Oak Ridge National Laboratory

Exploring EBC temperature limits for IGTs

M. J. Ridley, M. J. Lance, T.G. Aguirre, K. A. Kane*, B. A. Pint

Corrosion Science & Technology Group
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6156

*now Johns Hopkins Applied Physics Laboratory

UTSR, September 2022, San Diego, CA

Acknowledgments

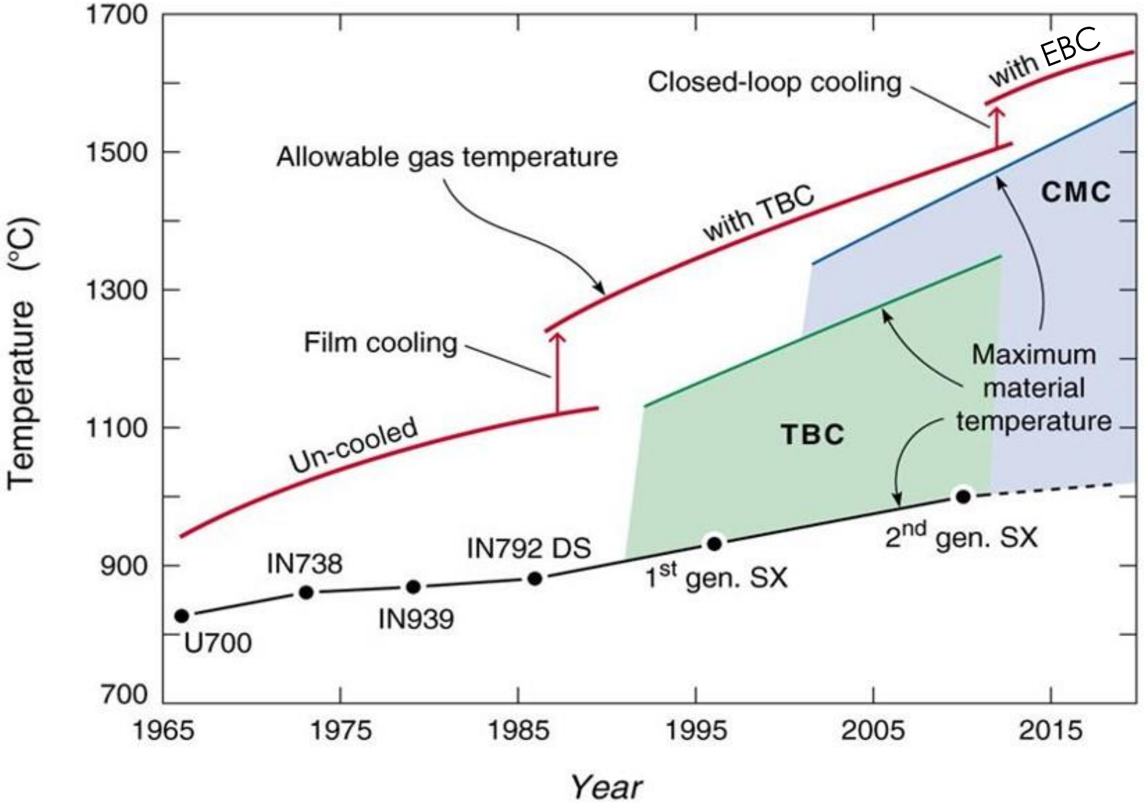
- Funding from U.S. DOE, Office of Fossil Energy and Carbon Management, Advanced Turbine Program
  - Rich Dennis, Manager; Rin Burke, Project Monitor
- ORNL Team
  - G. Garner, B. Johnston, J. Wade - oxidation experiments
  - T. Geer, V. Cox, C. O’Dell – metallography
  - T. Lowe – SEM
  - Y. Su – TEM
  - E. Lara-Curzio, J. A. Haynes, R. Lowden, D. Mitchell – input on CMCs
- Collaborations
  - Stony Brook Univ., Center for Thermal Spray Research (on-going)
    - S. Sampath and E. Garcia-Granados
  - NASA Glenn Research Center (just starting)
    - K. Lee and B. Harder
  - 1st industrial collaboration (just concluded)
  - 2nd industrial collaboration (initiated)

OAK RIDGE National Laboratory

Enabling CMCs for combustion environments requires protective environmental barrier coatings (EBCs)

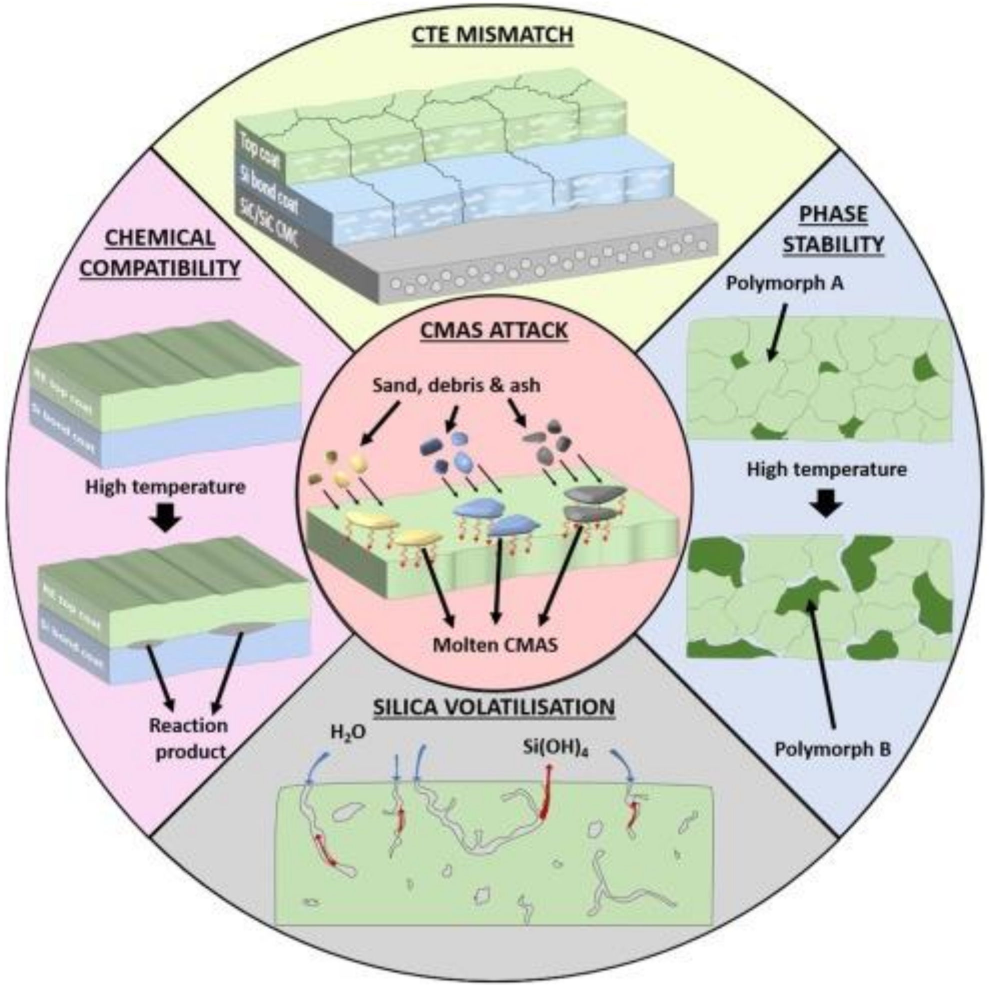
- CMCs (SiC fiber / SiC matrix) are alternatives to Ni-base superalloys for hot-section turbine components (static and rotating)
- Lightweight, high-temperature stability + strength
- **SiC volatilizes in steam – EBC required for mitigation**
- **$Yb_2Si_2O_7$ (YbDS) EBCs with Si bond coat are research standard**

H. Wadley. *IPM Research Group Website*. Accessed 2018.



EBC failure modes need to be better understood for long term application

- Steam reaction: Si-based ceramics volatilize in steam
- **Bond Coat Oxidation: Weakens interface, promotes delamination**
- Thermal Stability: Phase/property changes during operation
- Thermal Expansion Mismatch
- CMAS: Infiltration of molten particulate ingested into engine
- Foreign Object Damage



Tejero-Martin et al., J. Eur. Cer. Soc. (2021).

How do we develop a lifetime model for EBCs?

Lifetime Modelling of EBCs

- Kinetics/Thermo, FEM

Material Changes

- EBC/Si/SiC
  (chemistry, thickness, roughness, density)

Laboratory Testing

- Experimental (Methodology, geometry, cycling)
- Environmental
  (T, P, v, atm)

How do we develop a lifetime model for EBCs?

Lifetime Modelling of EBCs

- Kinetics/Thermo, FEM

Material Changes

- EBC/Si/SiC (chemistry, thickness, roughness, density)

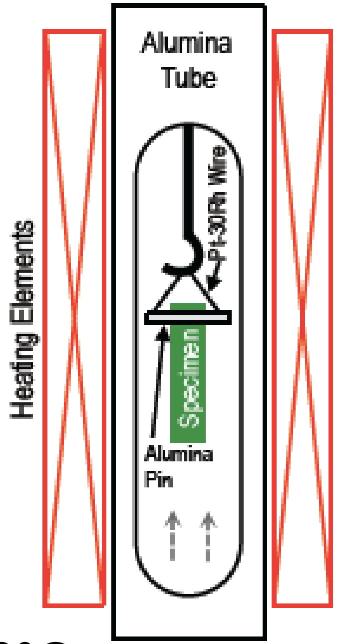
Laboratory Testing

- Experimental (Methodology, geometry, cycling)
- Environmental (T, P, v, atm)

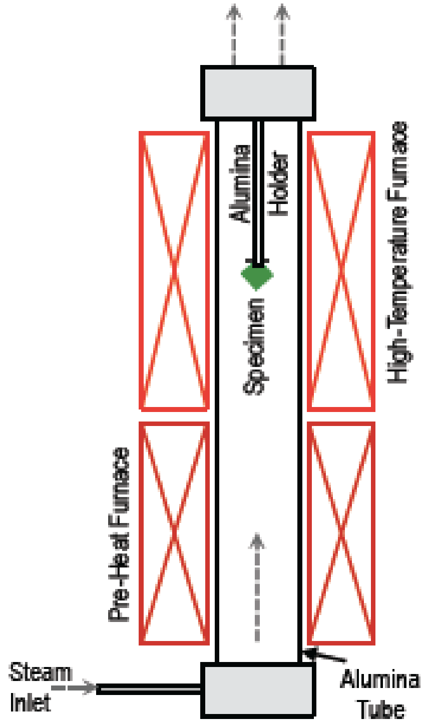
Capabilities: Focus on cyclic steam furnaces

