High-temperature slurry environmental barrier coating with graded HfO_2-$HfSiO_4$ topcoat

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S2: Environmental Barrier Coatings (II)

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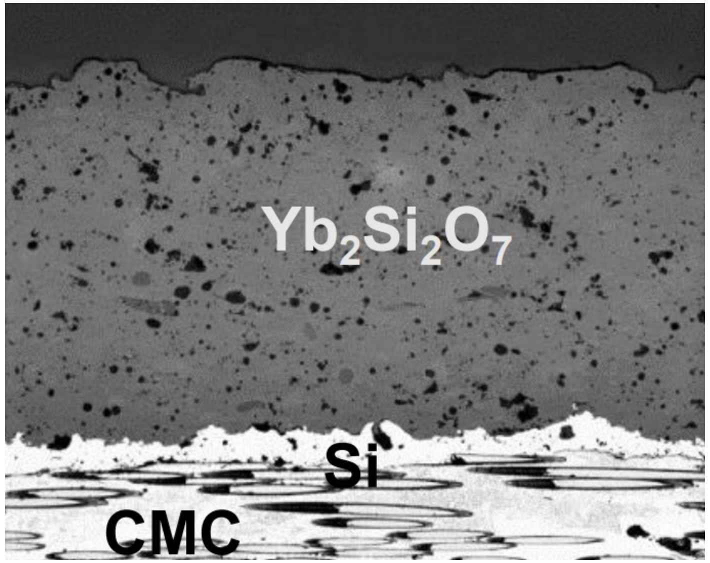
Background

- Current-generation environmental barrier coatings (EBCs) consist of a rare earth (RE) silicate ($RE_2Si_2O_7$; RE_2SiO_5) topcoat and a silicon bond coat
- Upper use temperature limited by melting point of Si (~1410°C)
- EBC operating temperature of **2700°F (1482°C)** desired



https://ntrs.nasa.gov/api/citations/20180004253

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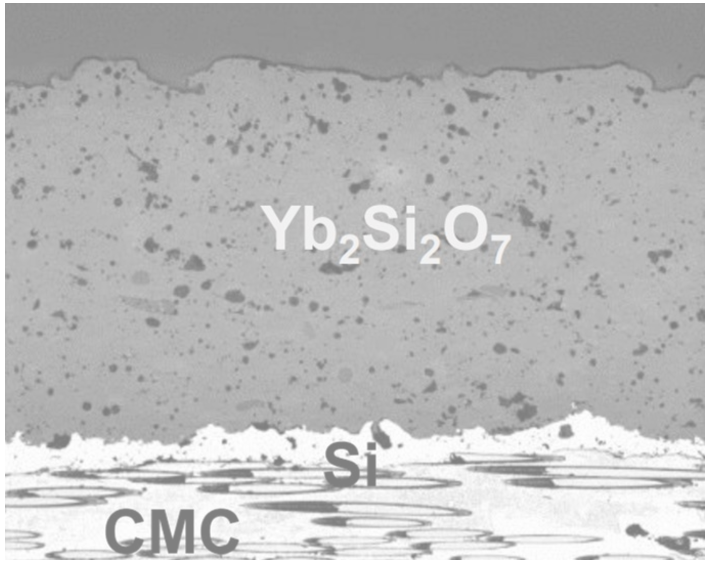

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Alternative bond coat materials necessary to reach EBC temperature goal

Background

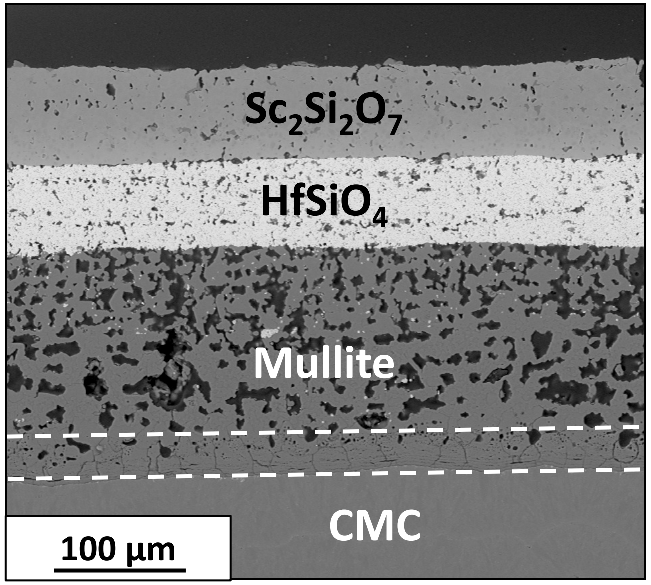
- A slurry-based oxide bond coat with significantly higher temperature capability has been developed at NASA Glenn Research Center

	Mullite	$RE_2Si_2O_7$, Al_2O_3, proprietary oxide	Si, SiC
Bond coat	balance	< 3 wt% (total)	< 30 wt% (total)

Background

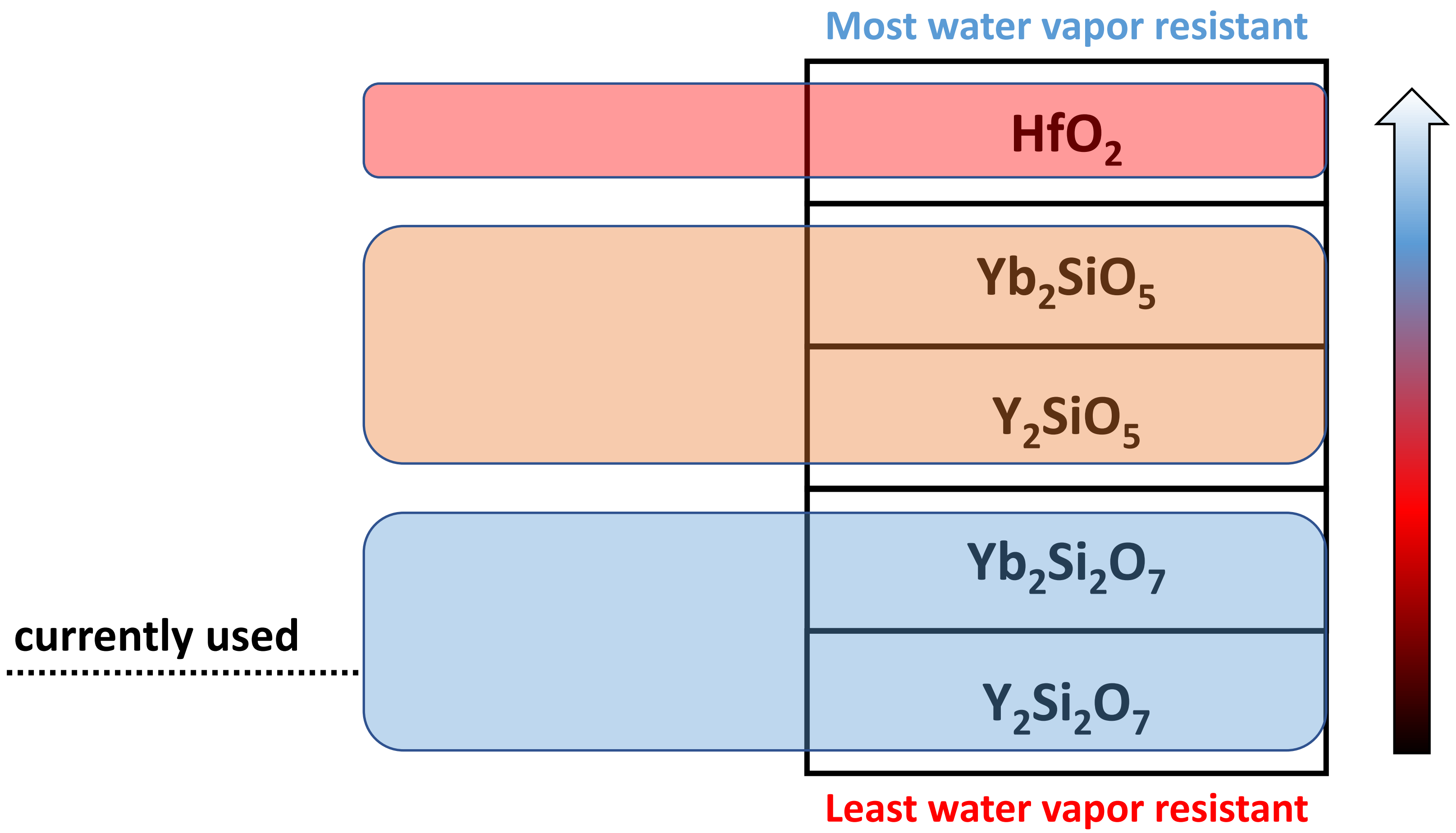
- A slurry-based oxide bond coat with significantly higher temperature capability has been developed at NASA Glenn Research Center
- Multilayer high-temperature EBC has been shown to be successful at temperatures ≥ 2700°F in oxygen, water-vapor-containing environments and under temperature gradients
  - Bond coat: mullite + sintering aids
  - Intermediate coat: $HfSiO_4$ + sintering aids
  - Topcoat: **$Sc_2Si_2O_7$** + sintering aids

1480°C, 1000 cycles, steam



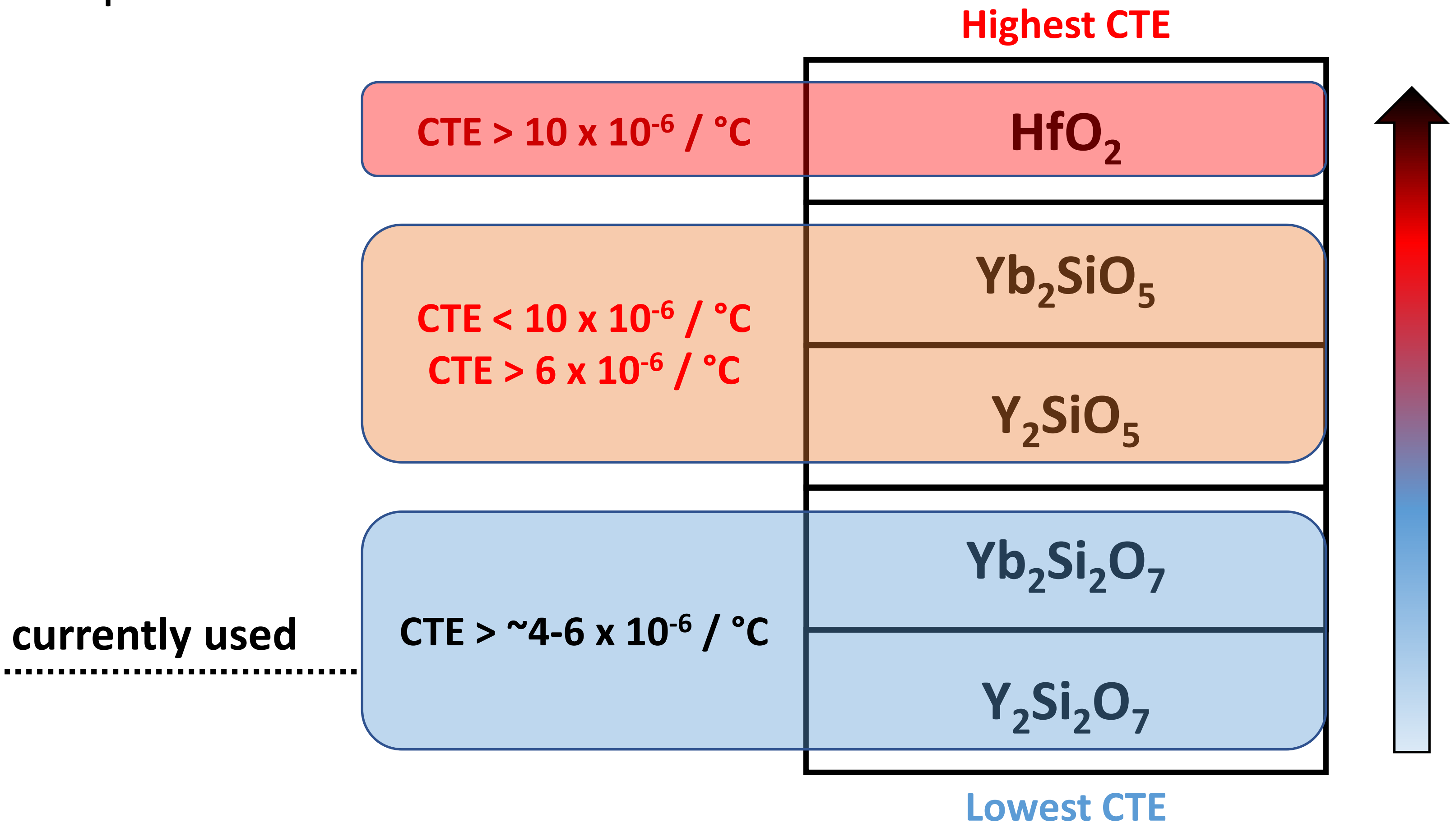
Motivation

- HfO_2 is desirable as an EBC topcoat due to its stability at high temperatures and in steam



