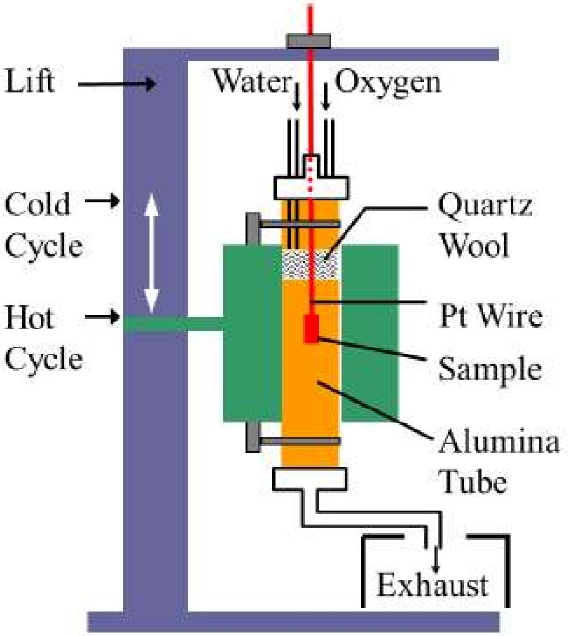
PS-PVD = plasma spray-physical vapor deposition

Cyclic steam oxidation

Steam oxidation-induced delamination is the most critical EBC failure mode.

- β → α SiO_2 phase transformation (~200°C), volume reduction
- CTE α SiO_2 = ~10 x 10^{-6} / °C





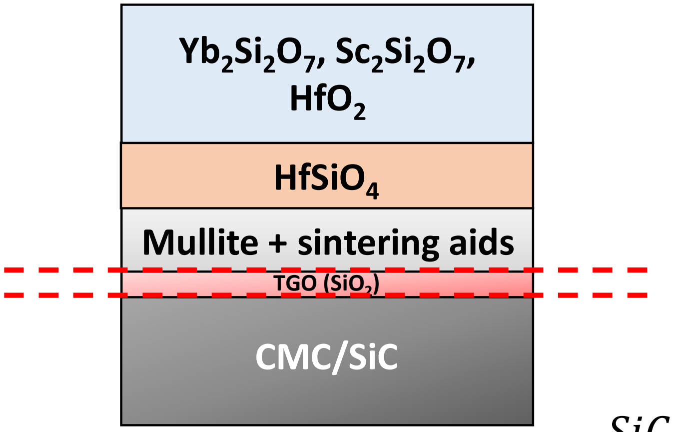
Lee et al., *J. Am. Ceram. Soc.* (2003).

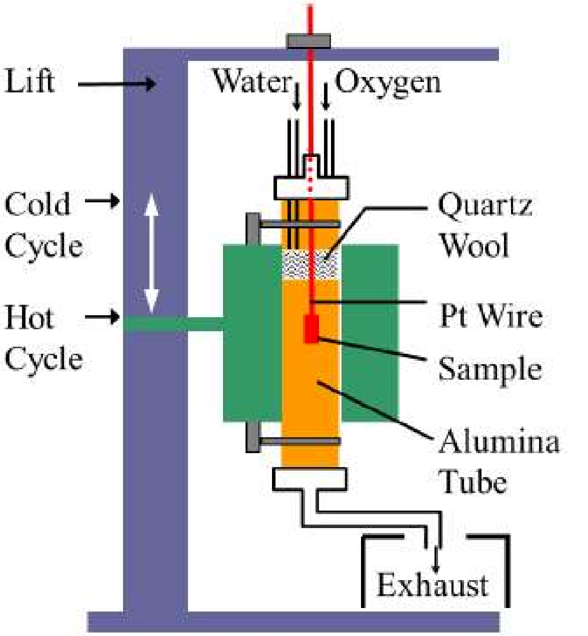
$$SiC + 3H_2O(g) \rightarrow SiO_2 + CO(g) + 3H_2(g)$$

Cyclic steam oxidation

Steam oxidation-induced delamination is the most critical EBC failure mode.