Nuclear Severe Accident Test Station

Rubotherm TGA



High Temperature Furnace



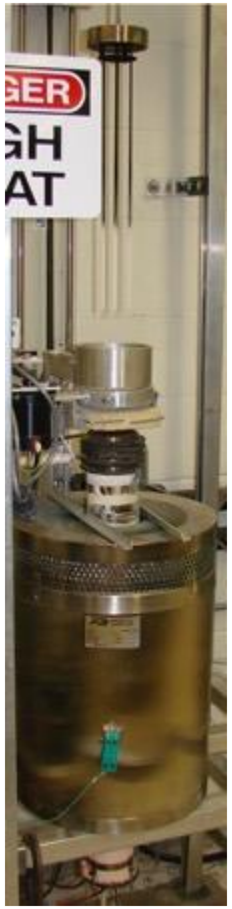
1500°C maximum

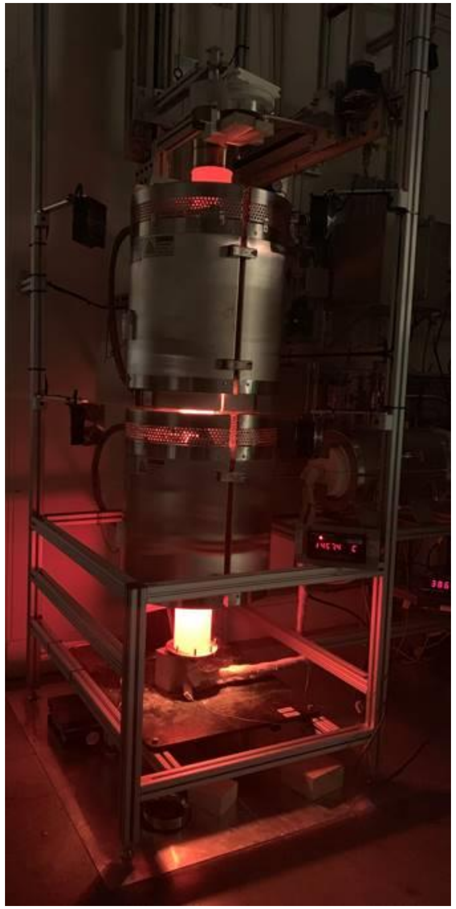
1700°C maximum

1-h cycles: automated cyclic rigs
Air + 90%H_2O, 10 min cool in lab. air

lid

furnace





2005 cyclic rig: 1350°C maximum

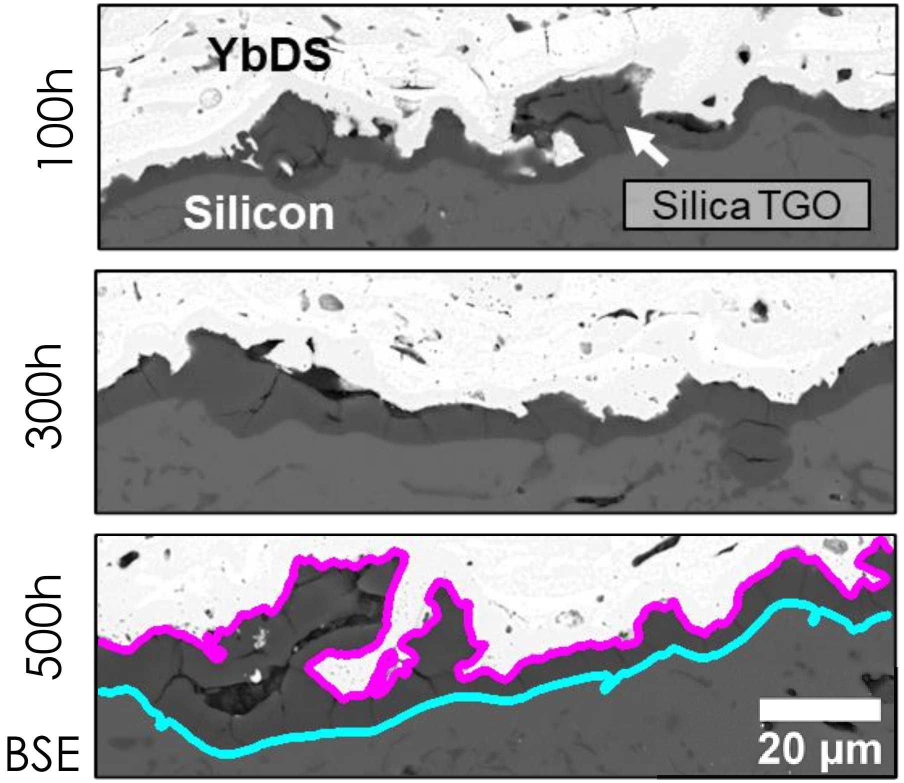
2019 cyclic rig: 1450°C maximum*

Methodology + software developed to measure kinetics

Non-uniform TGO in multilayer EBC

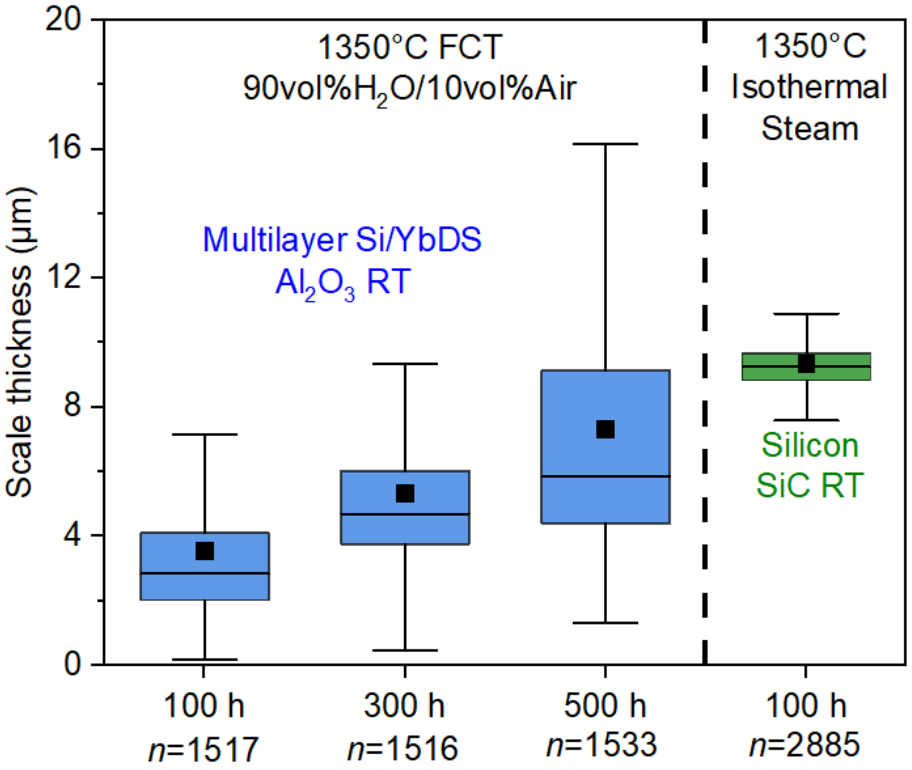
1. Undulating interface
2. APS Si microstructure defects

1350°C FCT in 90/10 H_2O/air



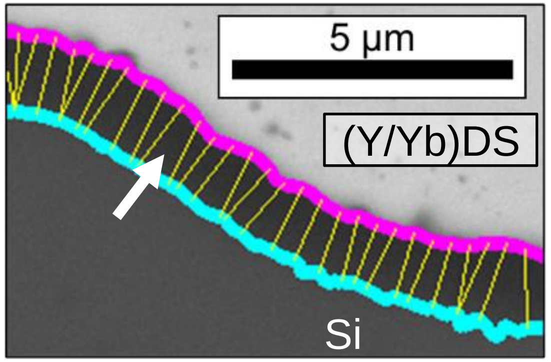
Open Source Software: https://github.com/TriplePointCat/SOFIA-CV

EBC: median better, distribution not normal



~900 µm span

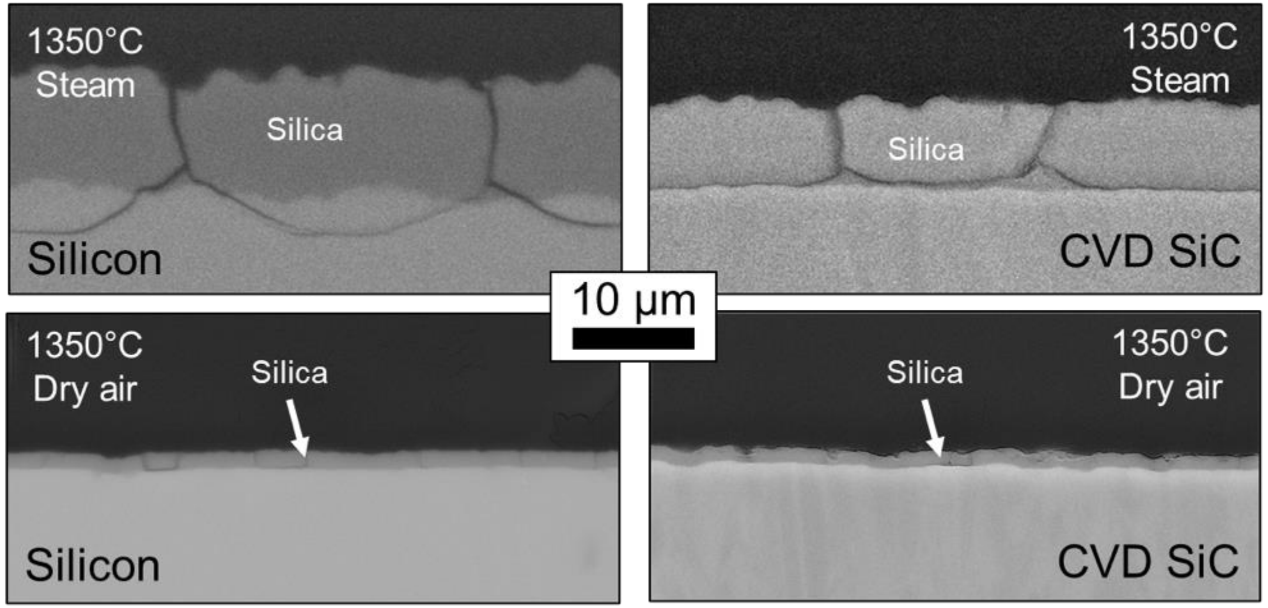
~1800 µm span



Based on 1500-3000 automated thickness measurements:

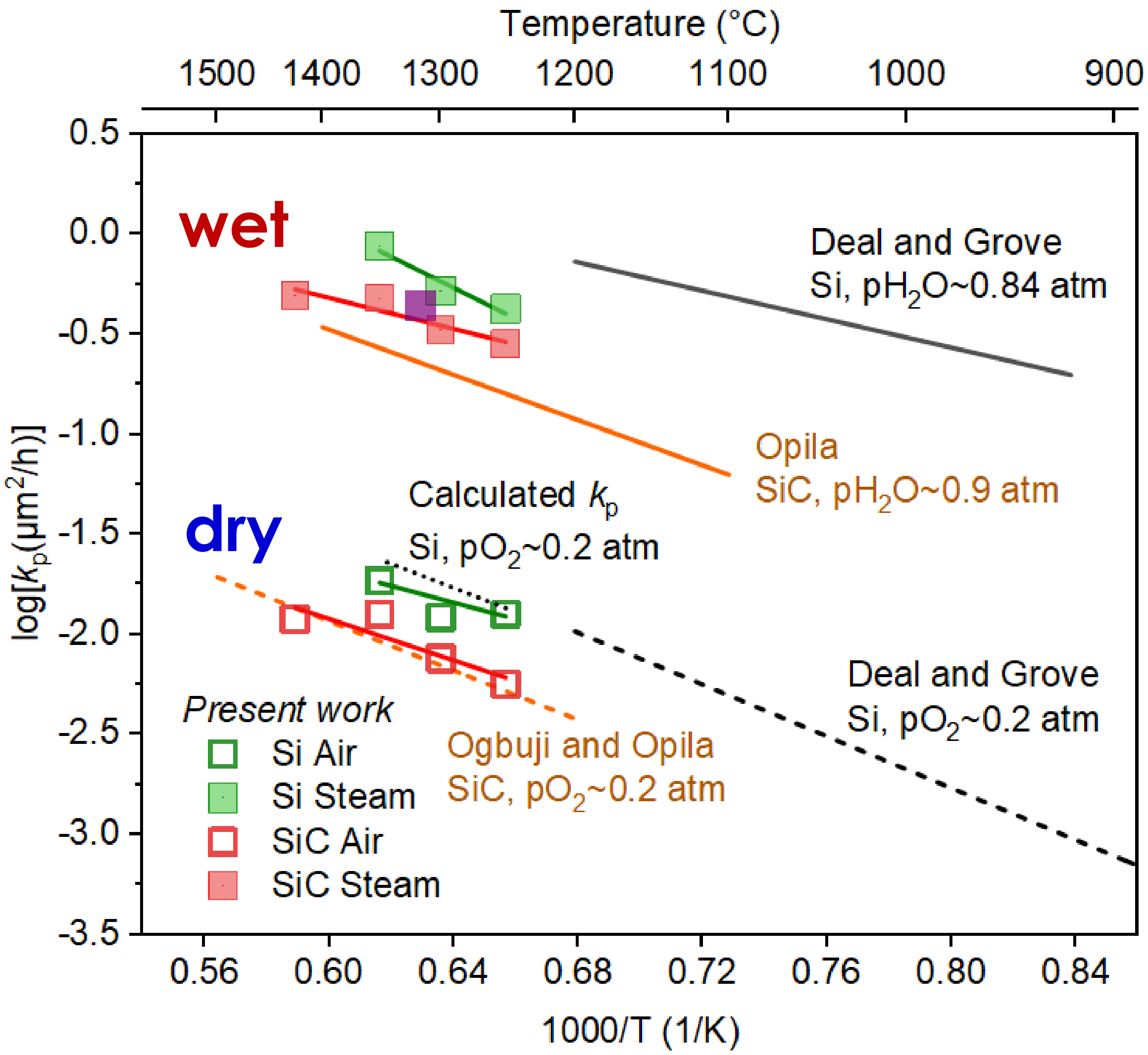
Methodology for assessing EBC performance is based on bare SiC/Si oxidation in air and steam

Silica in steam: EBCs to prevent evaporation – $Si(OH)_4$ AND reduce scale growth rate



Experiments performed in SiC reaction tube

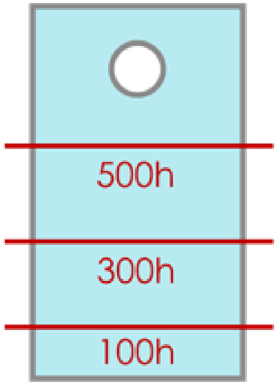
- Based on Harder (NASA)
- Defines upper and lower bounds for EBC performance

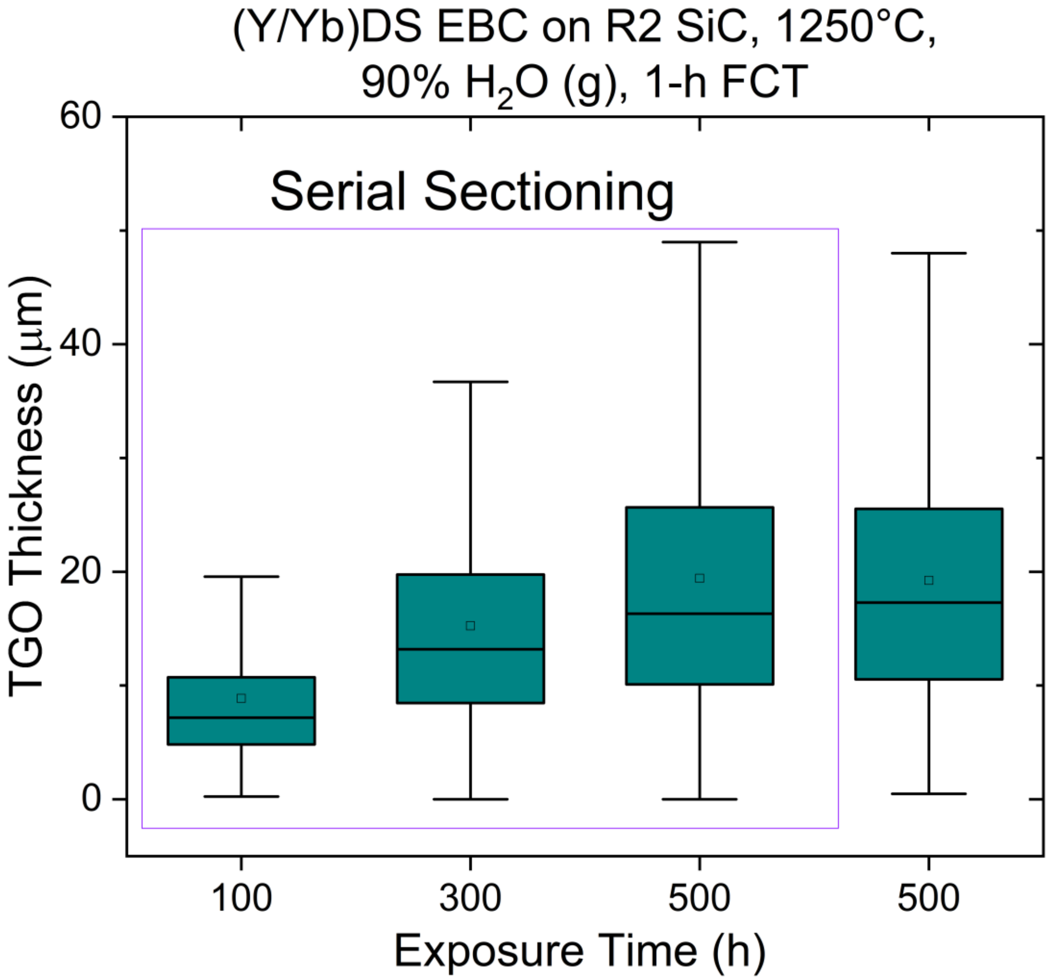


Kane, et al. *J. Amer. Ceram. Soc.* 105 (2022) 590

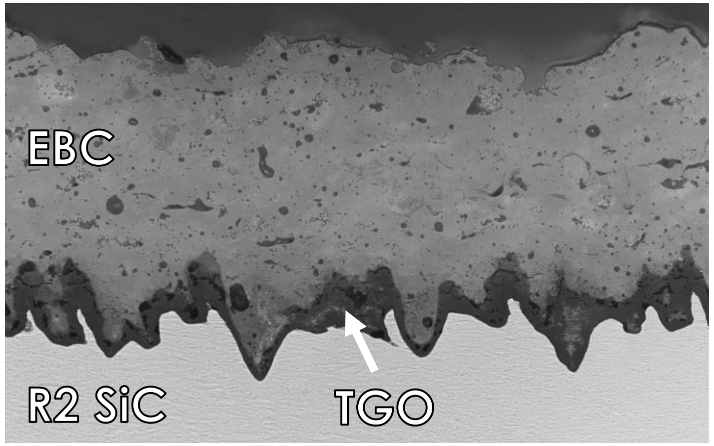
OAK RIDGE National Laboratory

Specimen geometry: Serial Sectioning does not impact on oxidation behavior up to 500h





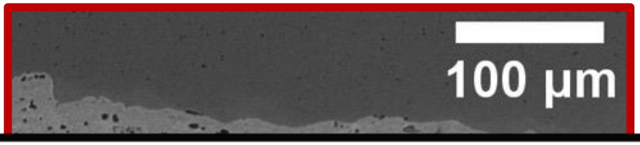
Optical Microscopy
1250°C, 500h



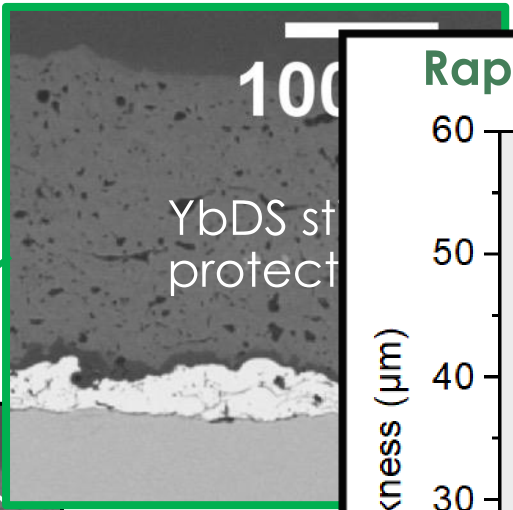
- "Fresh" edge of sample exposed upon sectioning has no impact
- 3-5 measurements/µm of TGO over 7-9 mm total sample length
- **Cost & sample efficient testing method**

OAK RIDGE National Laboratory

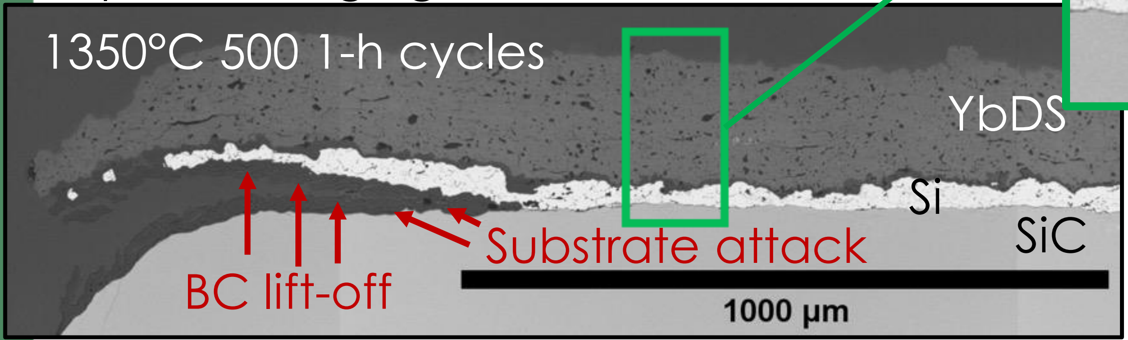
Specimen geometry: Long term impact?