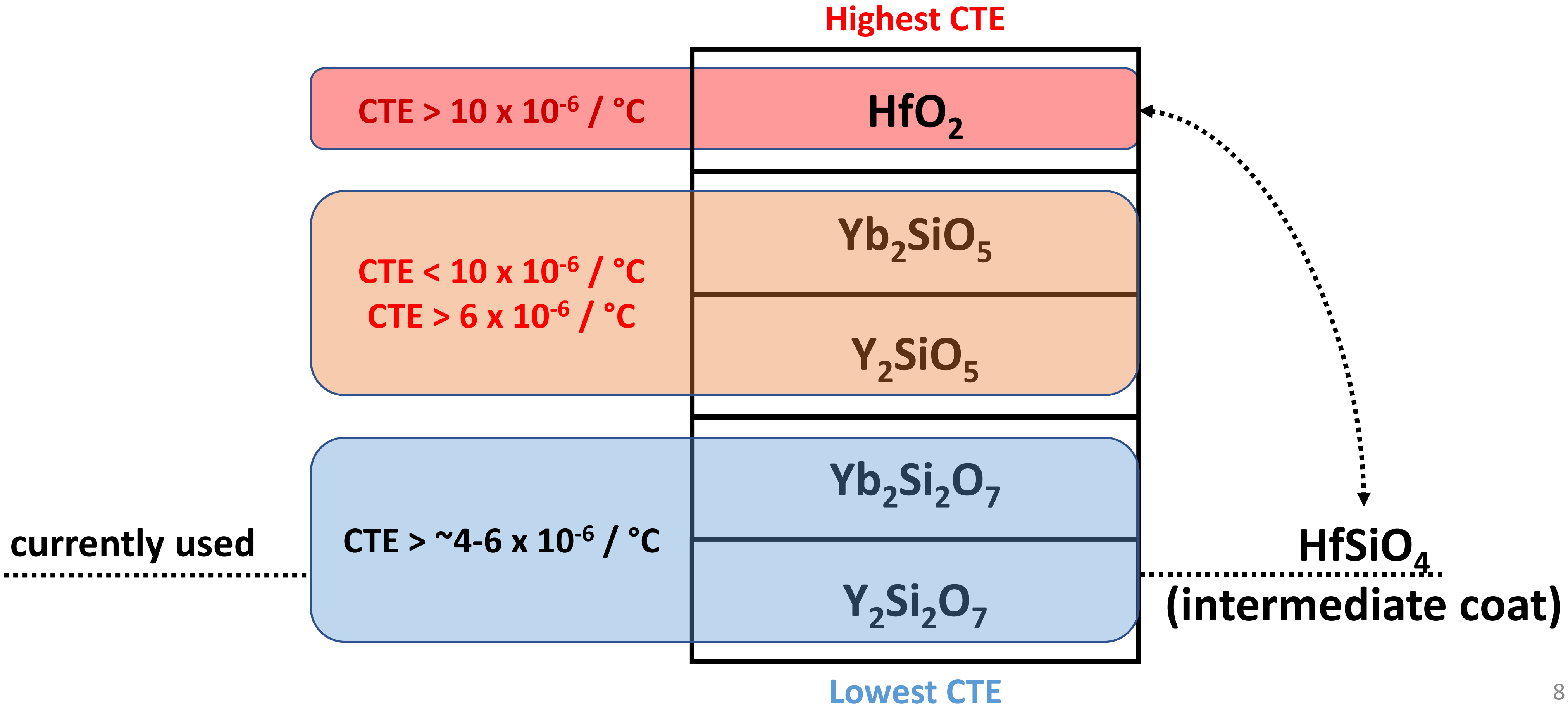
Motivation

- However, the thermal expansion coefficient (CTE) of HfO_2 is large and highly anisotropic



Objective

- Prepare **$HfSiO_4$-HfO_2** gradient topcoat layer with $HfSiO_4$ intermediate coat and high-temperature, mullite-based bond coat via slurry process



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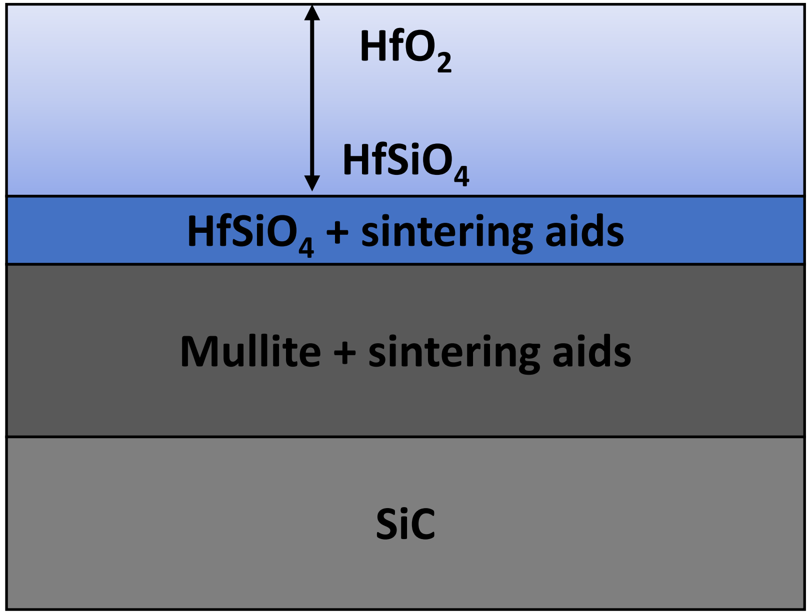

Objective

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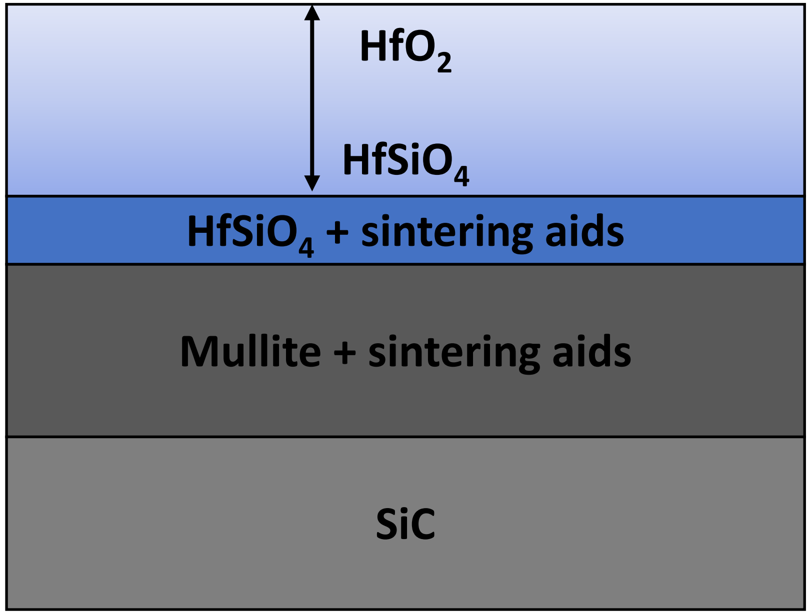
- Determine viability of this system via steam cycling at 2700°F



Experimental

- Bondcoat (BC), intermediate coat (IC), and topcoat powders mixed and milled
- Milled powders prepared as slurry with ethanol, polyethyleneimine (PEI) dispersant, and polyvinyl butyral (PVB) binder
- Coating layers deposited on Hexoloy® SA coupons via spin coating
- Dried coupons sintered 3 h/1520°C, annealed 20 h/1480°C in air (all layers)

	Base Material	Sintering Aids	Amount
Topcoat	HfO_2 + $HfSiO_4$	Si, mullite, $RE_2Si_2O_7$	TBD
Intermediate coat (IC)	$HfSiO_4$	Si	2 wt%
Bond coat (BC)	Mullite	Al_2O_3, $Yb_2Si_2O_7$, proprietary oxide	< 3 wt% (total)
		Si, SiC	< 30 wt% (total)

KN Lee, DL Waters, U.S. Patent 11325869, 10 May 2022.

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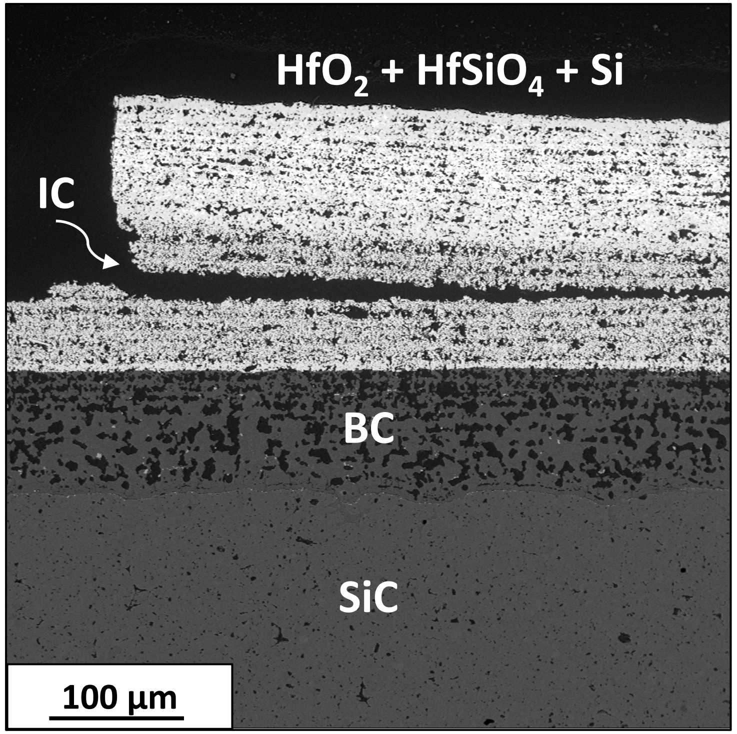
- Coating layers deposited on Hexoloy® SA coupons via spin coating
- Dried coupons sintered 3 h/1520°C, annealed 20 h/1480°C in air (all layers)
- Samples exposed in a steam cycling rig (1 hour hot, 30 min cool) at ~1480°C
  - 90 vol% H_2O/10 vol% O_2
  - 10 cm/s gas velocity

Results: Single-layer topcoat

- HfO_2 + **20 wt% $HfSiO_4$** + 1.5 wt% Si → spallation by <u>100</u> cycles at 1480°C
  - Silicon added to topcoat as sintering aid, densifier

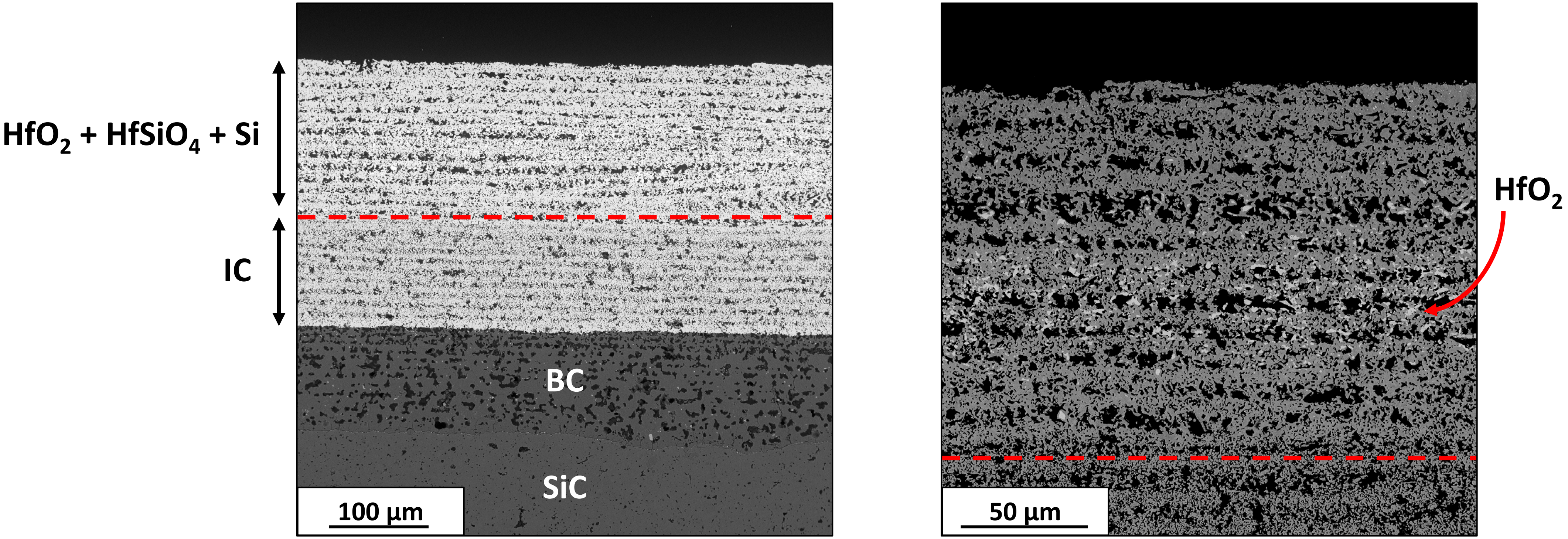
1480°C, 100 cycles, steam



Results: Single-layer topcoat

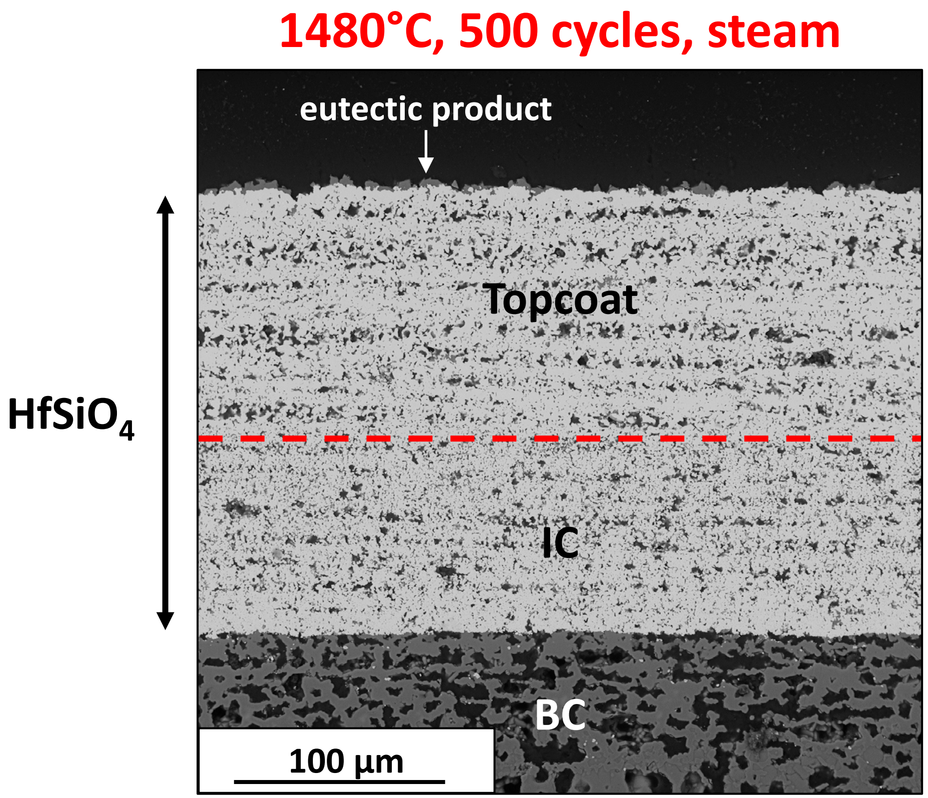
- HfO_2 + **30 wt% $HfSiO_4$** + 1.5 wt% Si → limited spallation after <u>500</u> cycles at 1480°C