- Cyclic steam oxidation rig used to evaluate EBC viability
  - Pt-Rh hang wire and basket to hold samples
  - 90 vol% H_2O/10 vol% O_2, 10 cm/s gas velocity
  - 1 hour hot cycle and 30 min cool cycle (<200°C)





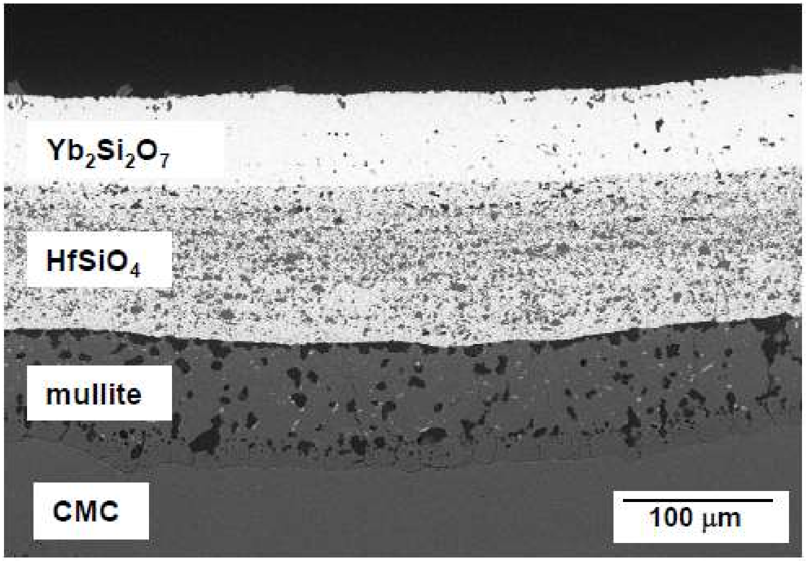
Lee et al., *J. Am. Ceram. Soc.* (2003).

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

$RE_2Si_2O_7$ (RE=Yb, Sc) topcoat for next-generation EBCs

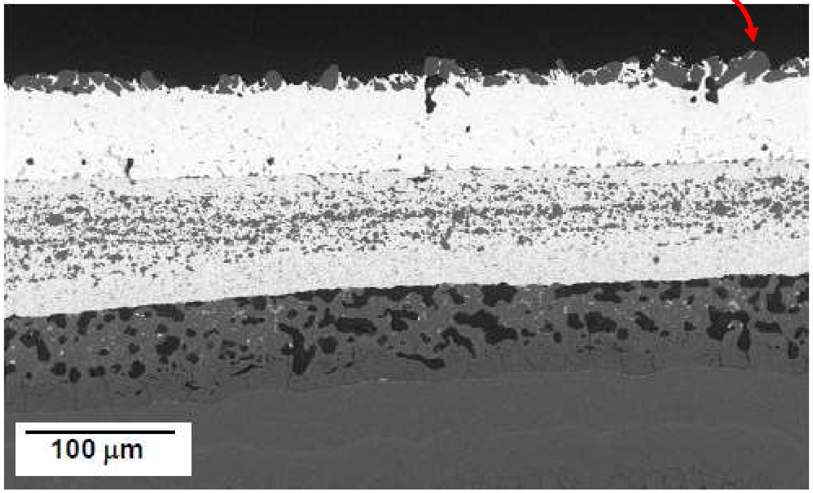
Yb$_2$Si$_2$O$_7$ topcoat

500 cycles, 1427°C



1000 cycles, 1427°C

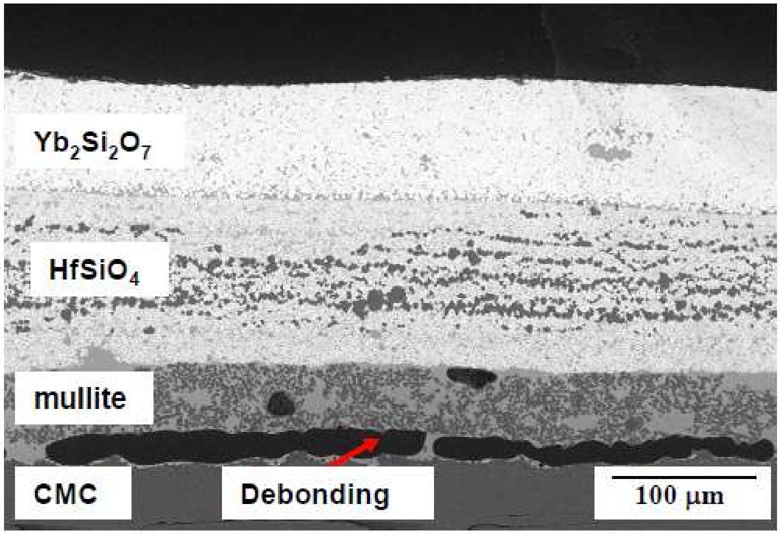
eutectic product



Addition of proprietary oxide to bond coat allows for **1000** successful cycles of EBC with Yb$_2$Si$_2$O$_7$ topcoat at 1427°C. Eutectic moves from bond coat to surface of topcoat during testing.