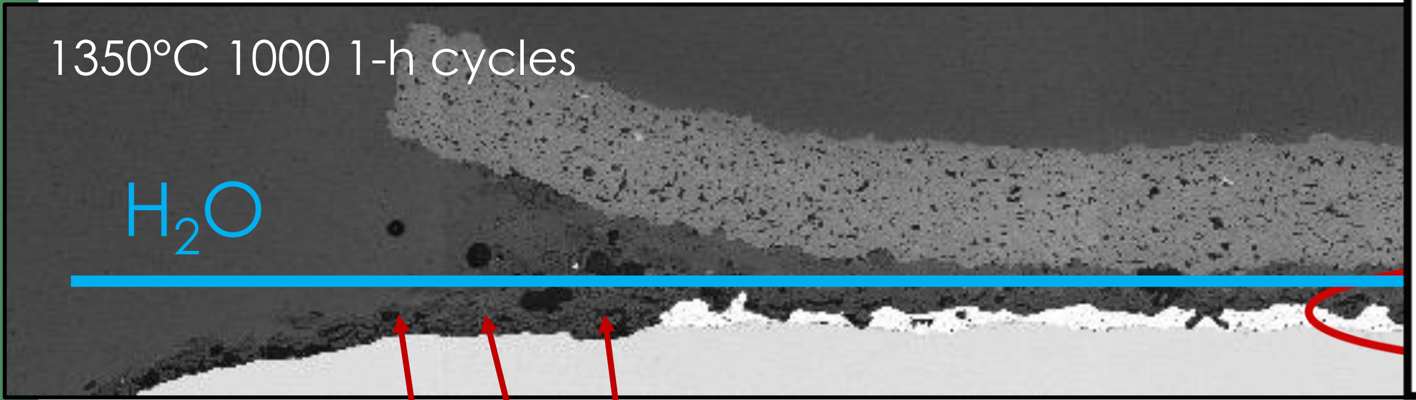
Circular & Rectangular Geometries
Bond coating lift-off observed after 1250°, 1300°, and 1350°C FCT, extent dependent on Temp. and time



Optical Imaging



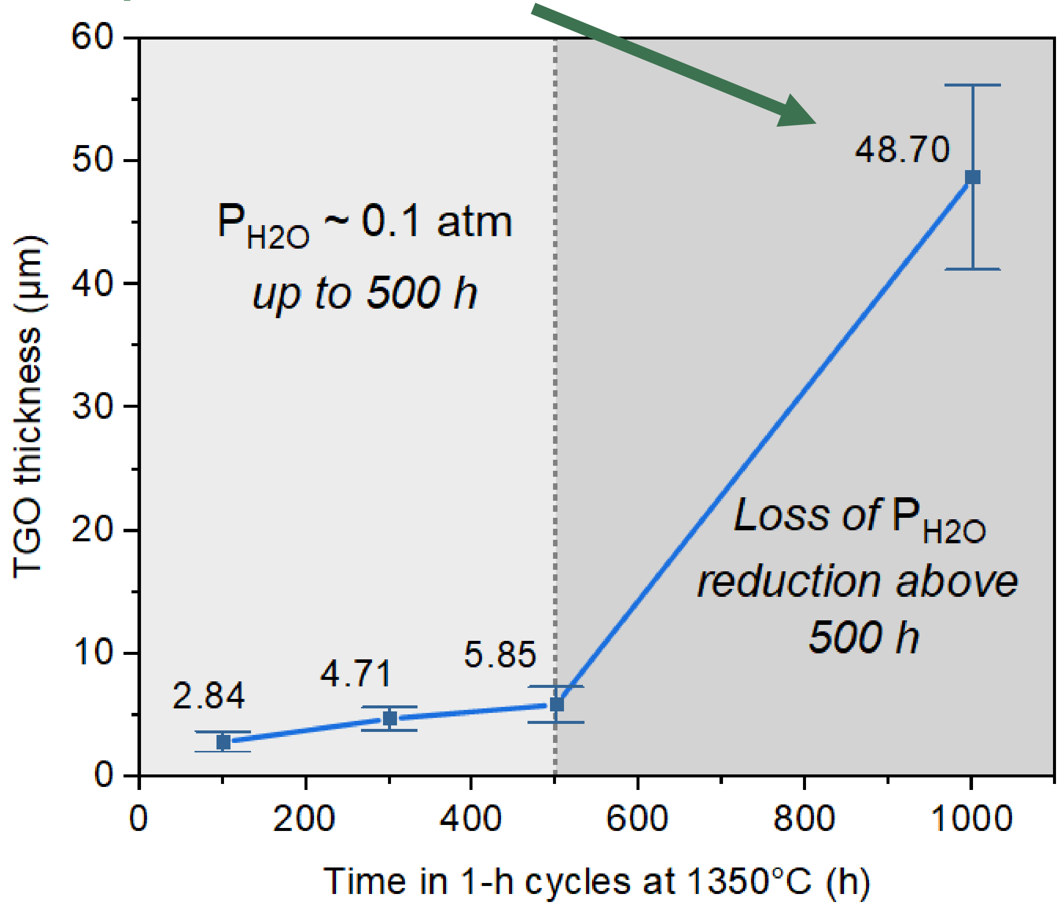
Direct
tran
=



BC destroyed at edge

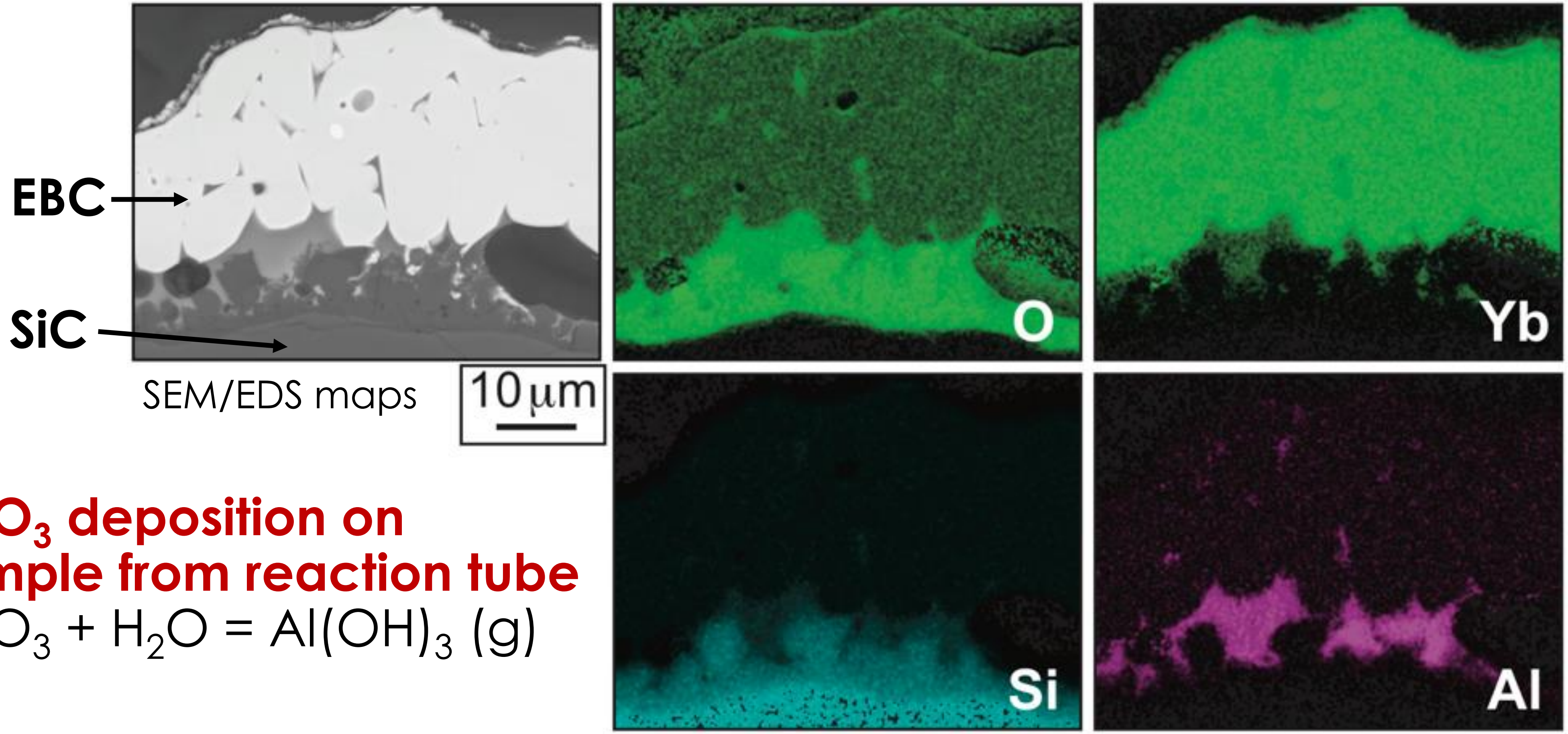
BC 100% consumed

Rapid increase in Ox. rate with YbDS EBC



Breakaway oxidation generally occurs above ~800 1-h cycles

Furnace ware contamination is a concern
Example: Al contamination in 1425°C steam from tube/holder



SEM/EDS maps

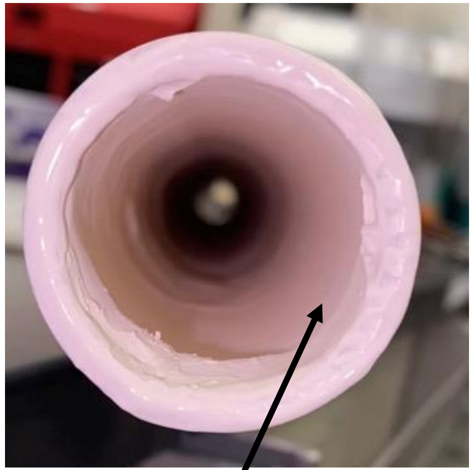
Al_2O_3 deposition on sample from reaction tube

$Al_2O_3 + H_2O = Al(OH)_3$ (g)

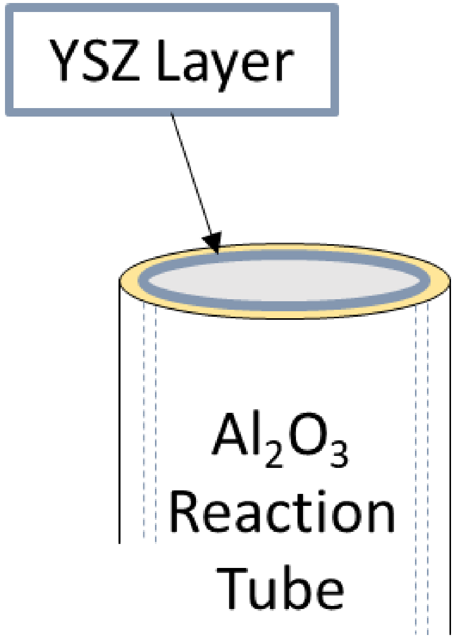
1st gen. YbDS EBC after 100h, 1425°C, 100% steam

Mitigating high-temp furnace impurities – Protective coating for furnace ware?