1480°C, 100 cycles, steam



Results: Single-layer topcoat

- HfO_2 is completely transformed into $HfSiO_4$ by 500 cycles
  - Si (in topcoat) + O_2 → SiO_2 + HfO_2 → $HfSiO_4$
  - 50/50 vol% HfO_2/$HfSiO_4$ expected in topcoat based on reaction of Si in topcoat alone



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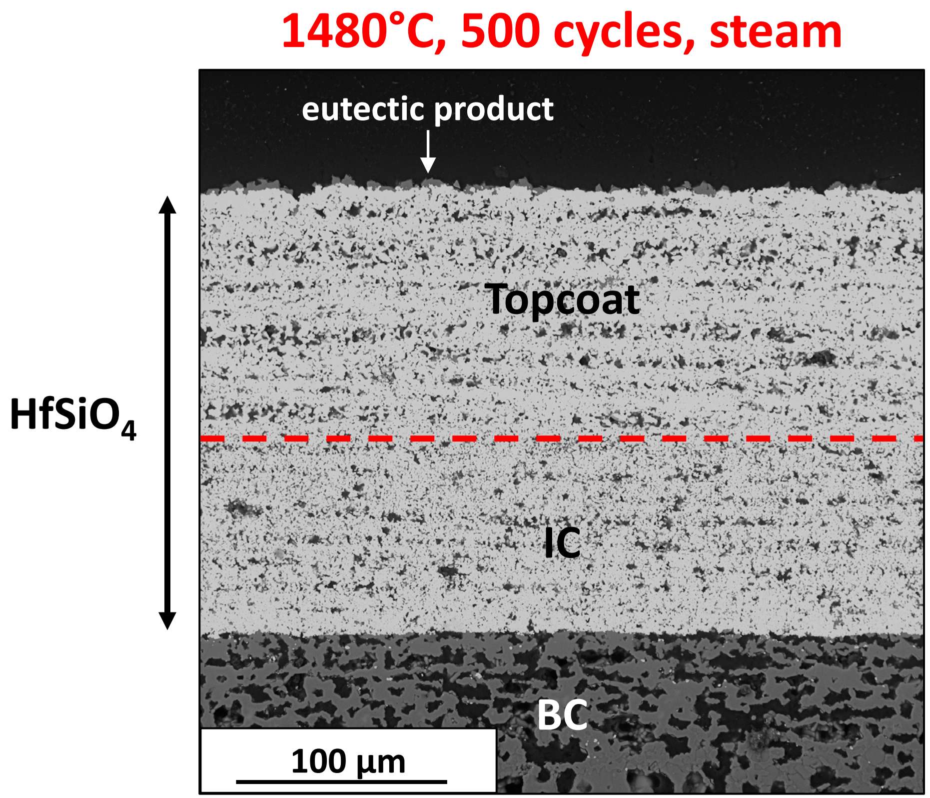
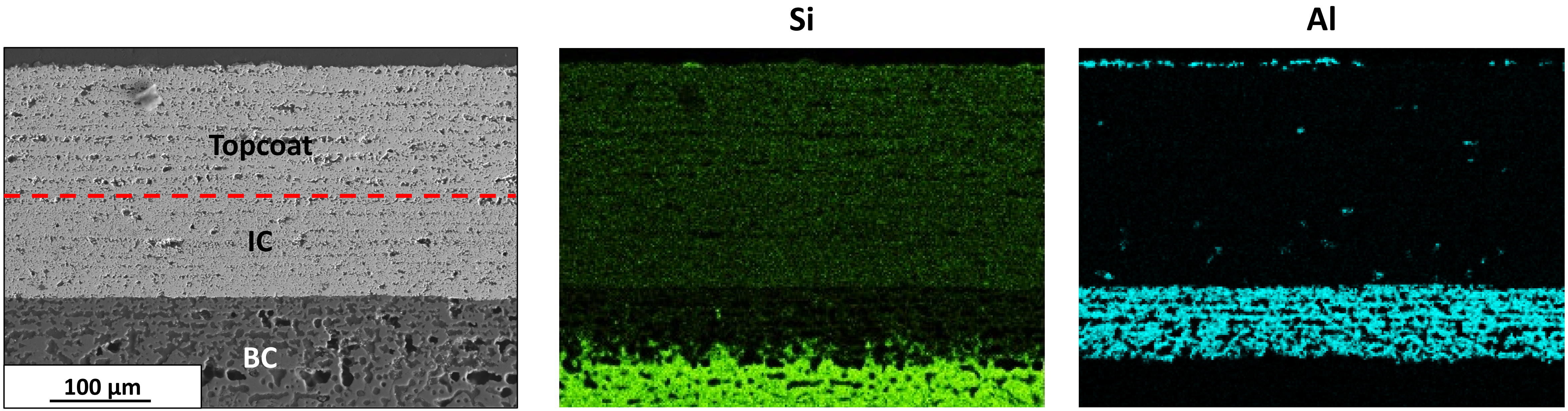
  - Full transformation suggests that Si/SiO_2 from BC is transported to topcoat via eutectic



Results: Single-layer topcoat

- Energy dispersive spectroscopy (EDS) maps confirm that eutectic moves from BC to topcoat



Results: Single-layer topcoat

- HfO_2 is completely transformed into $HfSiO_4$ by 500 cycles
  - $Si + O_2 \rightarrow SiO_2 + HfO_2 \rightarrow HfSiO_4$
  - Eutectic product from sintering aids (containing SiO_2) moves up

- Addition of mullite + $Yb_2Si_2O_7$ or $Sc_2Si_2O_7$ to single-layer topcoat results in "bubbling"/cracking after 100 cycles

HfO_2 + 30 wt% $HfSiO_4$ + 1.5 wt% Si + 2.5 wt% mullite/$Yb_2Si_2O_7$ mixture

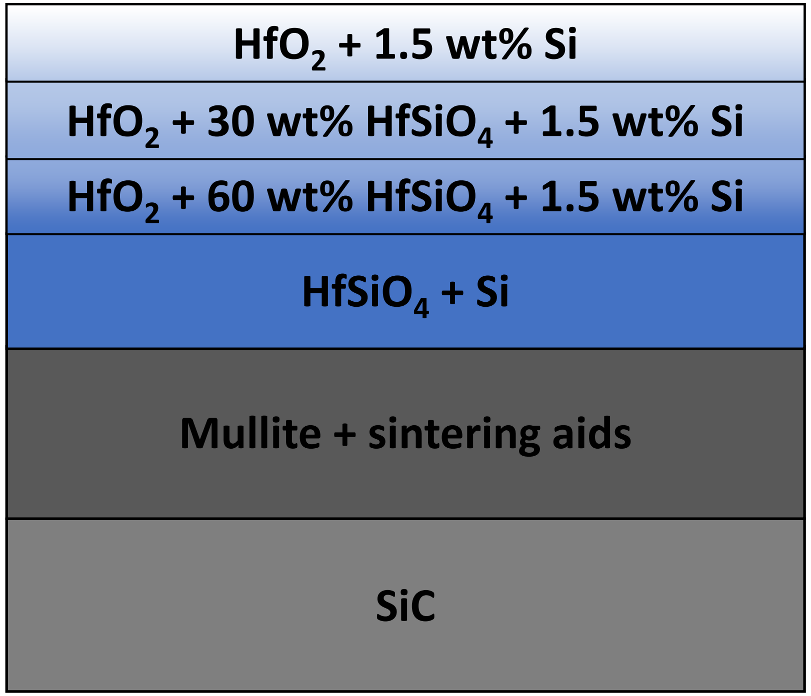
1480°C, 100 cycles, steam

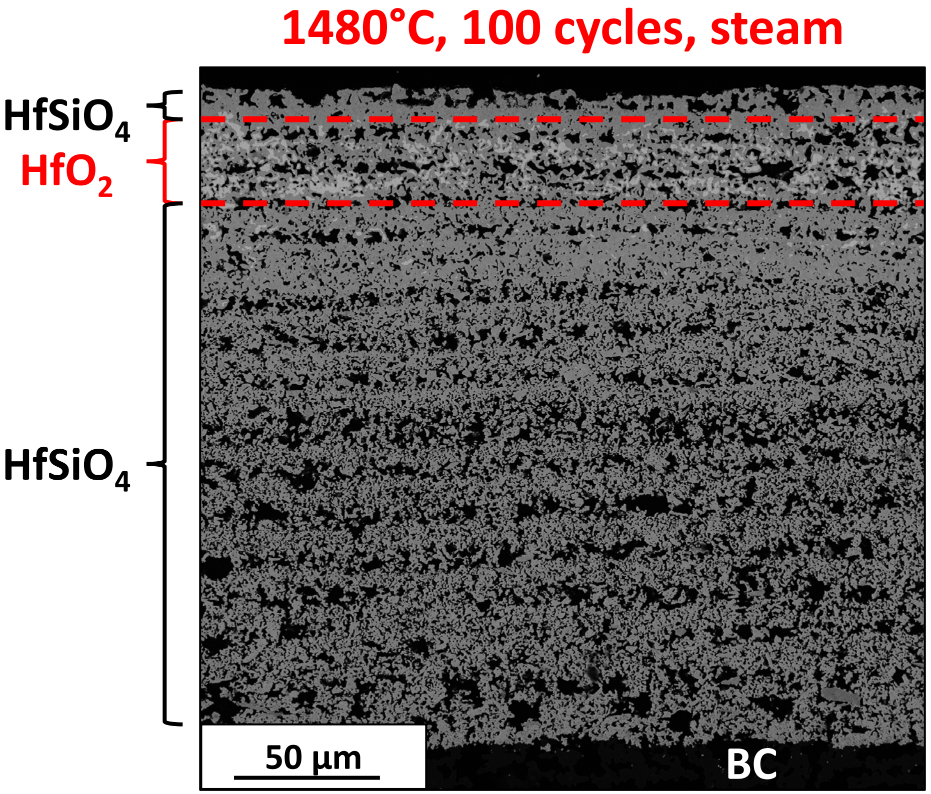
1"

½"

Results: Three-layer topcoat

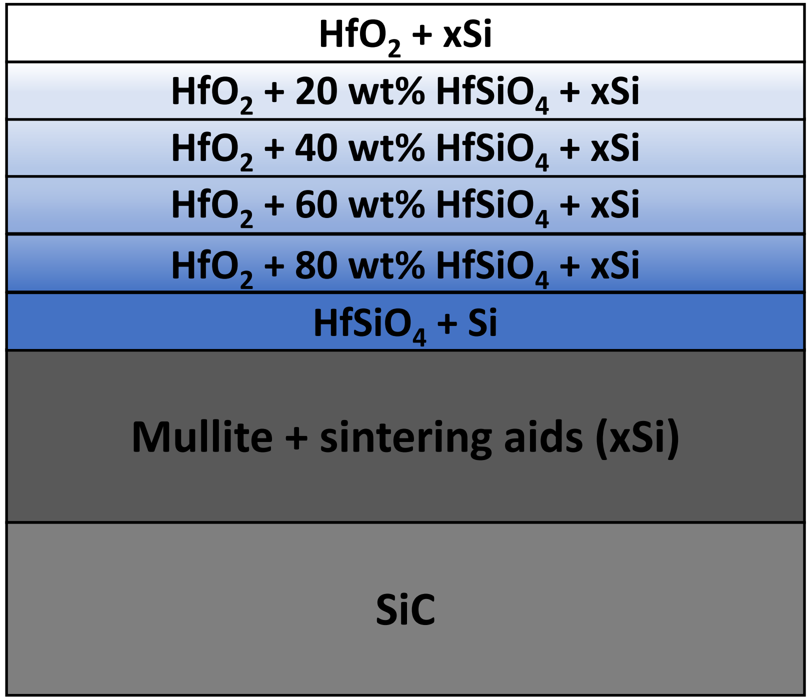
- Very little HfO_2 remaining in three-layer coating after 100 cycles





Results: Five-layer topcoat

- Presence of SiO_2 in topcoat results in transformation of HfO_2 to $HfSiO_4$
  - Silicon in topcoat oxidizes to form SiO_2, reacts with HfO_2 to form $HfSiO_4$
  - Silicon/SiO_2 in bond coat is transported to topcoat



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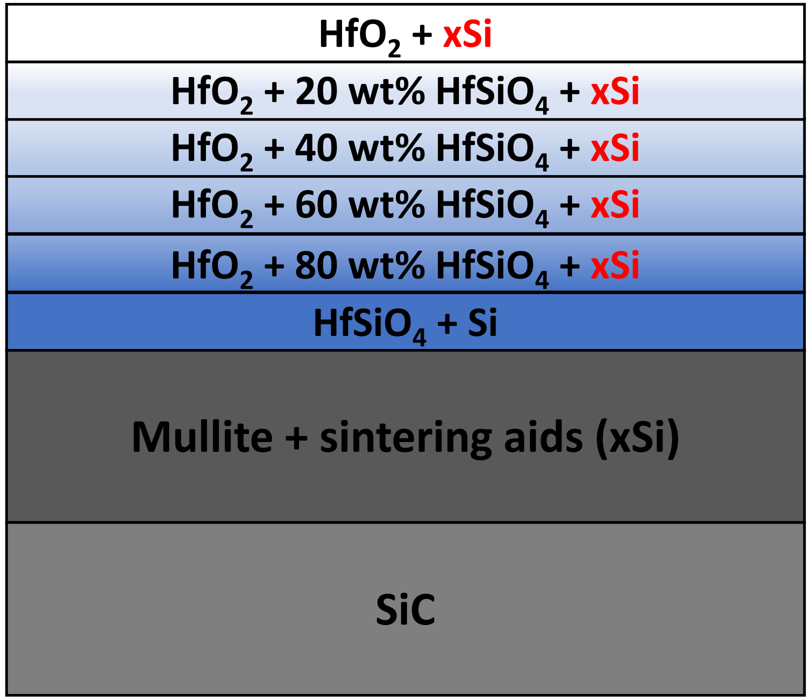

1) What is the minimum amount of Si needed in each layer of the topcoat?