$Yb_2Si_2O_7$ topcoat

67 cycles, 1480°C



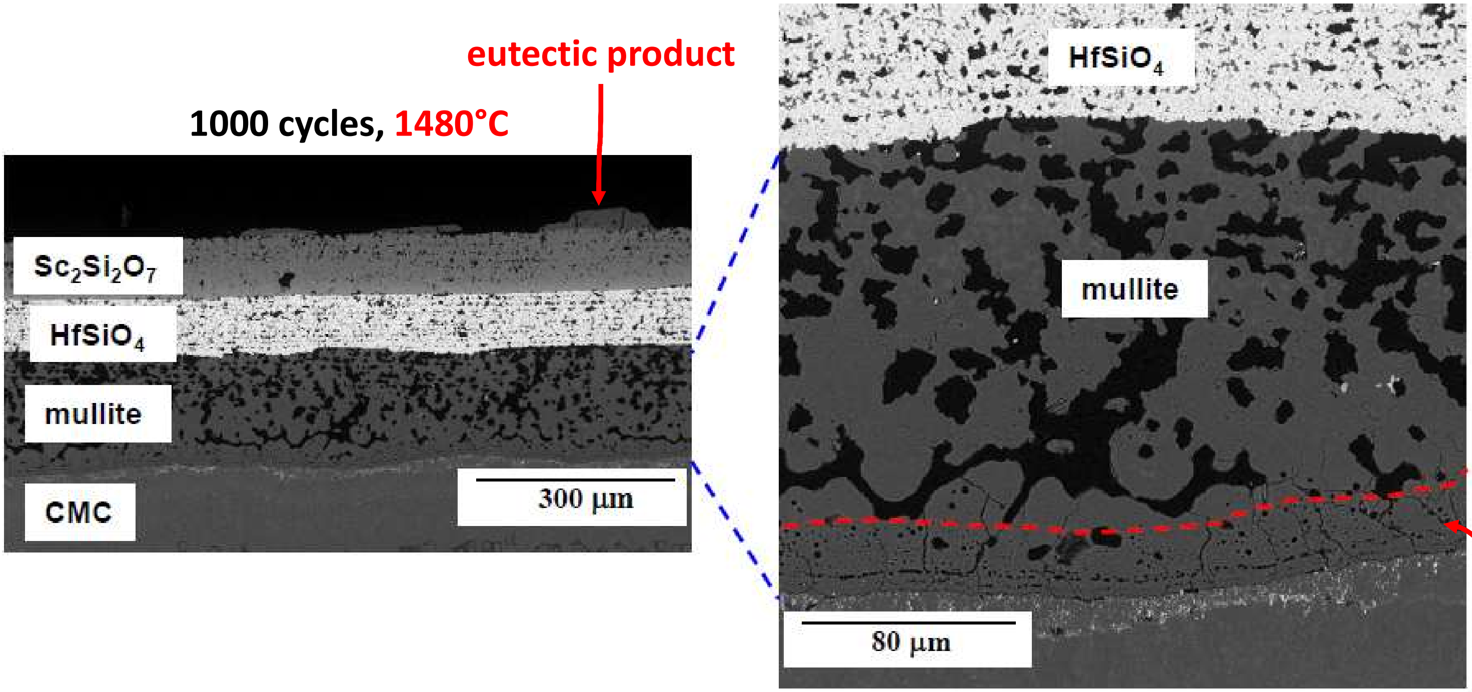
after sintering (1520°C, 3 h) and annealing (1480°C, 20 h), air

YbDS/YbMS topcoat on Hexoloy

Debonding observed by **67 cycles** at 1480°C. Eutectic formation and spread limits use temperature of $Yb_2Si_2O_7$.