Al_2O_3 Reaction Tube

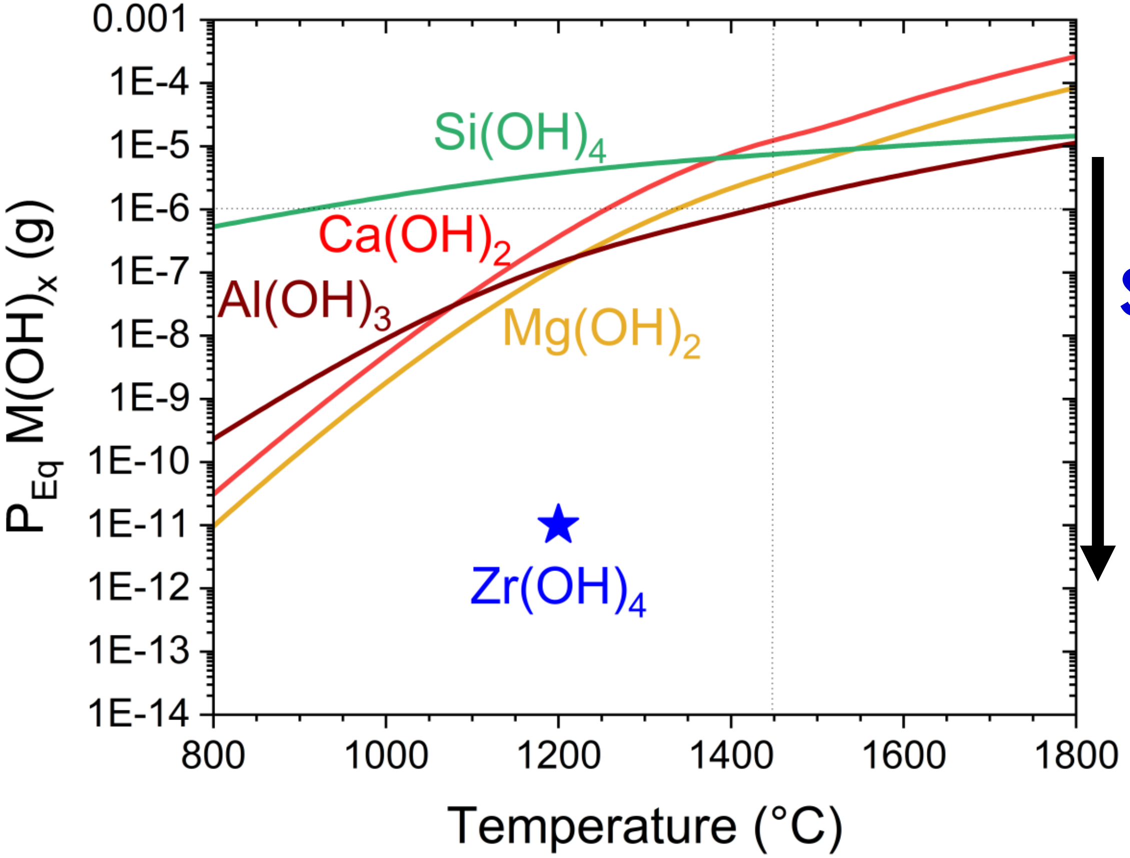


YSZ Layer



Protective ZrO_2 barrier to slow down steam reaction with furnace ware

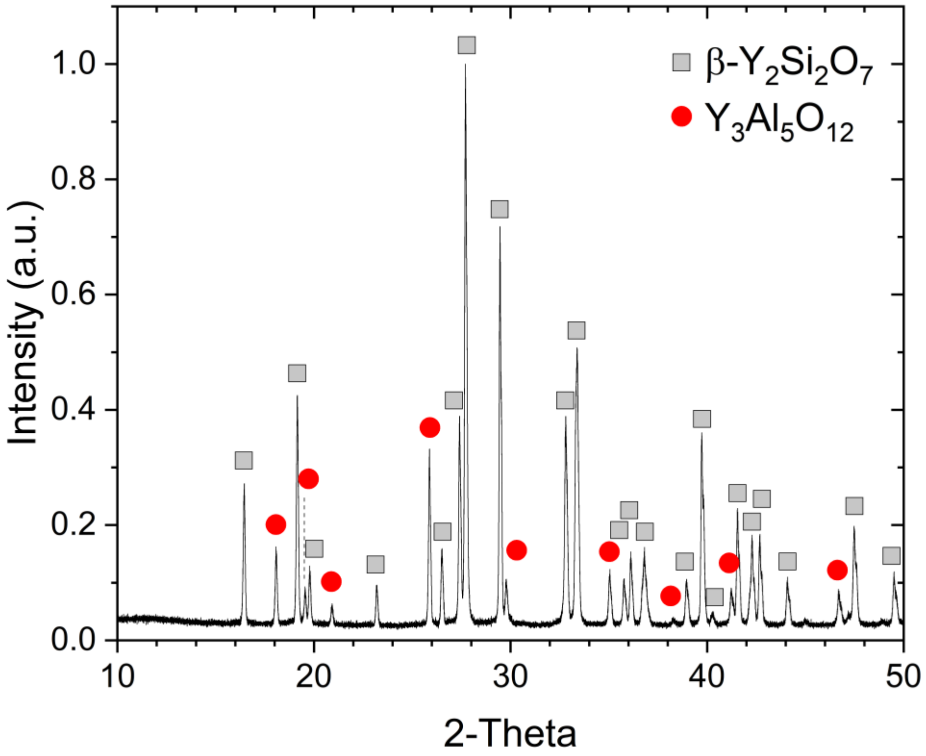
Data from: Meschter, Opila, Jacobson, Ann. Rev. of Mat. Res. (2013)



Stability in steam

Reaction tube impurities can be mitigated by coating tube with steam-resistant layer

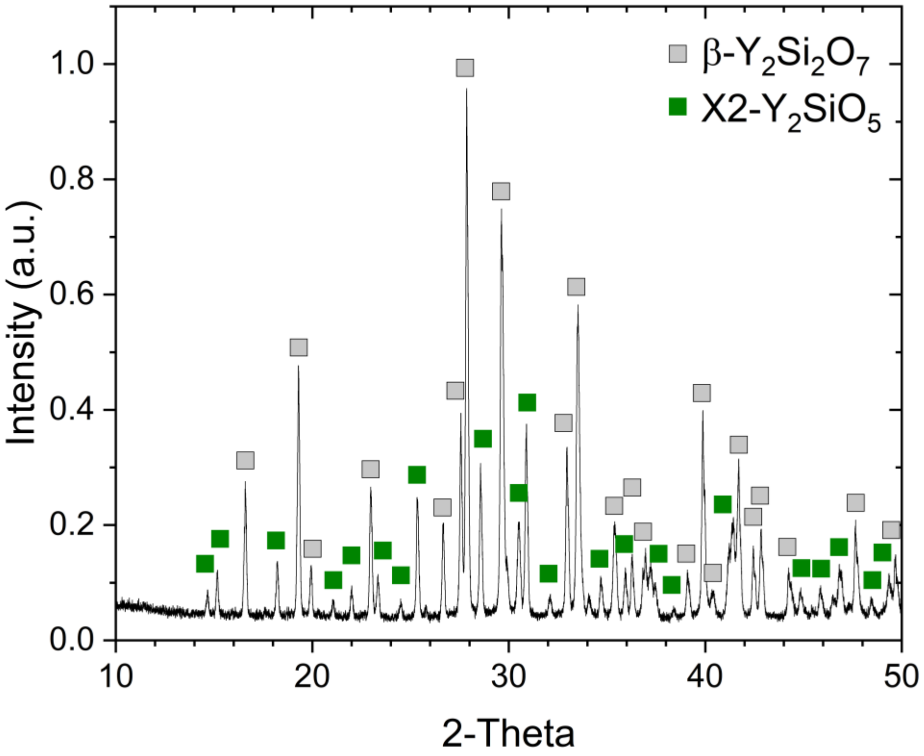
Al_2O_3 Reaction Tube



Al_2O_3 deposition from furnace ware

$Al_2O_3 + H_2O = Al(OH)_3$ (g)

YSZ-Coated Al_2O_3 Reaction Tube



Realistic steam reaction occurs

$Y_2Si_2O_7 + H_2O = Y_2SiO_5 + Si(OH)_4$ (g)

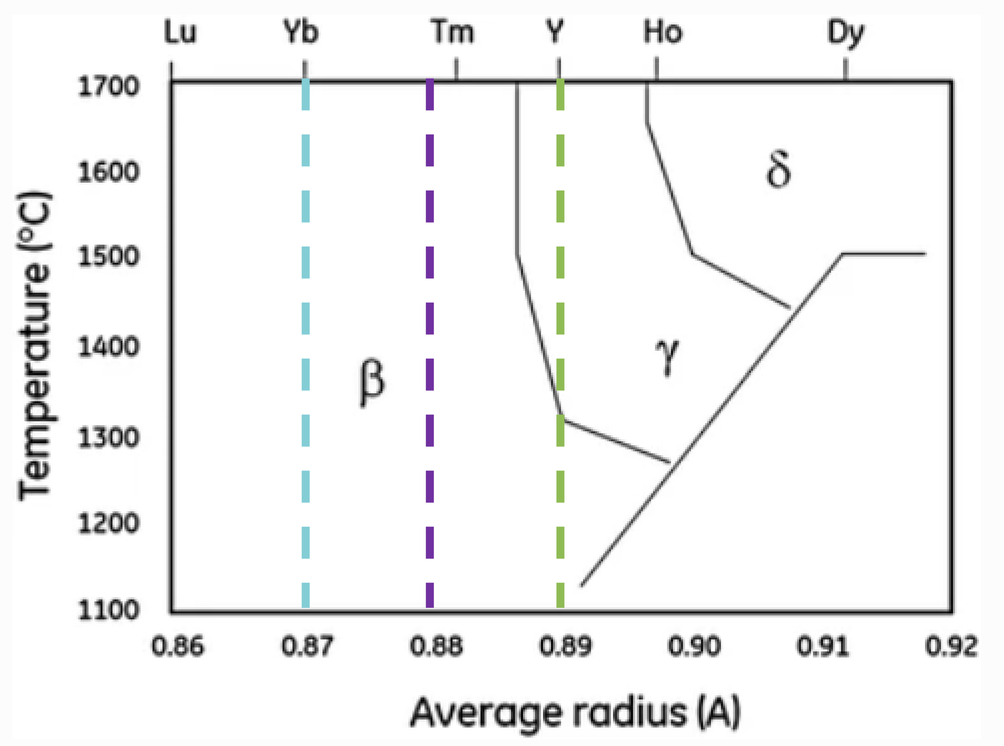
How do we develop a lifetime model for EBCs?