Results: Five-layer topcoat

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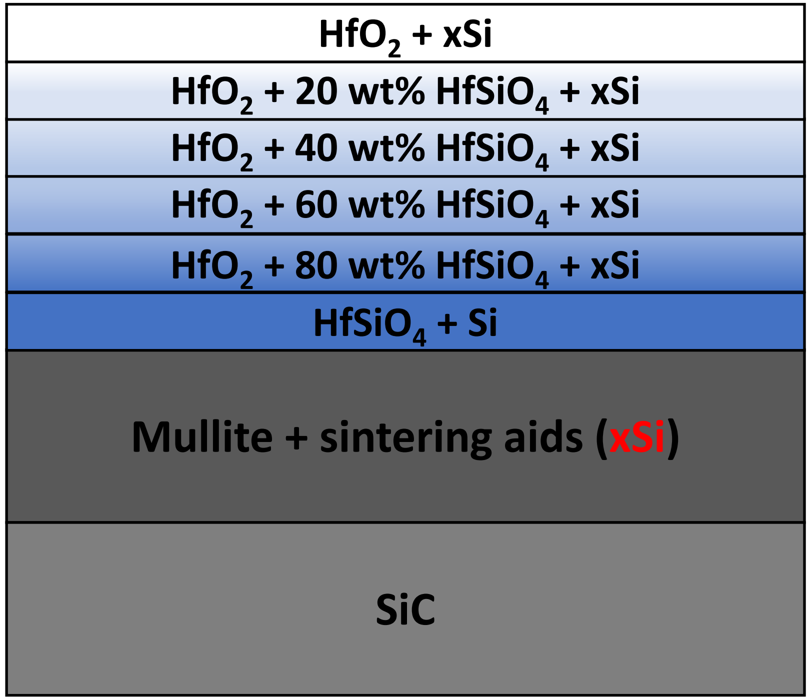
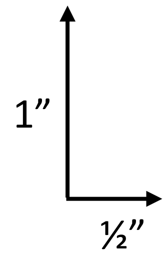


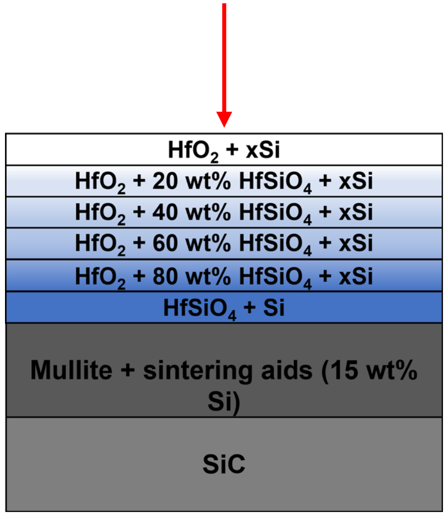
1) What is the minimum amount of Si needed in each layer of the topcoat?
2) What is the minimum amount of Si needed in the bond coat?

Results: Si in topcoat

- Bond coat composition kept constant (+15 wt% Si, other sintering aids)
- Minimum of 1.5 wt% Si necessary for topcoat (each layer)



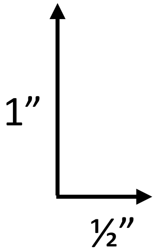
1480°C, ≤ 100 cycles, steam



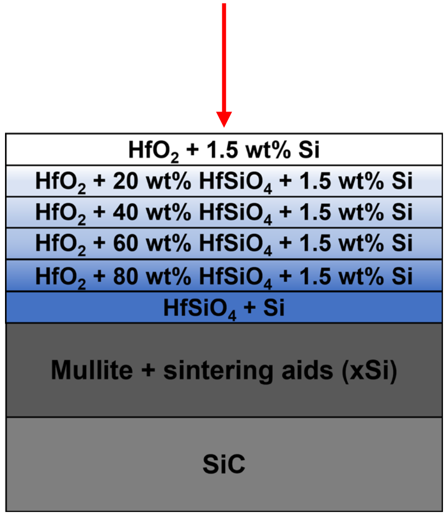
x = 0 wt% Si | **x = 0.5 wt% Si** | **x = 1 wt% Si** | **x = 1.5 wt% Si**

Results: Si in bond coat

- Topcoat layer compositions kept constant (+1.5 wt% Si each layer)
- Minimum of 15 wt% Si necessary for bond coat



As-processed (3 h/1520°C, 20 h/1480°C, air)



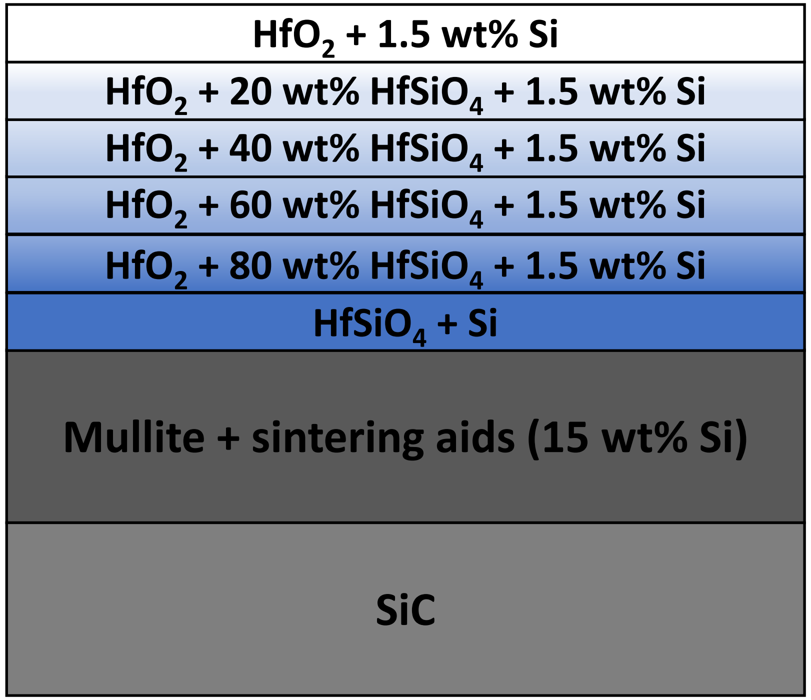
x = 0 wt% Si

x = 12.5 wt% Si

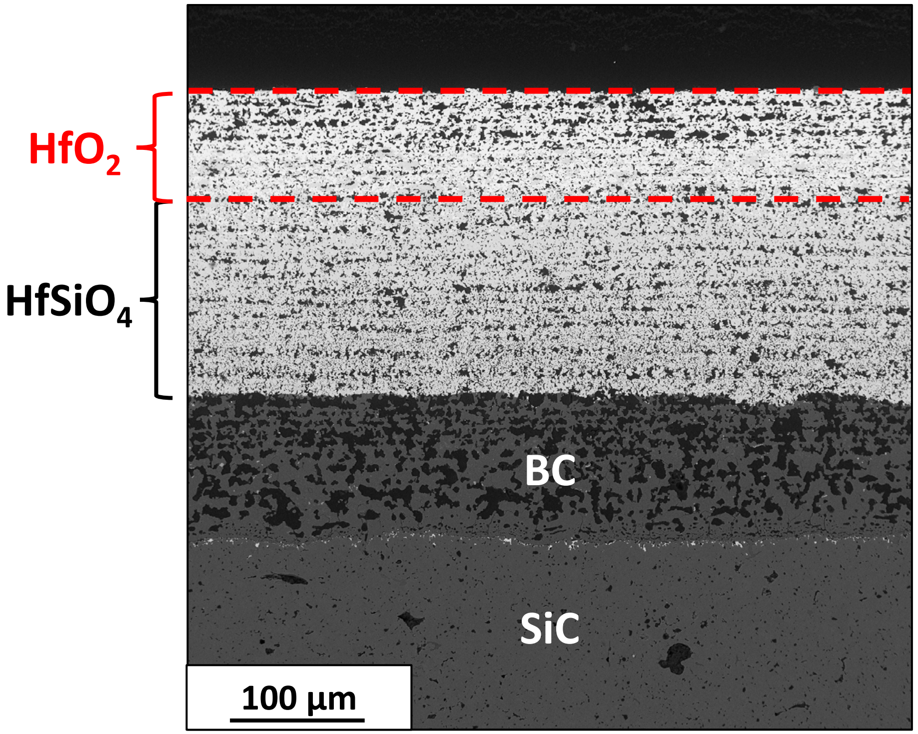
x = 15 wt% Si

Results: Five-layer topcoat

- BC = +15 wt% Si, topcoat layers = +1.5 wt% Si
- ~150 μm thick region containing HfO_2 remains at surface after 100 cycles at 1480°C



1480°C, 100 cycles, steam



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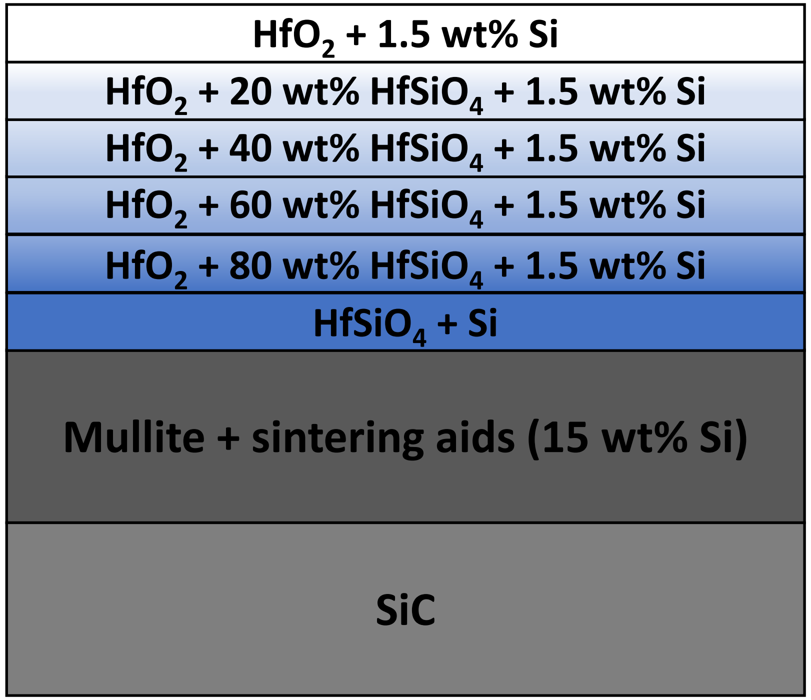
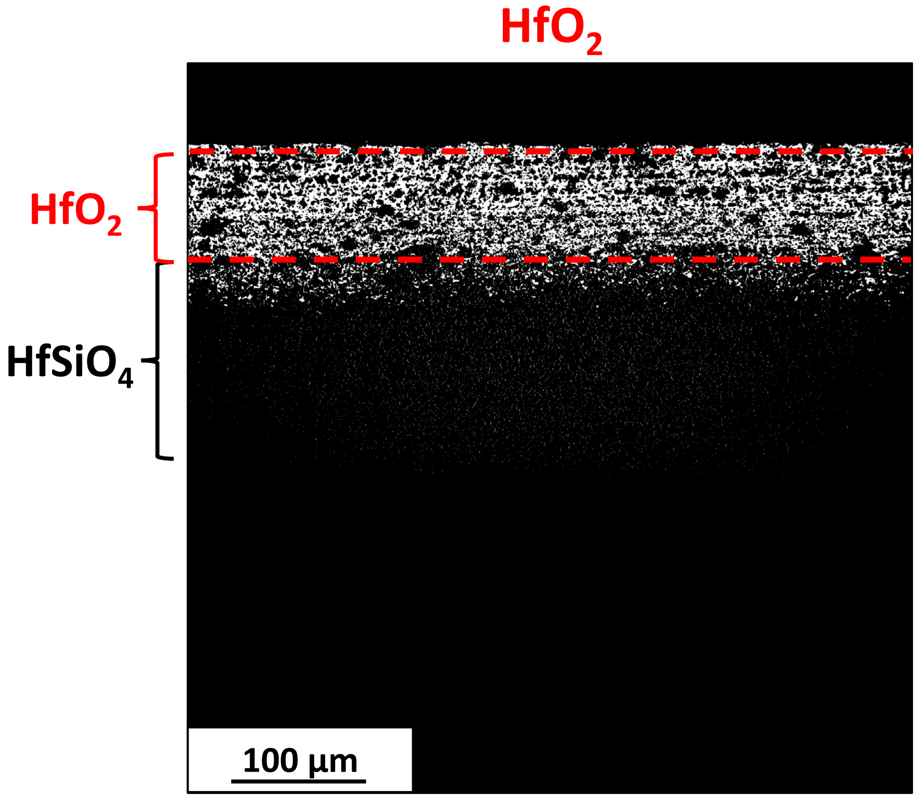
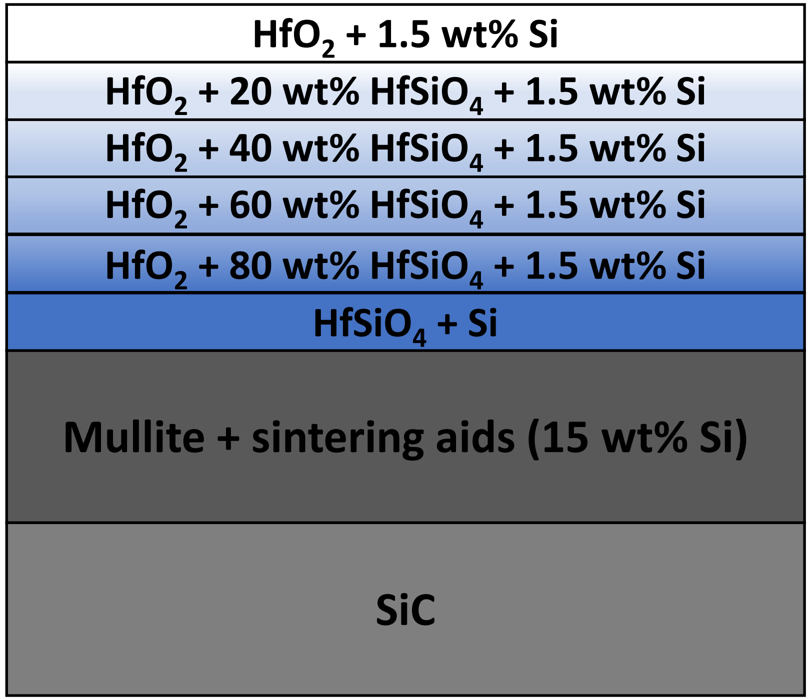