$Sc_2Si_2O_7$ topcoat

1000 cycles, 1480°C



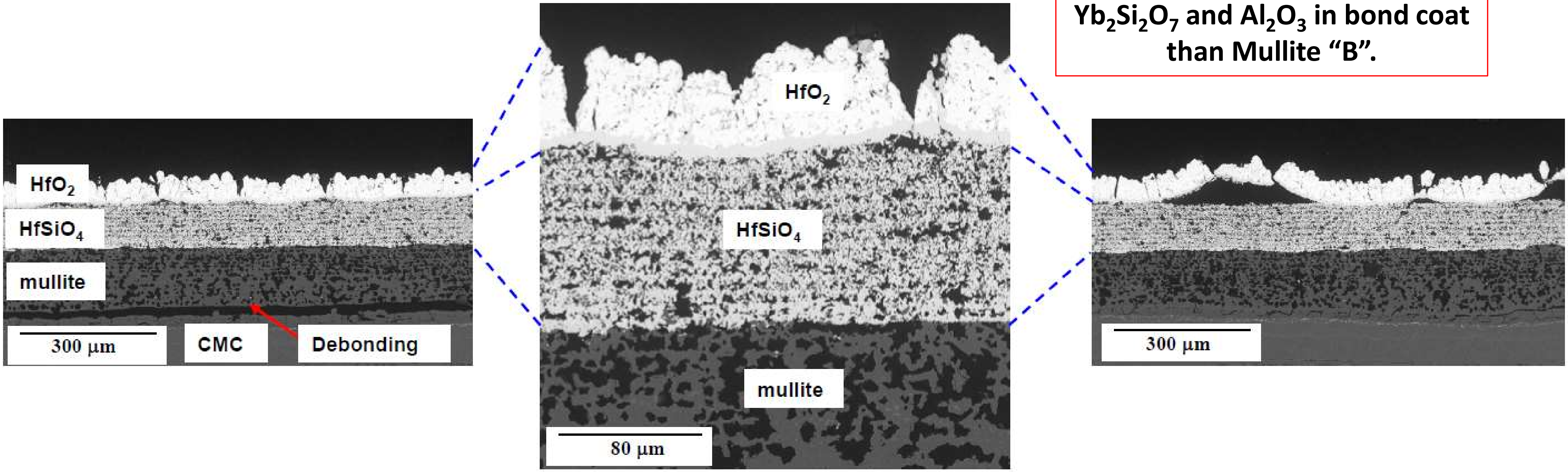
No spallation after **1000 cycles** at 1480°C. Bond coat shows some signs of distress (pore coalescence).

HfO_2 topcoat for next-generation EBCs

PS-PVD HfO_2 topcoat

Mullite “A” contains less $Yb_2Si_2O_7$ and Al_2O_3 in bond coat than Mullite “B”.

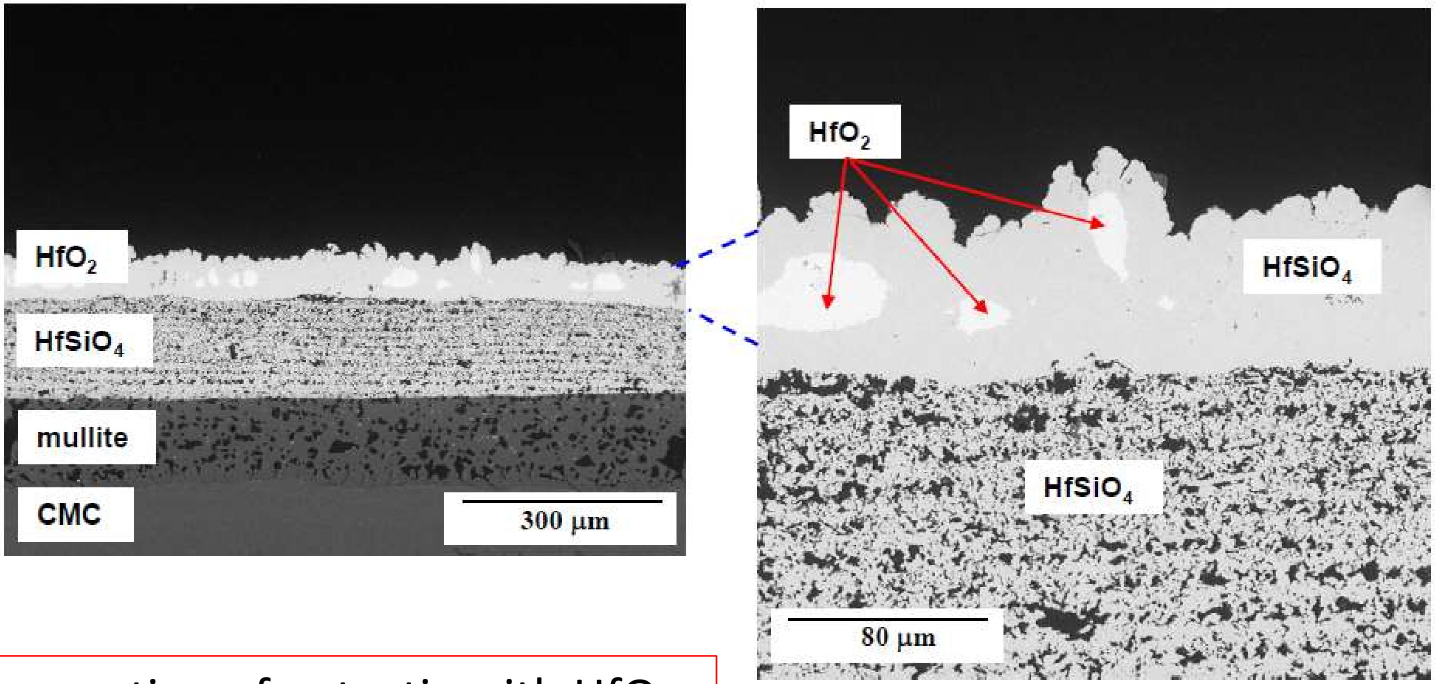
500 cycles, 1480°C, Mullite “A”