Lifetime Modelling of EBCs	Kinetics/Thermo, FEM	
Material Changes	EBC/Si/SiC (chemistry, thickness, roughness, density)	
Laboratory Testing	Experimental (Methodology, geometry, cycling)	Environmental (T, P, v, atm)

Oak Ridge National Laboratory

How does YbDS compare to commercial mixed $(Yb/Y)_2Si_2O_7$?

Phase Stability Plot



$Yb_2Si_2O_7$		$Y_2Si_2O_7$		$(Yb/Y)_2Si_2O_7$
↑ \$16.4/kg Yb_2O_3	+	↓ \$3.4/kg Y_2O_3	=	↓ Lower cost
✓ Single Phase		× Multi phase		✓ Single Phase
✓ Low CTE		× High CTE		✓ "medium" CTE
↓ Volatility		↑ Volatility		↑ Volatility
↓ CMAS Resist.		↑ CMAS Resist.		↑ CMAS

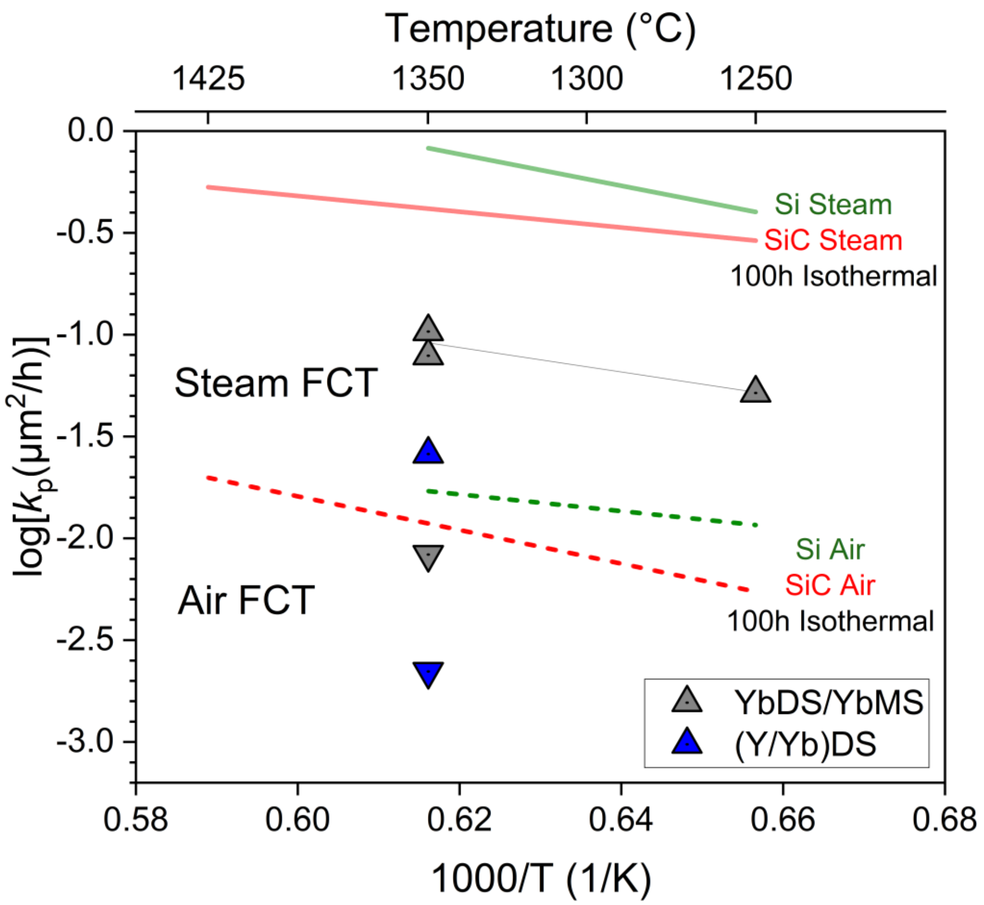
Mixing YbDS to YDS can stabilize desired β-phase EBC

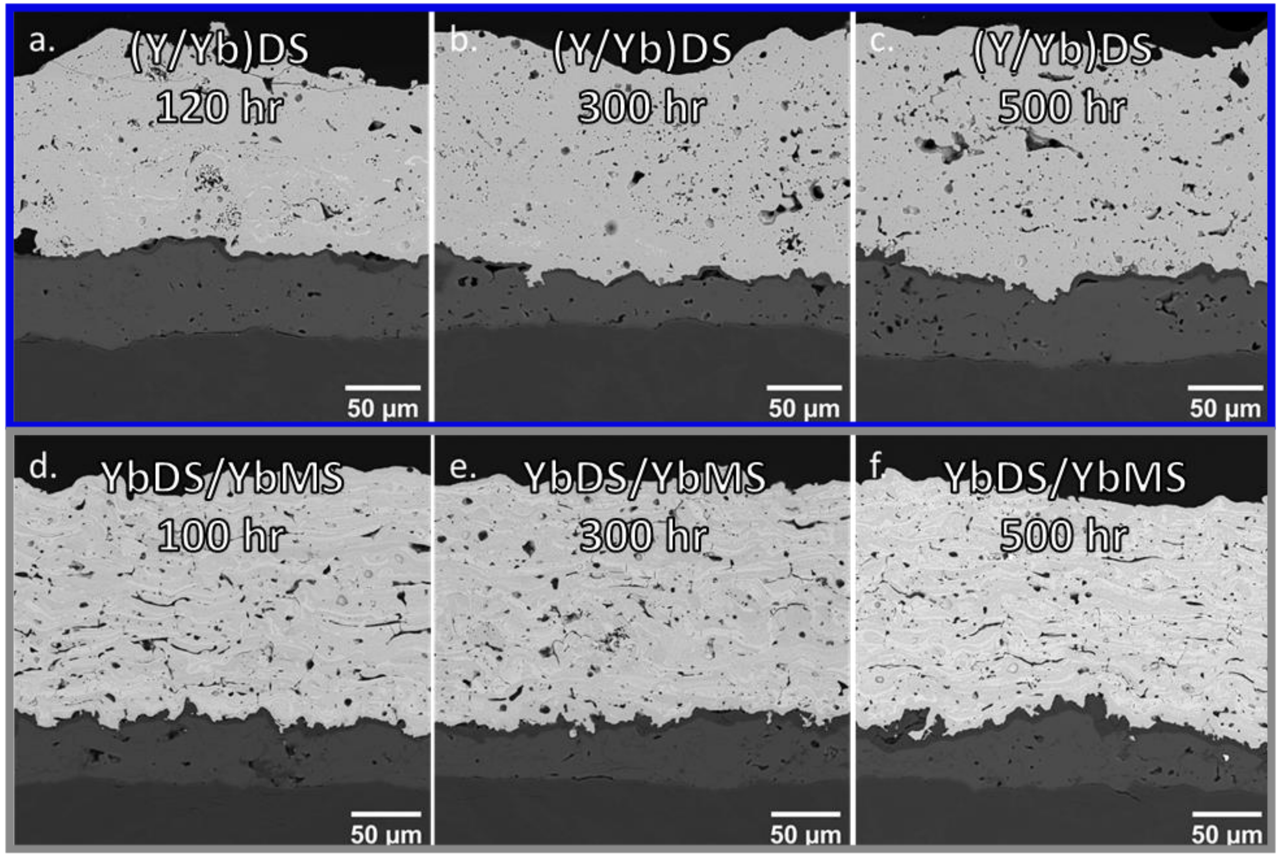
Is (Y/Yb)DS phase stable through furnace cycle testing (FCT)?

Does EBC composition or thickness influence TGO kinetics?

(Y/Yb)DS has lower rates than YbDS in both air and steam

Ridley, MJ, et al. JACERS. (2022).



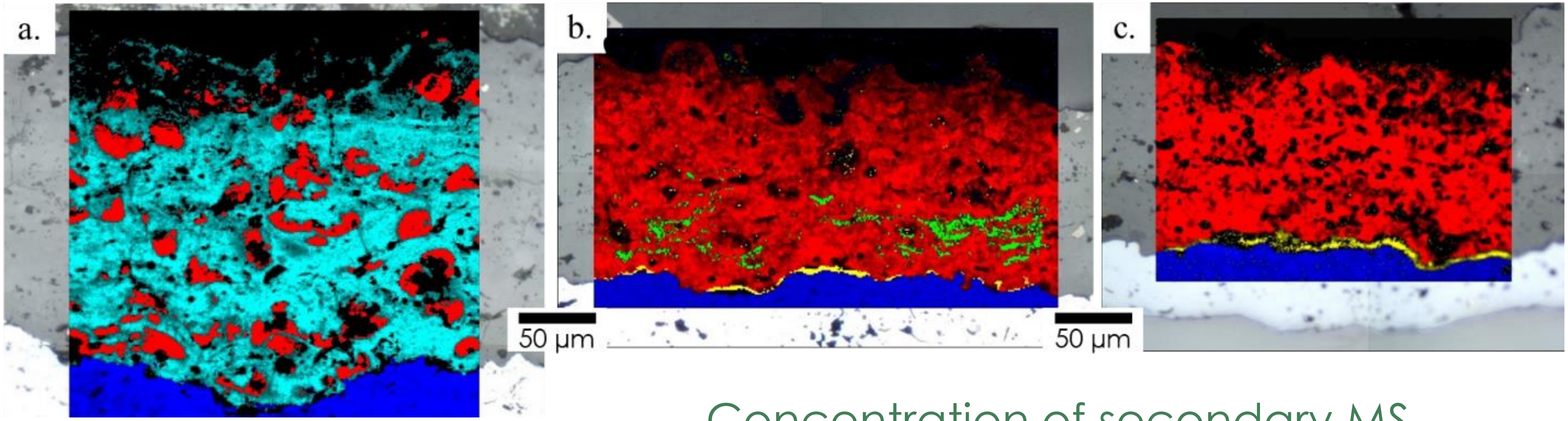


- Only one temperature (1350°C)
- Manufactured at different locations using similar CVD SiC substrates
- Further study needed for mechanistic understanding
  - Porosity, monosilicate changes