Results: Five-layer topcoat

- ~75 µm thick region containing HfO_2 remains near surface after 500 cycles
- Thin, dense $HfSiO_4$ layer observed at surface
- Pore coalescence in bond coat



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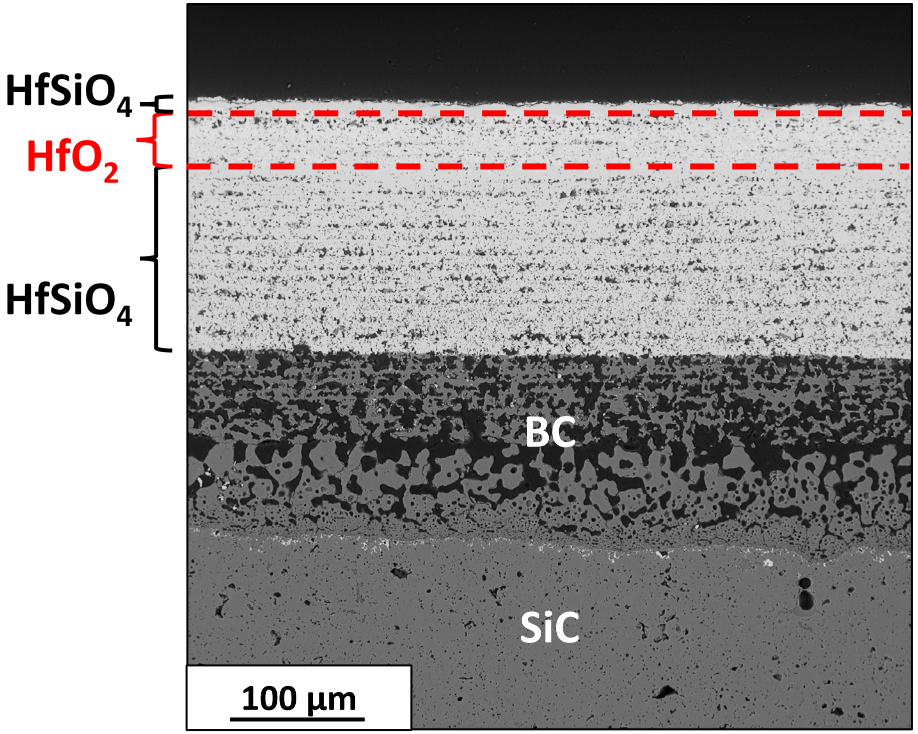

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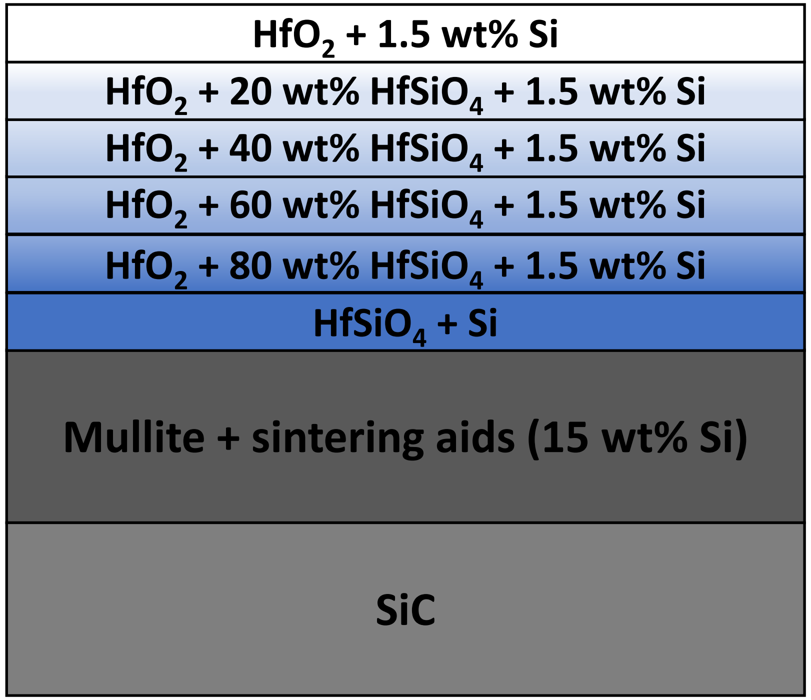

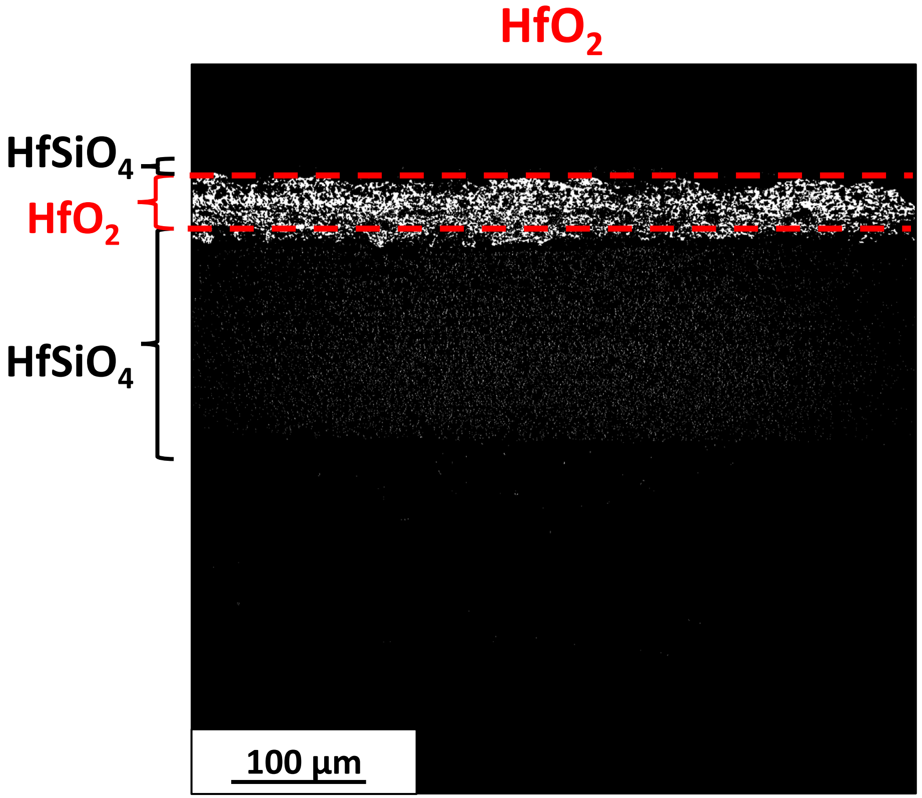

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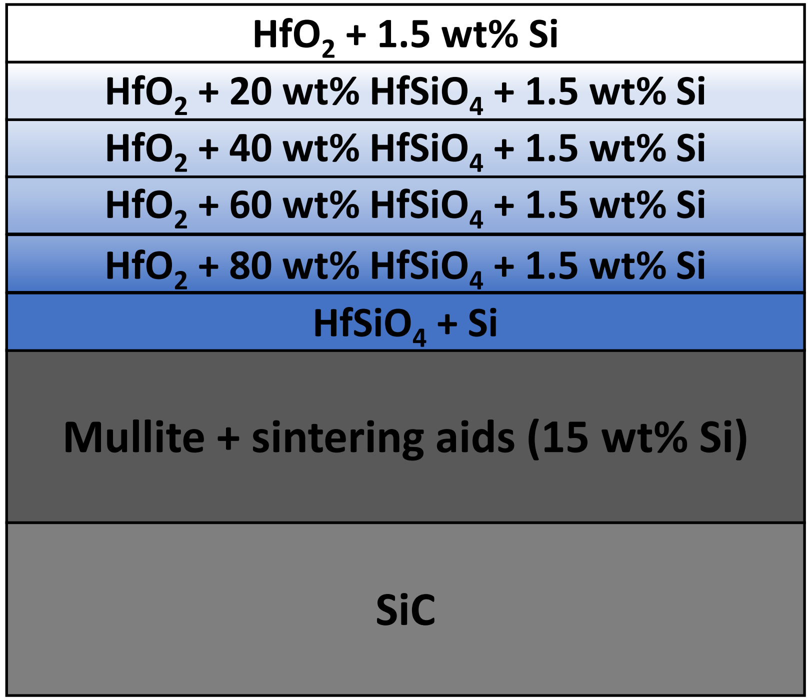
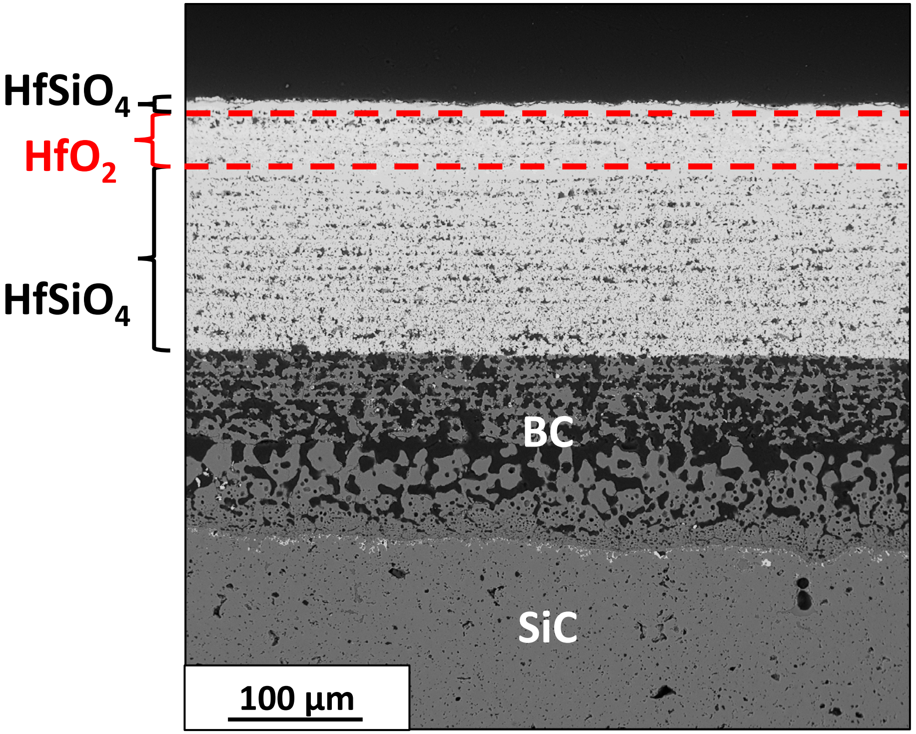
EBC layers are porous. Can we add additional sintering aids or change the sintering regime?