- Moving eutectic reacts with HfO_2 to form $HfSiO_4$
- Severe topcoat debonding with some spallation
- Some debonding at bond coat/TGO interface observed

PS-PVD HfO_2 topcoat

500 cycles, 1480°C, Mullite "B"



- Excessive reaction of eutectic with HfO_2 to form $HfSiO_4$
- No debonding/spallation observed

Mullite "B" contains more $Yb_2Si_2O_7$ and Al_2O_3 in bond coat than Mullite "A".

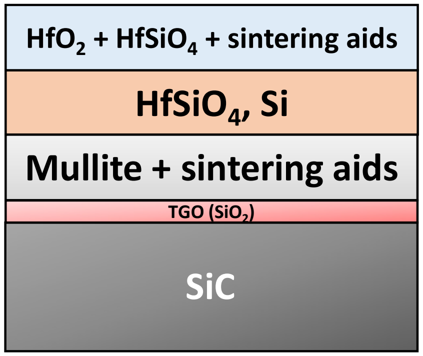
Slurry HfO_2 topcoat

- HfO_2 has high, anisotropic CTE
  - a = ~10, b = ~-1, c = ~17 x 10^{-6} / °C (1450°C, monoclinic; Haggerty et al.)
  - a = ~10, c = ~13 x 10^{-6} / °C (1450°C, tetragonal; Haggerty et al.)
- Can we produce HfO_2 as a slurry-based coating?

Haggerty et al., *J. Am. Ceram. Soc.* (2014).

Single-layer HfO_2 topcoat

- HfO_2 mixed with $HfSiO_4$ / sintering aids Si, mullite, $Yb_2Si_2O_7$



HfO_2 + $HfSiO_4$ + sintering aids

$HfSiO_4$, Si

Mullite + sintering aids

TGO (SiO_2)

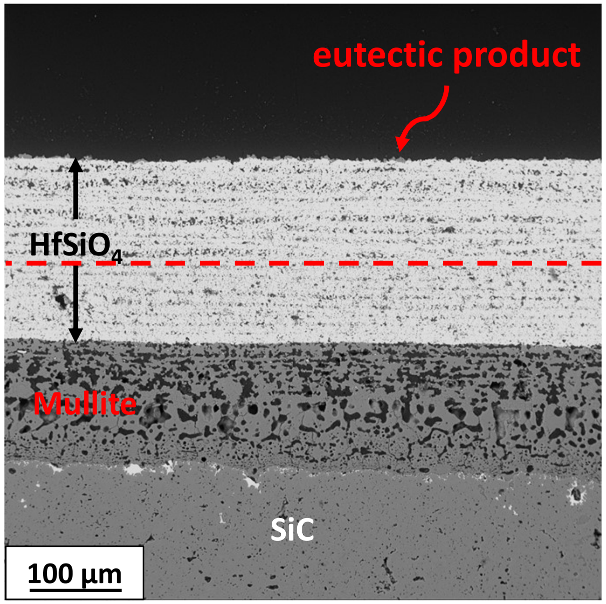
SiC

Single-layer HfO_2 topcoat

- **30 wt% $HfSiO_4$ + 1.5 wt% Si** → limited spallation after 500 cycles at 1480°C
  - 20 wt% $HfSiO_4$ + 1.5 wt% Si does not survive 100 cycles
  - Addition of 2.5 – 5 wt% mullite + $Yb_2Si_2O_7$/$Sc_2Si_2O_7$ mixture results in "bubbling"/cracking after 100 cycles

No observable HfO_2 remaining in topcoat layer by 500 cycles. HfO_2 reacts with Si, eutectic. Some debonding observed at bond coat/TGO interface.