OAK RIDGE National Laboratory

Raman can be used to map out phases of (Y/Yb)DS EBC after steam cycling at 1350°C

As-sprayed | 100 1-h FCT | 300 1-h FCT



Amorphous Y/Yb Silicate
β-(Y/Yb)DS
(Y/Yb)MS
a-cristobalite SiO_2
Silicon

Concentration of secondary MS phase decreases and porosity increases – **not observed in air FCT**

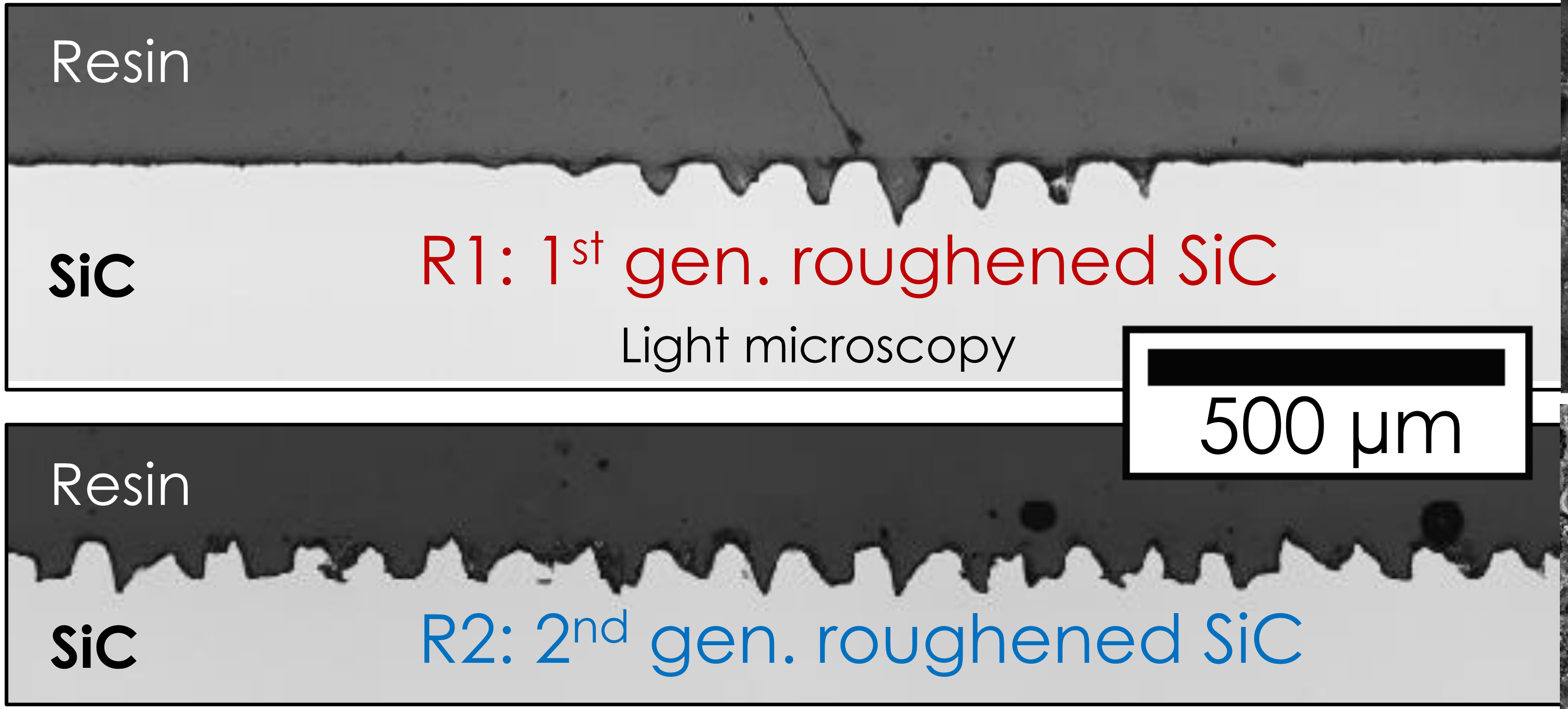
Silica TGO is crystalline after 100h exposure time

Can laser roughening impact EBC adhesion and reaction kinetics?

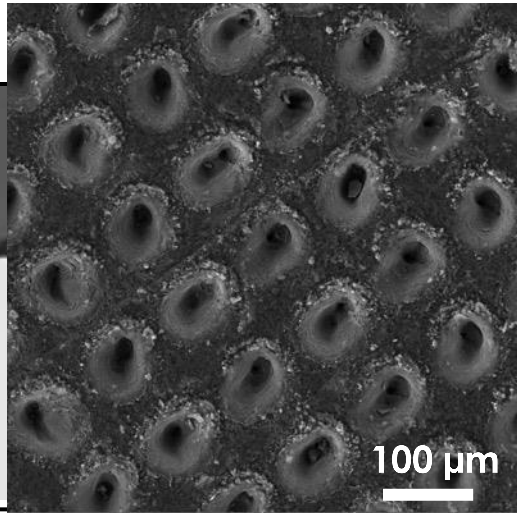
Si bond coat melts at ~1410°C → Upper Temp Limit

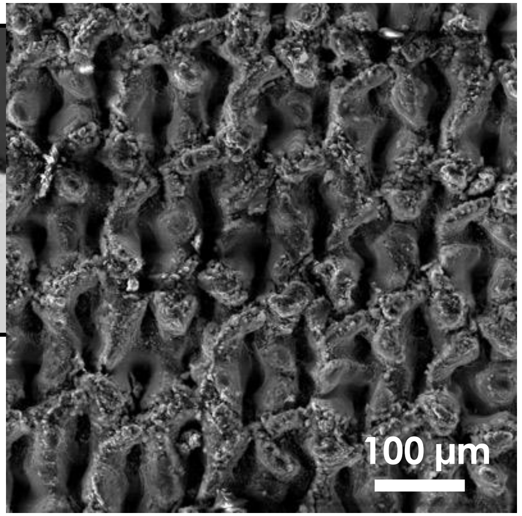
Can EBCs perform without Si interlayer?

Roughened SiC interface to encourage adhesion



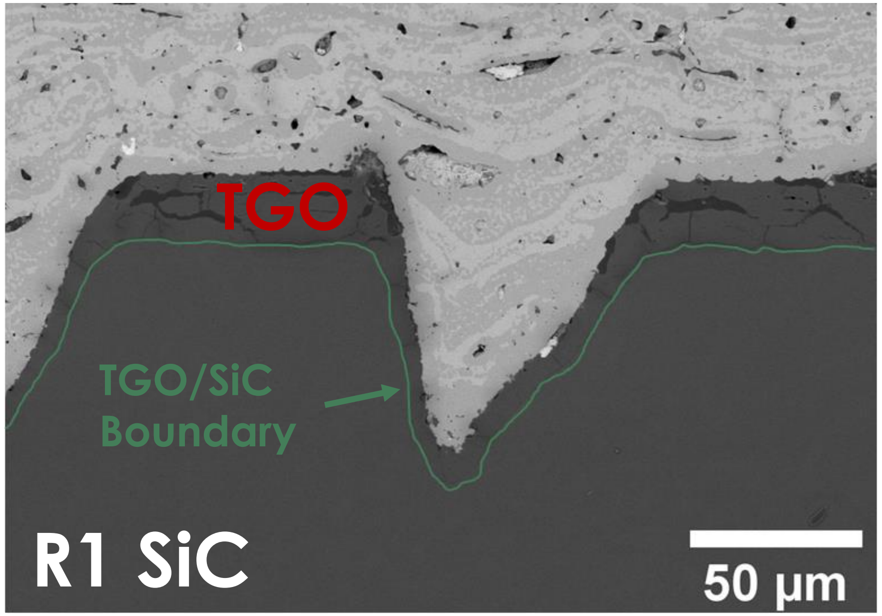
SEM BSE plan views



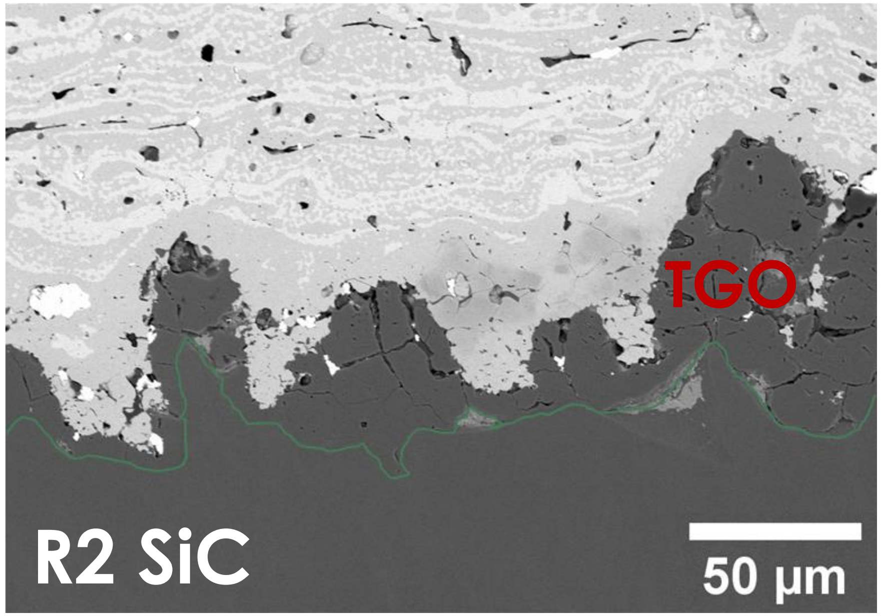


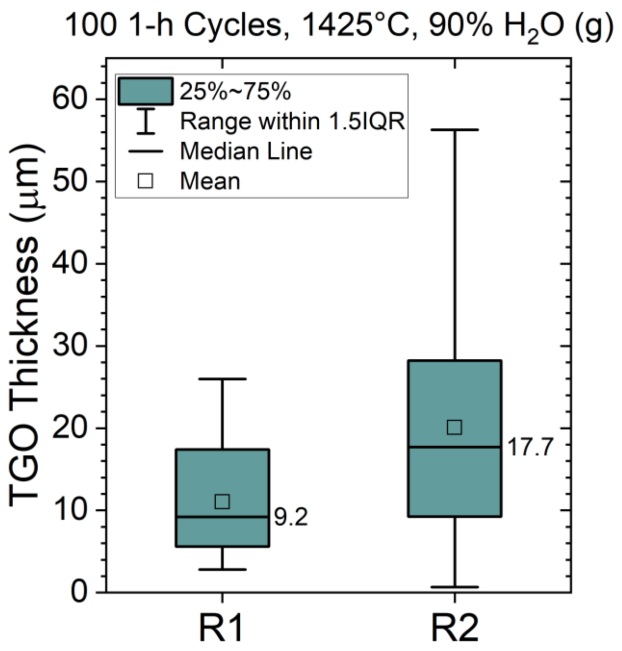
R1 vs. R2 in 90% Steam: R2 performed poorly