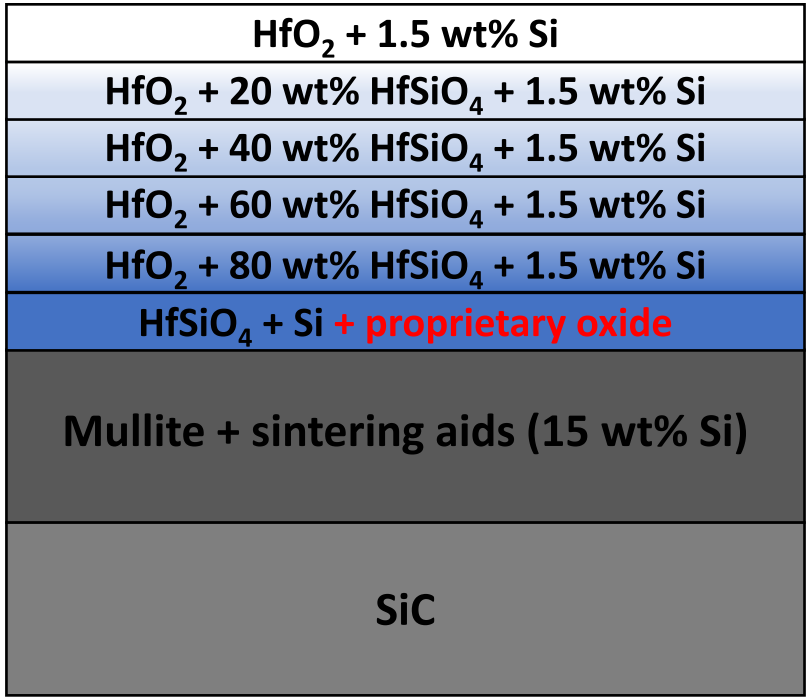


1480°C, 500 cycles, steam

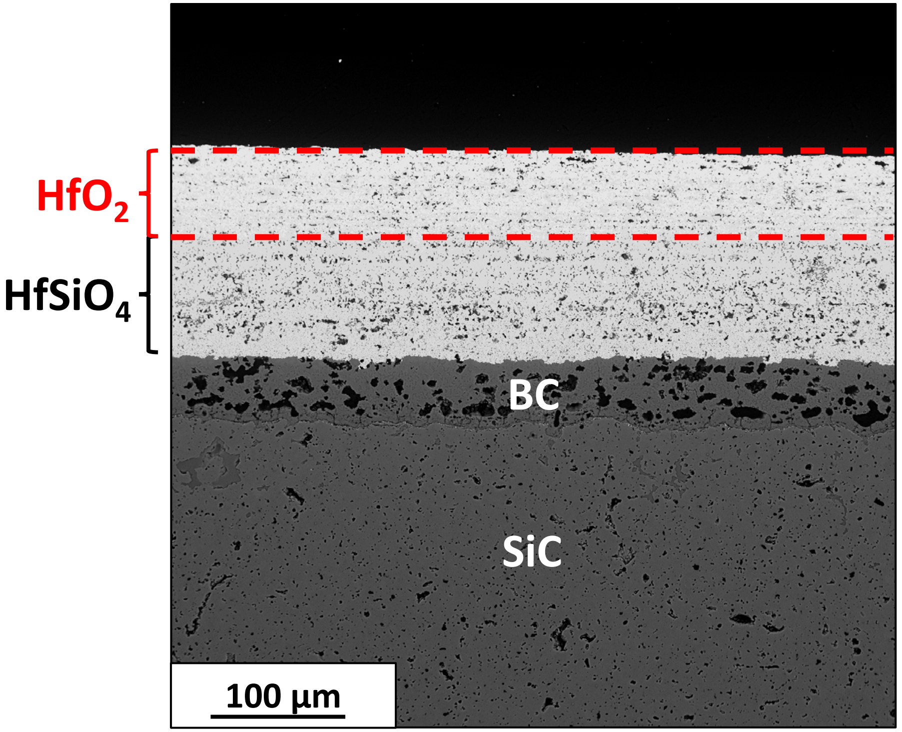


Results: Additional sintering aids

- Proprietary oxide added to intermediate coat (IC) in addition to 2 wt% Si
- Each layer (BC, IC, topcoat) sintered separately, 20 h anneal total



1480°C, 100 cycles, steam



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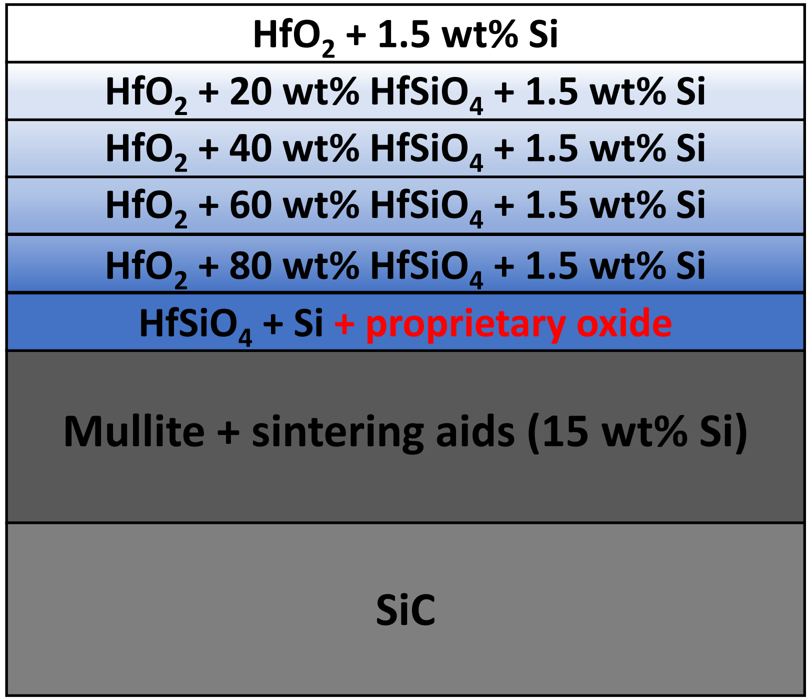
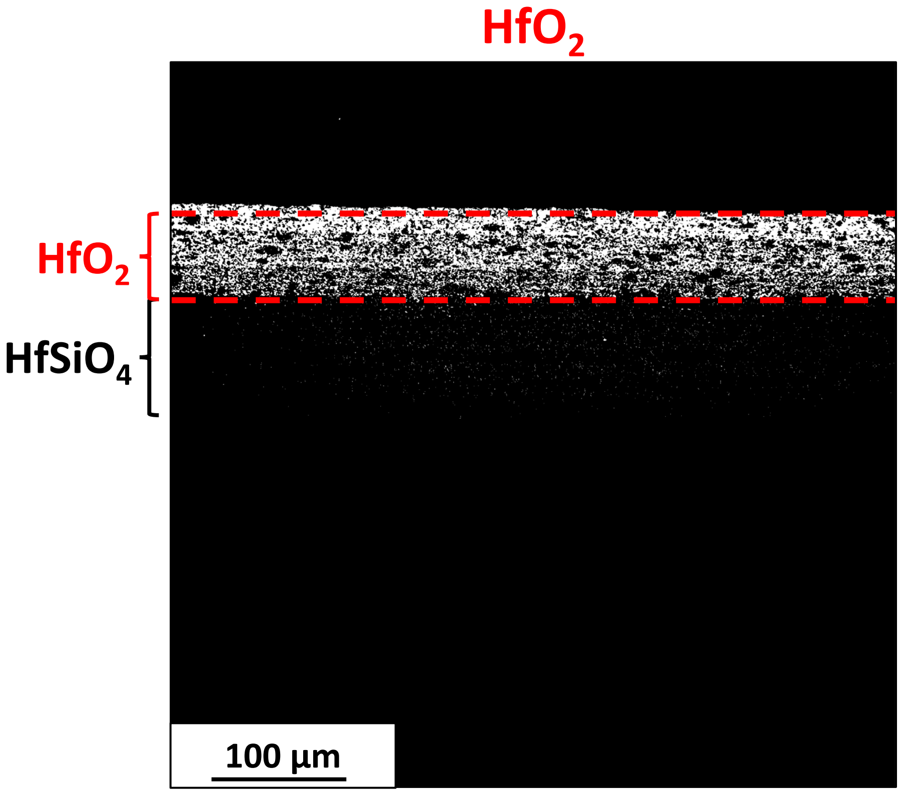
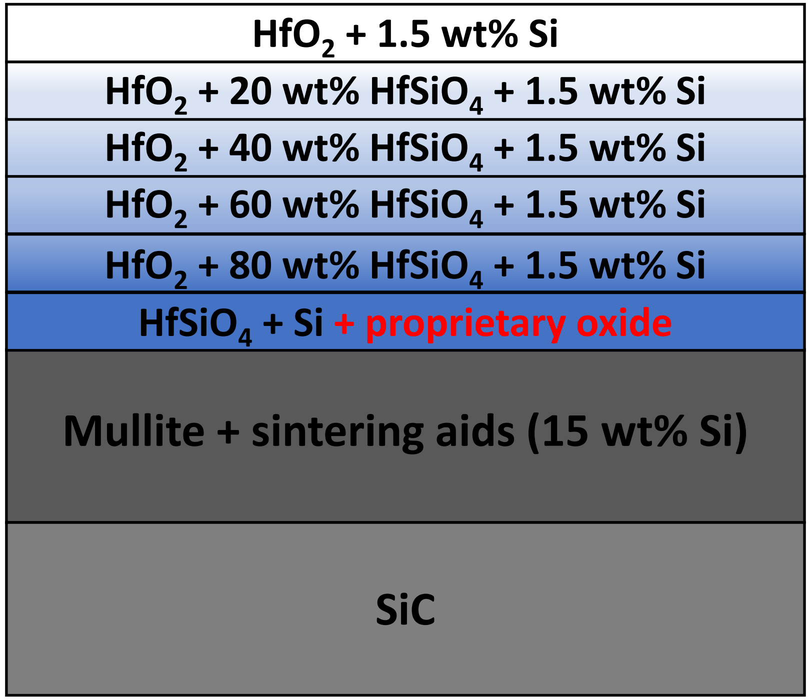


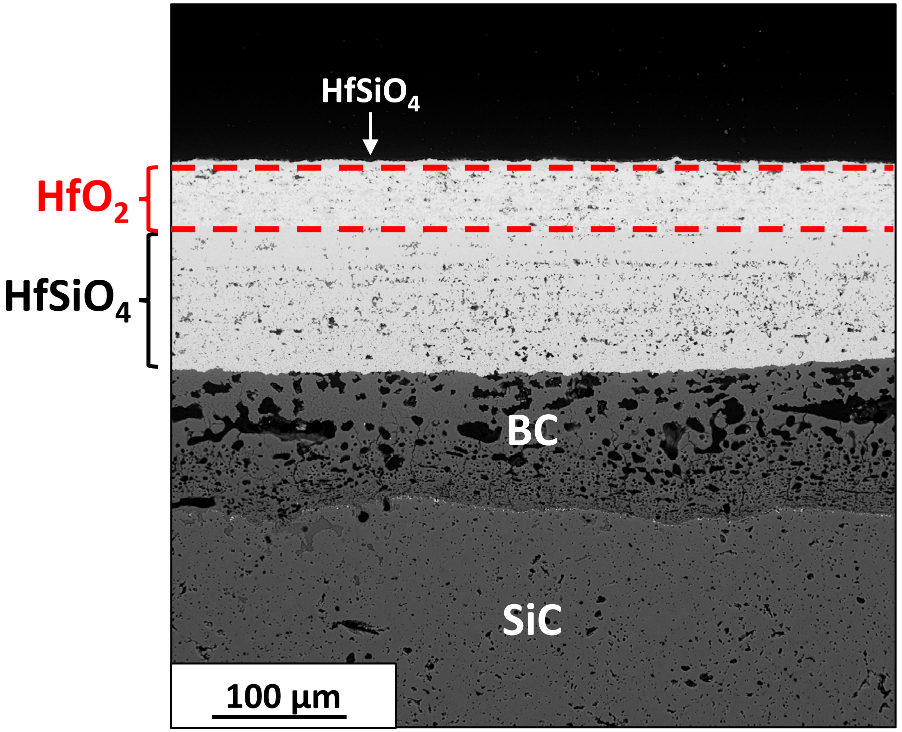


Results: Additional sintering aids

- Addition of oxide to IC seems to improve density of layer and adhesion to underlying BC
- HfO_2 remaining after 400 cycles



1480°C, 400 cycles, steam



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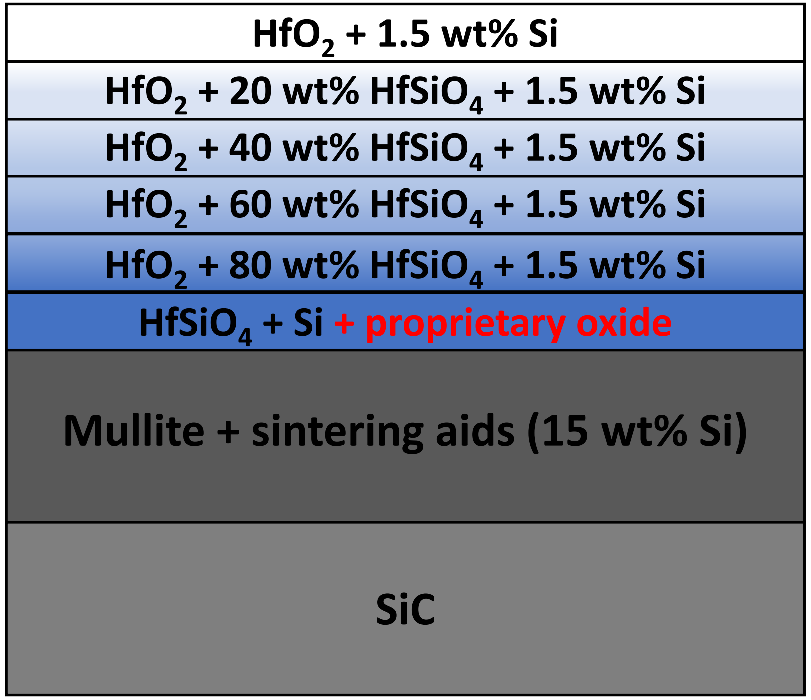