500 cycles, 1480°C



Graded HfO_2 topcoat

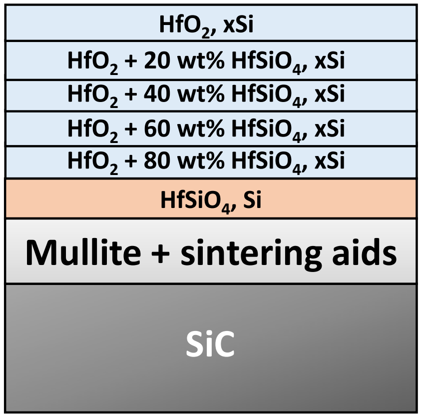
- HfO_2 as graded topcoat layer – up to five layers mixed with $HfSiO_4$, Si
  - Si content of ≥ 1.5 wt% needed as coating addition in each layer

100 cycles, 1480°C

x = 0 wt% Si

x = 0.5 wt% Si

x = 1.5 wt% Si



HfO_2, xSi

HfO_2 + 20 wt% $HfSiO_4$, xSi

HfO_2 + 40 wt% $HfSiO_4$, xSi

HfO_2 + 60 wt% $HfSiO_4$, xSi

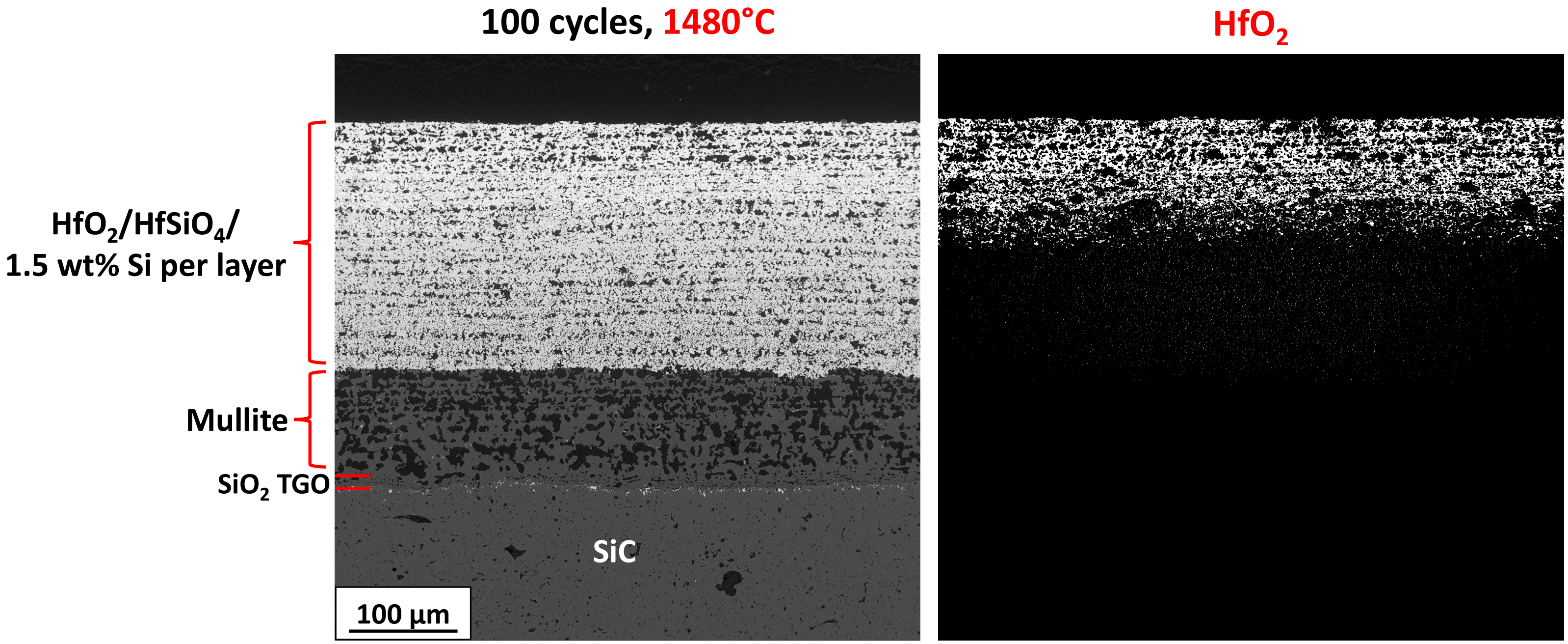
HfO_2 + 80 wt% $HfSiO_4$, xSi

$HfSiO_4$, Si

Mullite + sintering aids

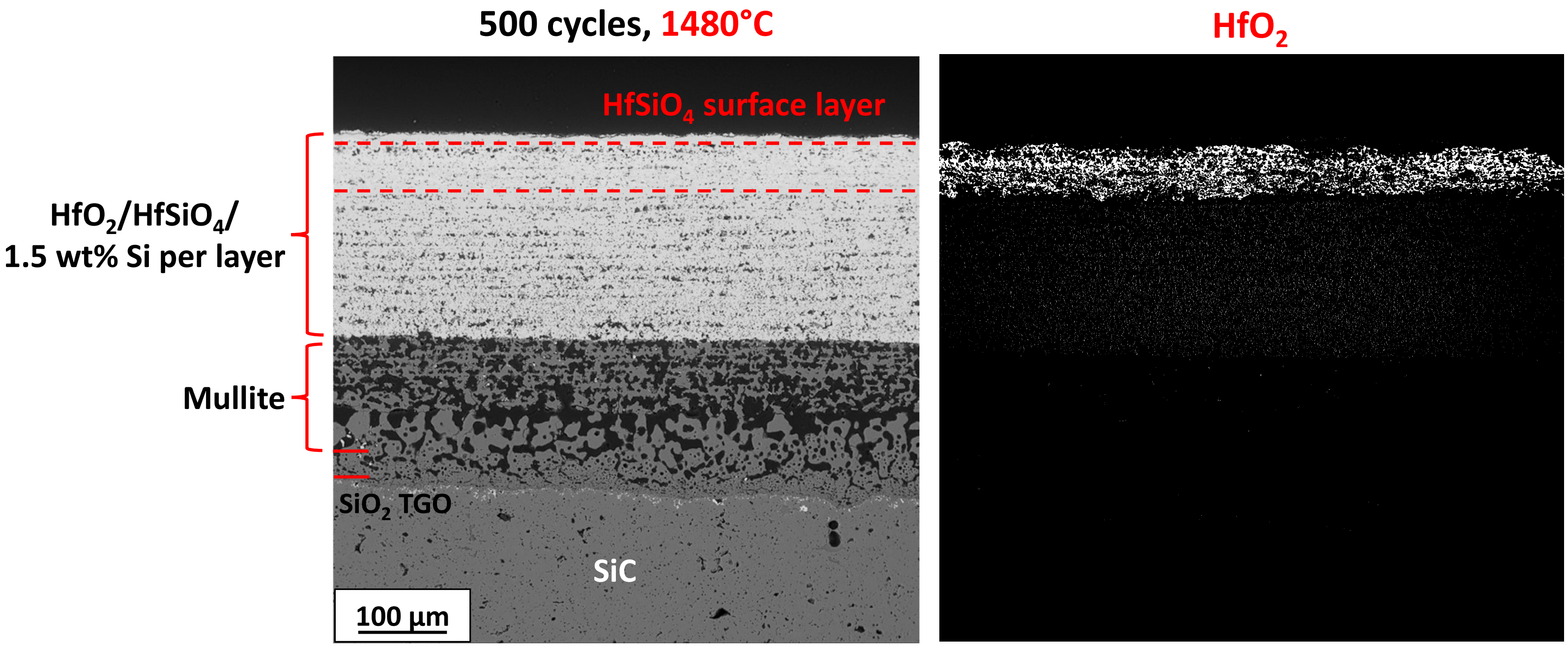
SiC

Graded HfO_2 topcoat