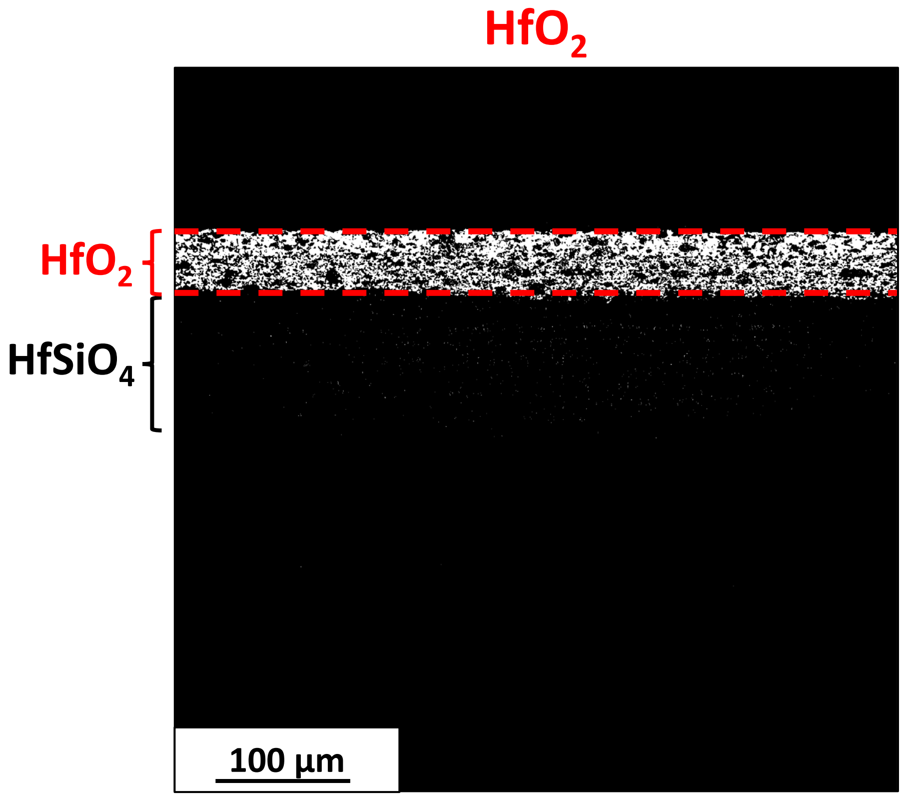

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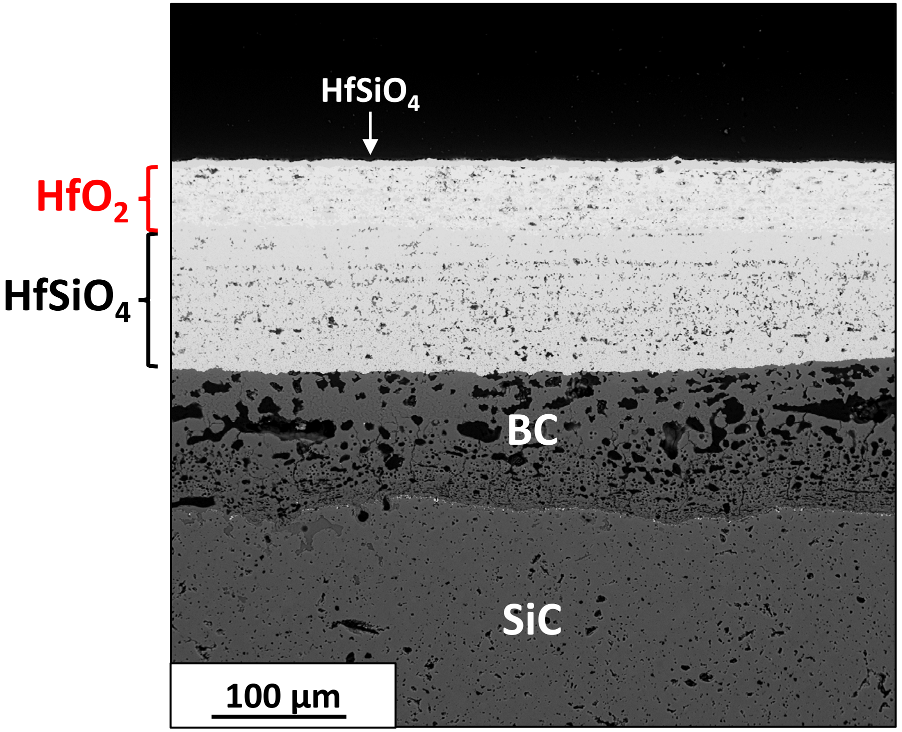
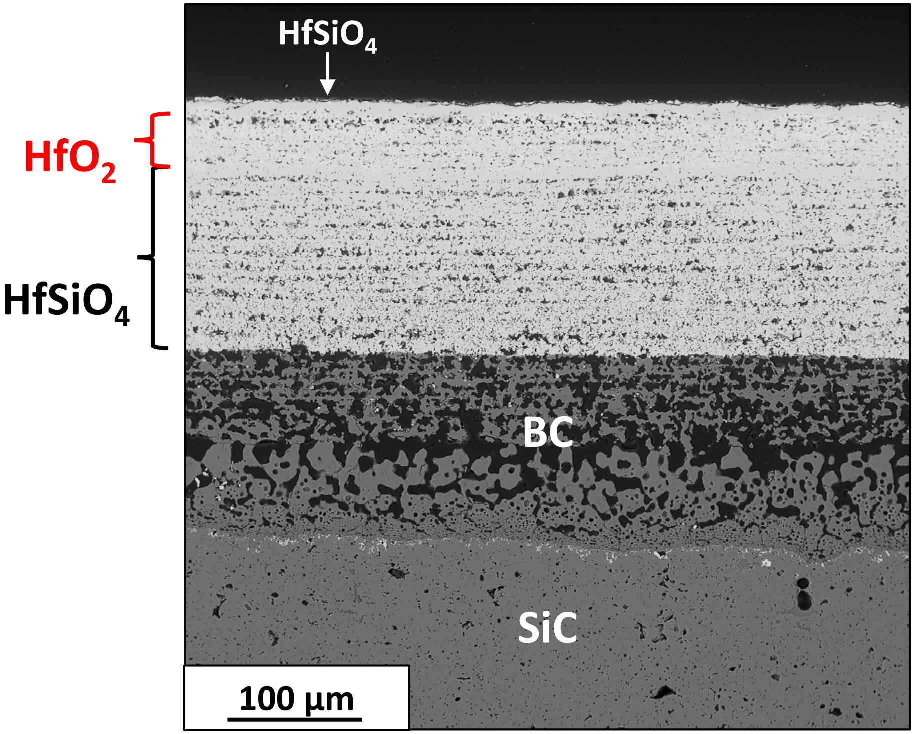


+ proprietary oxide / layers sintered separately

1480°C, 500 cycles, steam

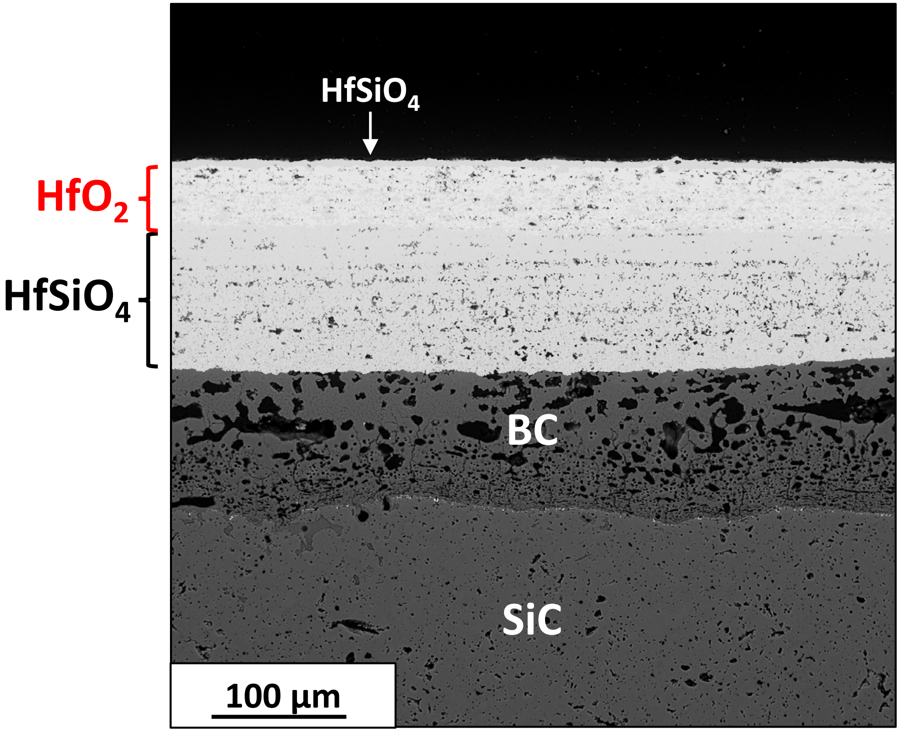


no proprietary oxide / one sintering schedule

BC/IC interface more coherent when proprietary oxide added to IC

Results: Additional sintering aids

1480°C, 400 cycles, steam



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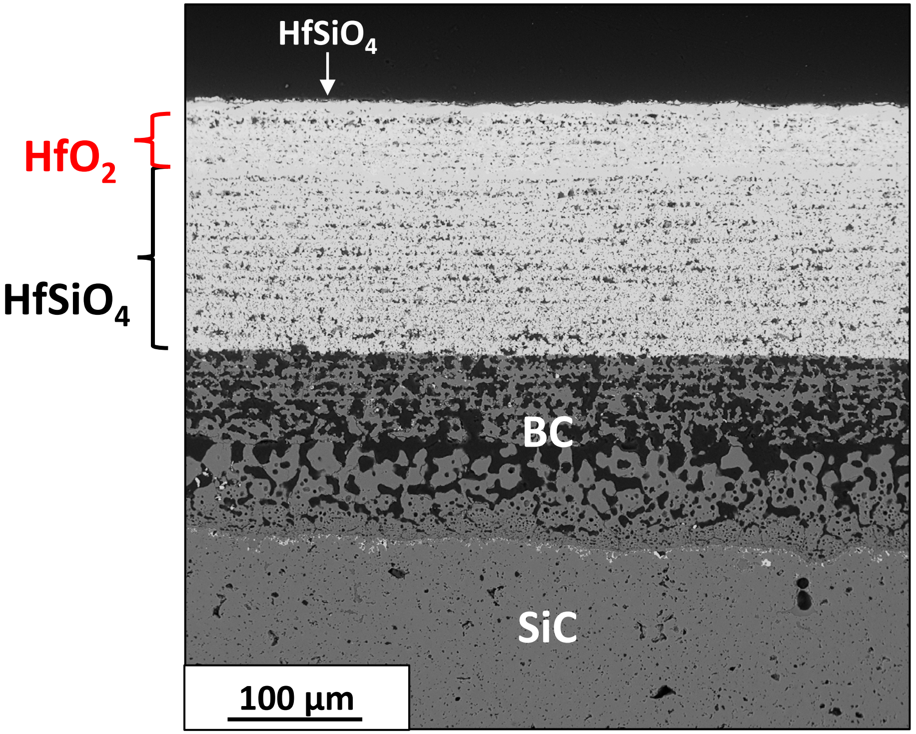
1480°C, 500 cycles, steam

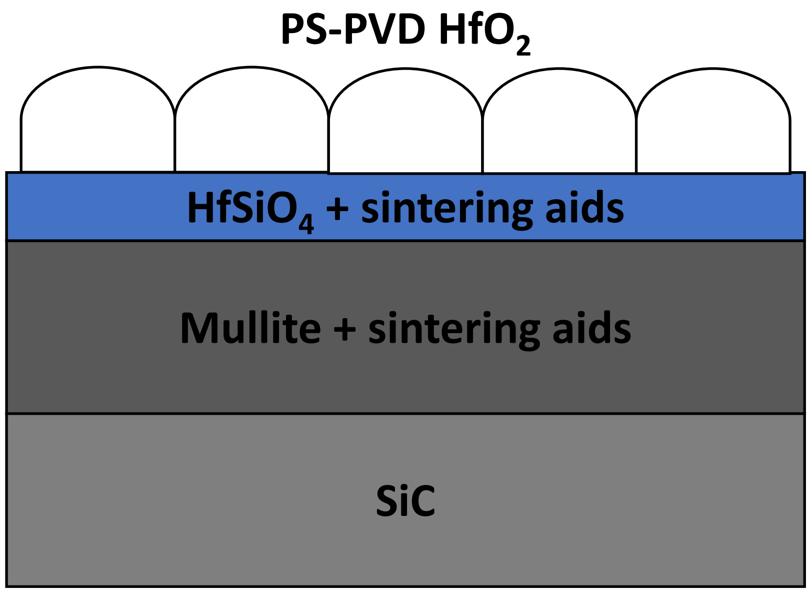


no proprietary oxide / one sintering schedule

EBC layers appear denser when proprietary oxide added / layers sintered separately

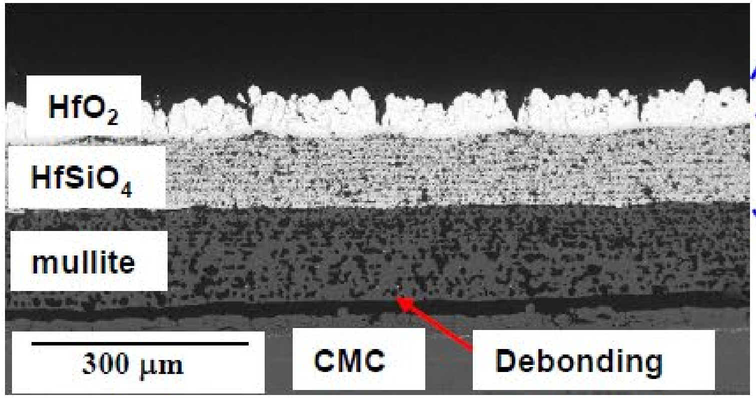
Results: Comparison to PS-PVD HfO_2

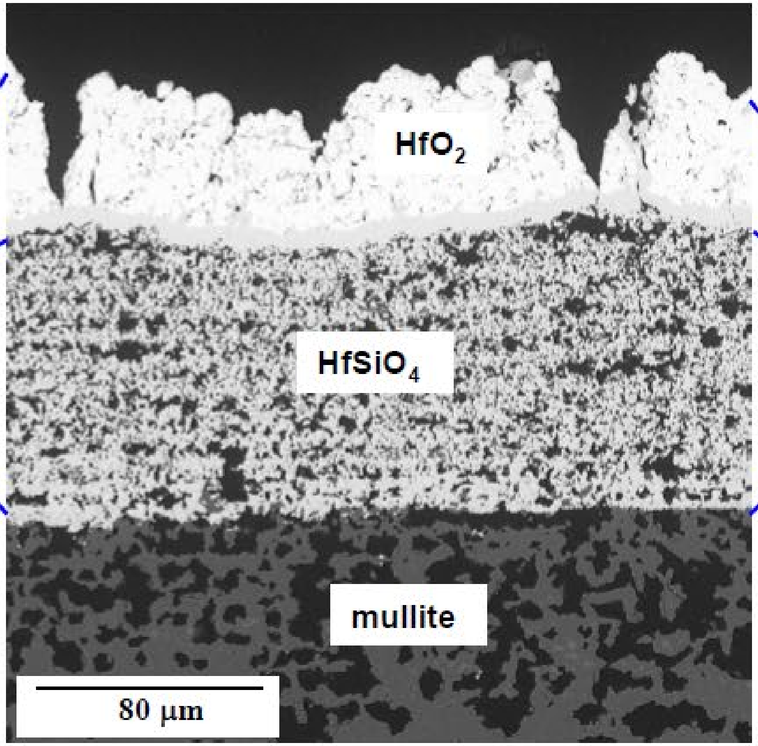
How does HfO_2 deposited by plasma spray-physical vapor deposition (PS-PVD) compare to slurry HfO_2 under similar conditions?