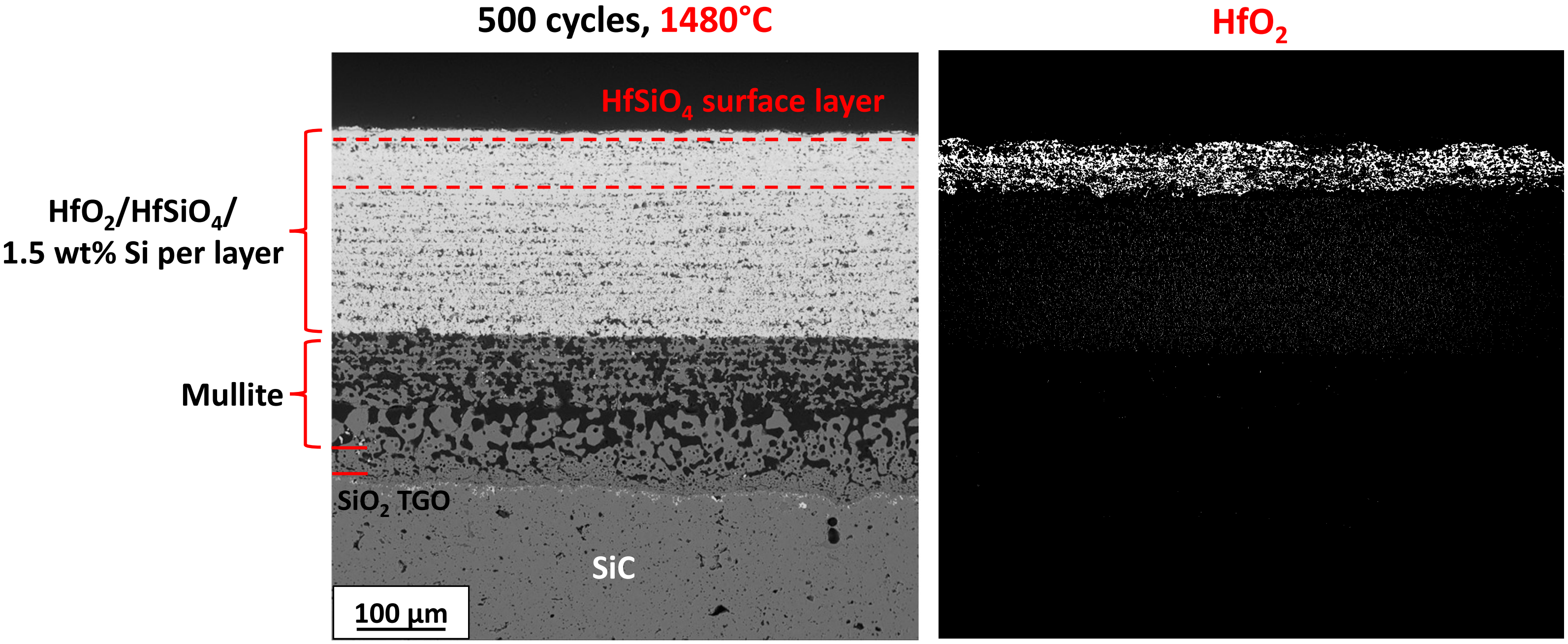
HfO_2 reacts with Si, eutectic after **100 cycles** at 1480°C, but ~150 µm thick region containing HfO_2 remains at surface.

Graded HfO_2 topcoat



HfO_2 near surface of topcoat ~75 µm thick following **500 cycles** at 1480°C. Thin, dense $HfSiO_4$ layer observed at surface. Pore coalescence near bond coat/TGO.

Graded HfO_2 topcoat



Future work needed to optimize sintering aid type/amount in bond coat and topcoat for graded HfO_2 to minimize reaction to form $HfSiO_4$.

Next-generation EBCs – takeaways

- Oxide-based bond coat needed to enable next-generation EBCs
  - Mullite-based bond coat with 1000 h capability at 1480°C has been successfully demonstrated
- Oxidation life and temperature capability are key challenges with mullite-based bond coat
  - Sintering aid type/concentration can be optimized
- $Sc_2Si_2O_7$ currently shows most promise as topcoat layer
  - Reaction of $Yb_2Si_2O_7$ with eutectic and HfO_2 with eutectic is current issue
  - Graded $Sc_2Si_2O_7/Sc_2SiO_5/Sc_2O_3$ under development
  - Sc is expensive!
- Future work entails continued EBC optimization and rigorous durability testing under temperature gradient + thermal cycling