Results: Comparison to PS-PVD HfO_2

- Si/SiO_2 from bond coat reacts with HfO_2 to form $HfSiO_4$ at IC/topcoat interface
- Severe topcoat debonding with some spallation
- Some debonding at bond coat





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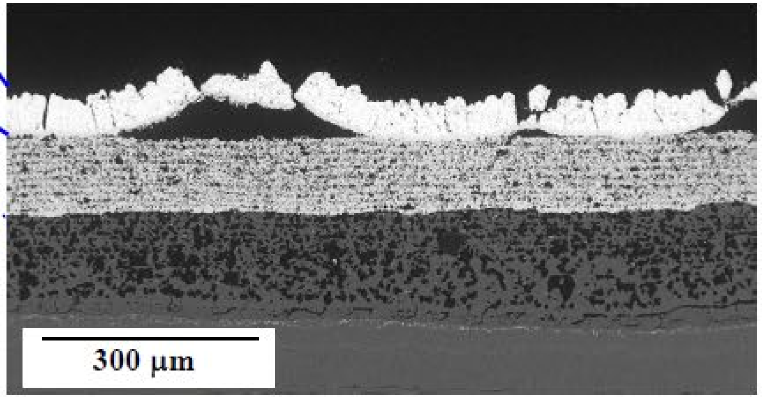
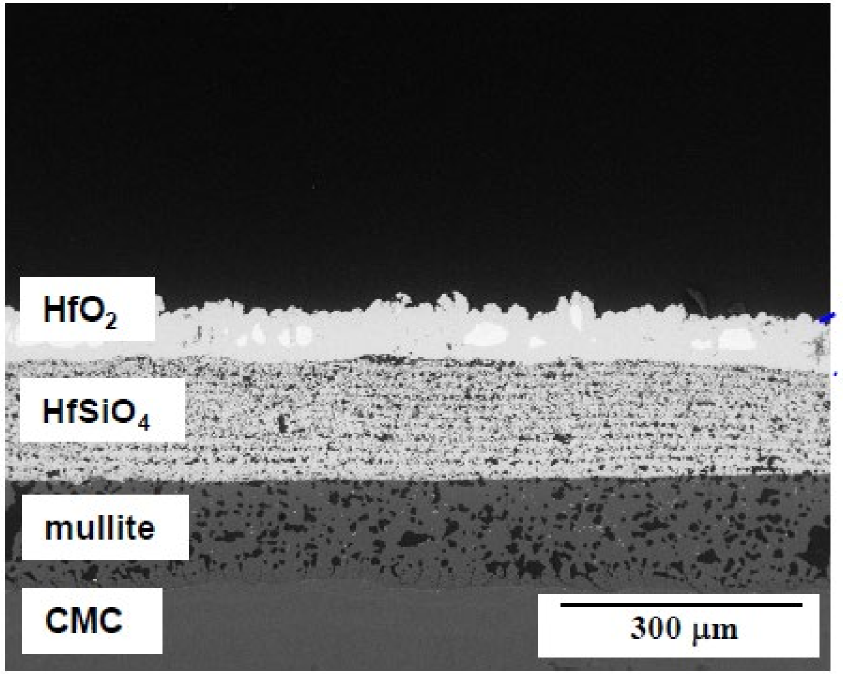
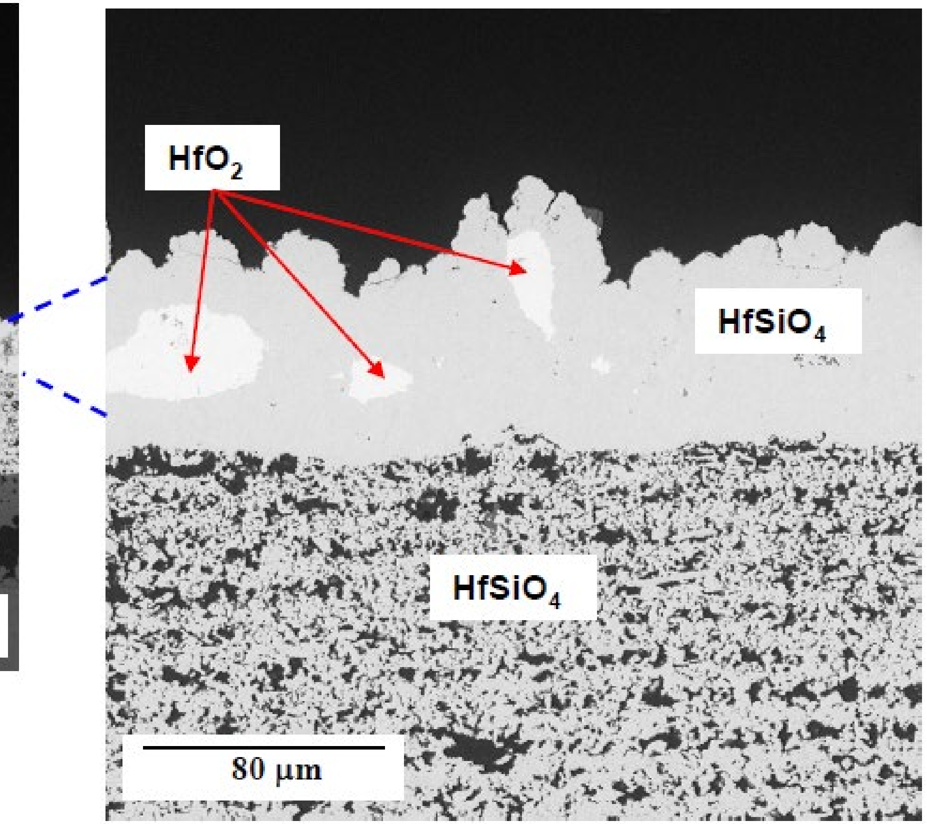


Results: Comparison to PS-PVD HfO_2

- Excessive reaction of Si/SiO_2 from bond coat with HfO_2 to form $HfSiO_4$ when amount of sintering aids in bond coat increased
- No debonding/spallation observed



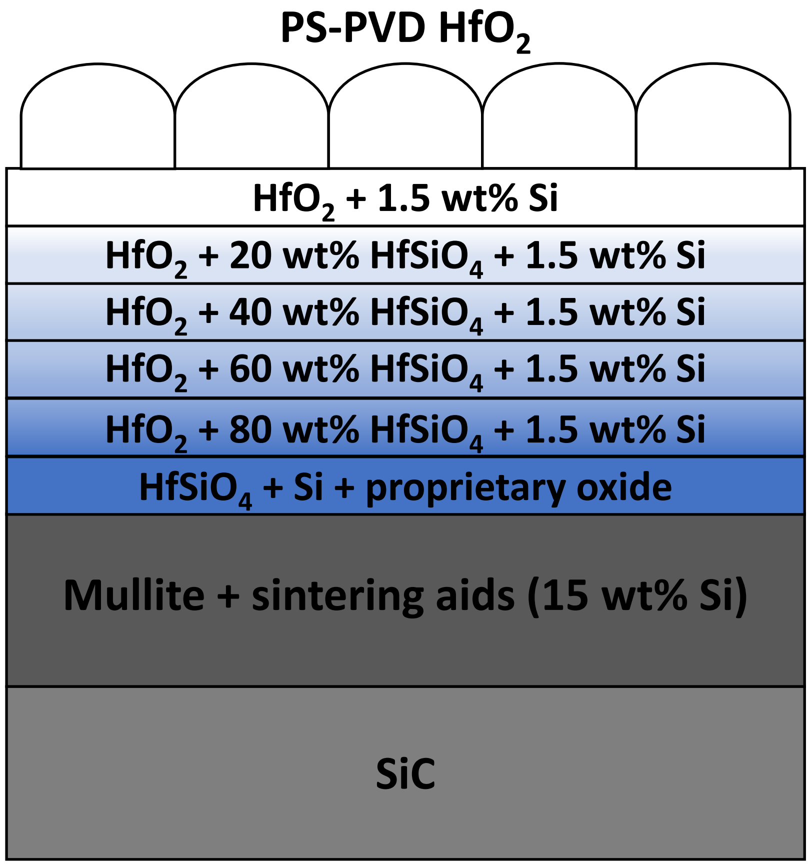
1480°C, 500 cycles, steam



Results: Comparison to PS-PVD HfO_2

PS-PVD HfO_2 topcoat undergoes similar issues as slurry HfO_2

Combined-process HfO_2 topcoat



Summary

- Si/SiO_2 content in topcoat, bond coat important with regards to CTE, reaction to form $HfSiO_4$
  - Five-layer topcoat system shows most promise
  - Minimum topcoat layer Si = 1.5 wt% (slurry)
  - Minimum bond coat Si = 15 wt% (slurry)
- Addition of proprietary oxide to intermediate coat results in better adhesion to bond coat, proprietary oxide/separate sintering of BC, IC, topcoat may increase density of layers
- PS-PVD topcoat shows similar trends to slurry topcoat
  - Increase in Si/SiO_2 content in bond coat = more $HfSiO_4$ formation in topcoat, better adhesion to underlying layers
- HfO_2 as single-layer EBC is unstable – however, still useful component of EBC system
  - Need to monitor thermally grown oxide (TGO) in optimized system
  - Outermost PS-PVD HfO_2 may be viable approach

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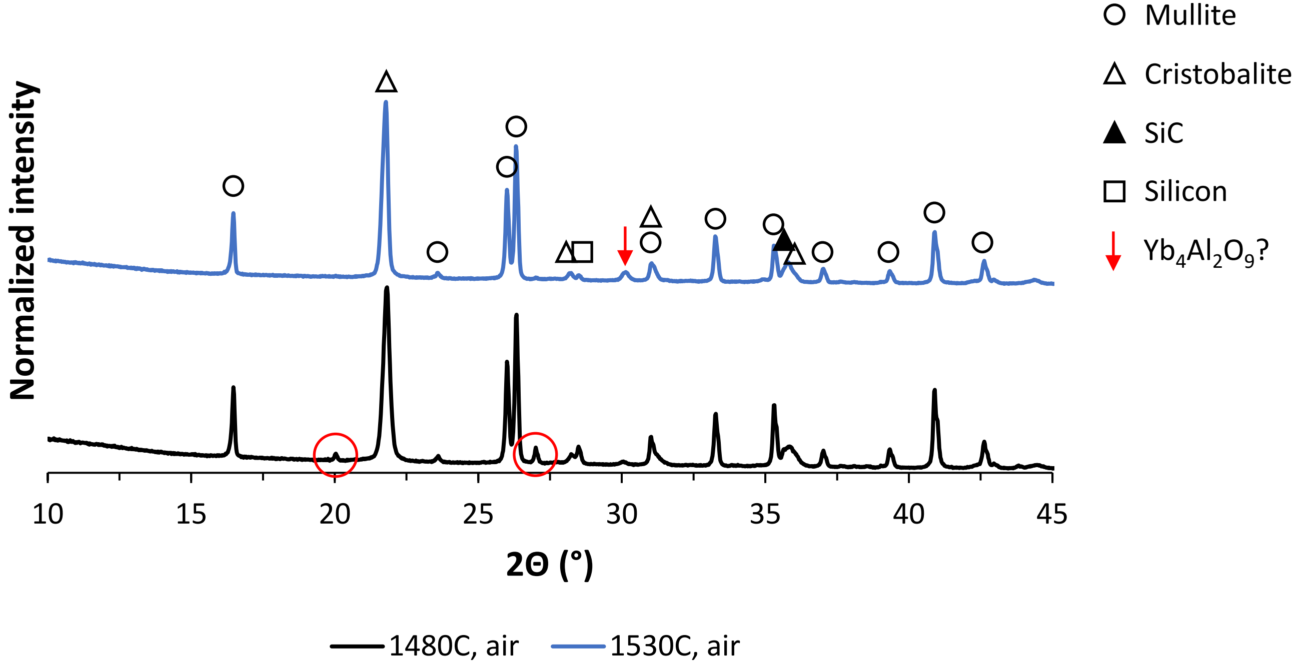
Backup

10 hours



	Mullite	Al_2O_3	$Yb_2Si_2O_7$	Si
Bond coat	balance	1 wt%	1 wt%	20 wt%