200 µm EBC on **R1 SiC**
1425°C, 100 1-h FCT, 90% H_2O (g)



200 µm EBC on **R2 SiC**
1425°C, 100 1-h FCT, 90% H_2O (g)



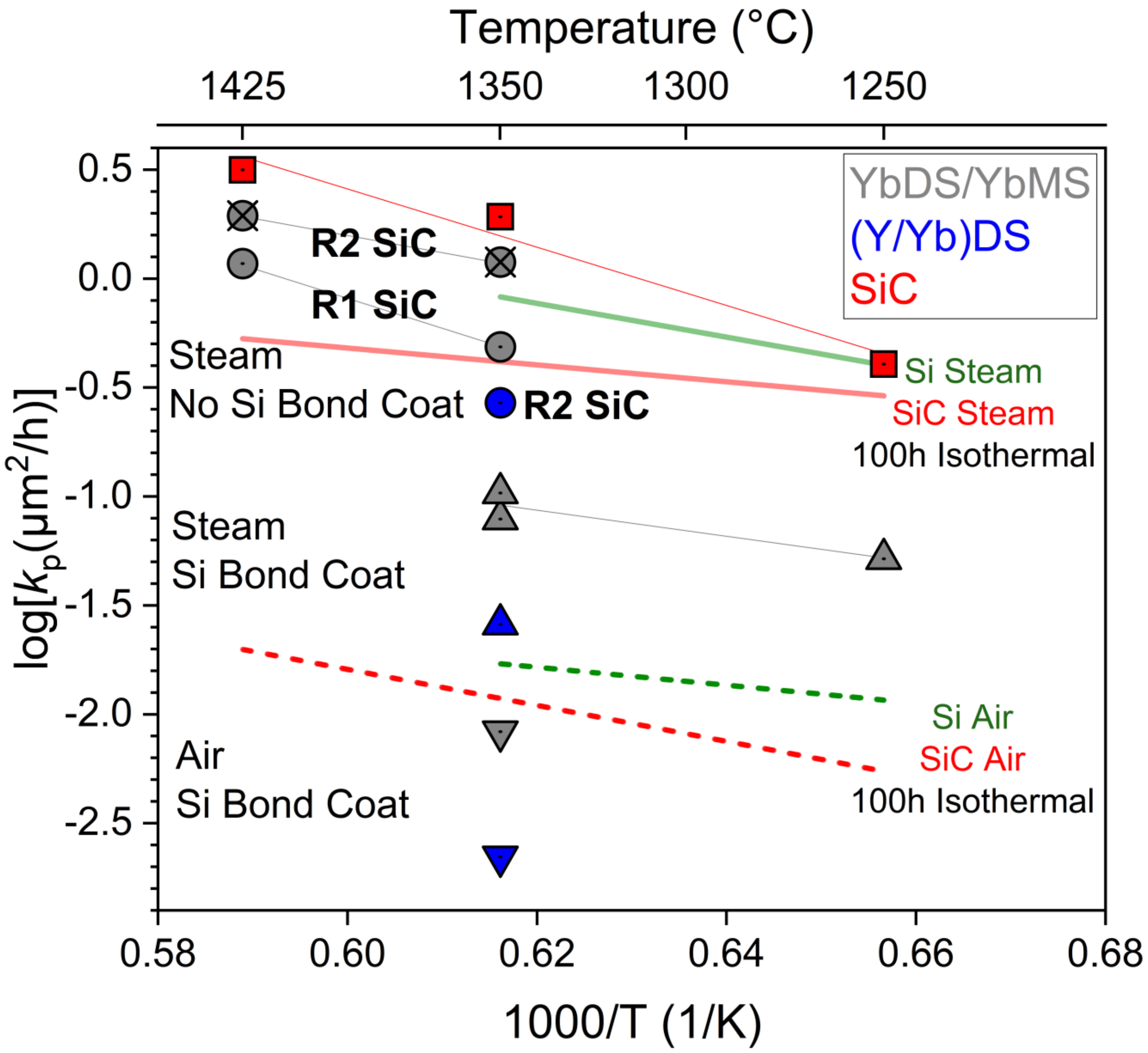


TGO thickness is dependent on local interface roughness

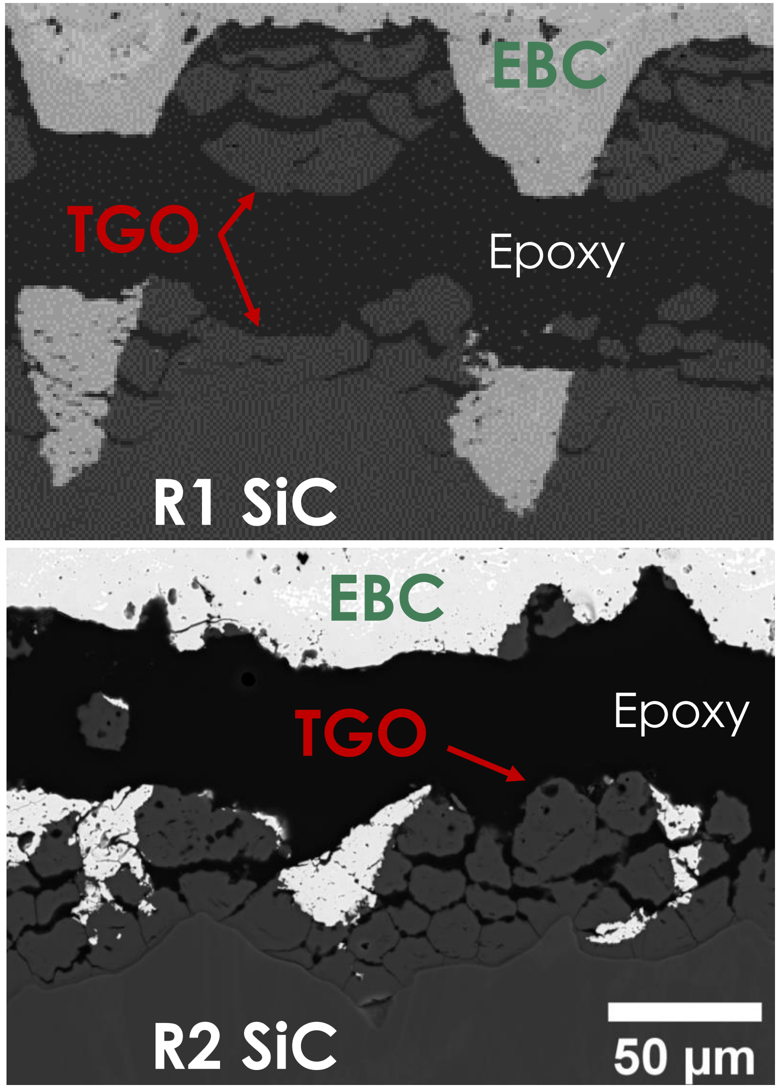
Crack network formation may accelerate oxidation

Enhanced roughness SiC leads to rapid oxidation

- (Y/Yb)DS EBCs consistently outperforms YbDS/YbMS in terms of oxidation resistance
- R1 SiC/EBC systems are more oxidation resistant than R2
- 1-h cyclic testing of SiC results in higher growth rates than isothermal testing
  - Cycle time matters!



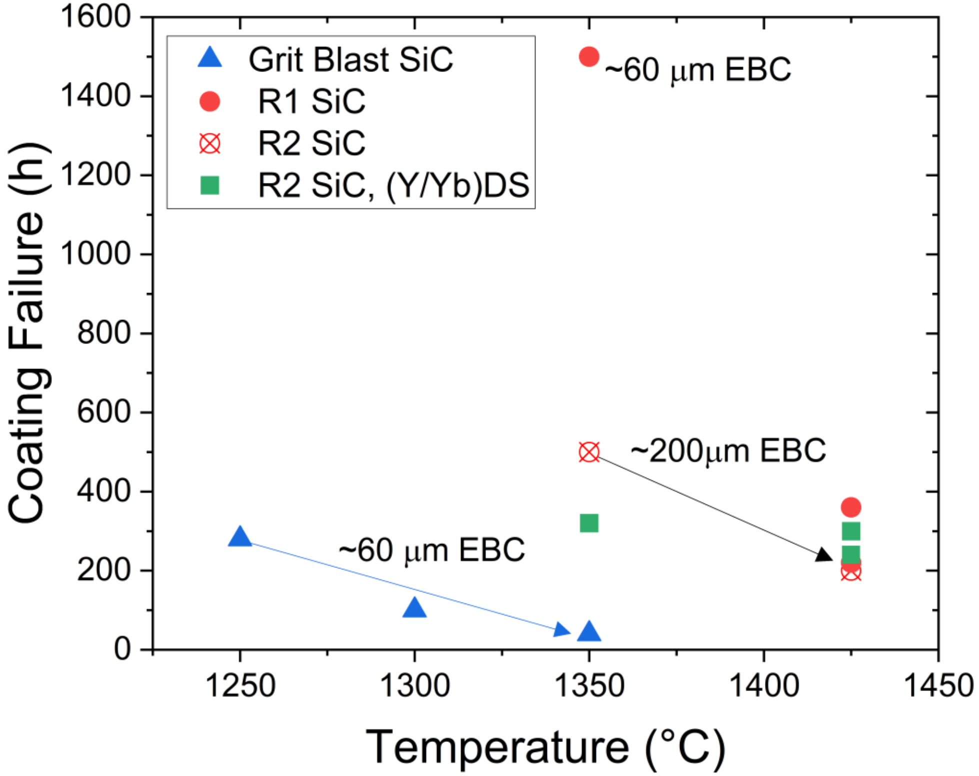
No bond coat EBC systems display failure after short exposure times



TGO crack networks decrease interface strength

Failed specimens have TGO thicker than the applied SiC roughness

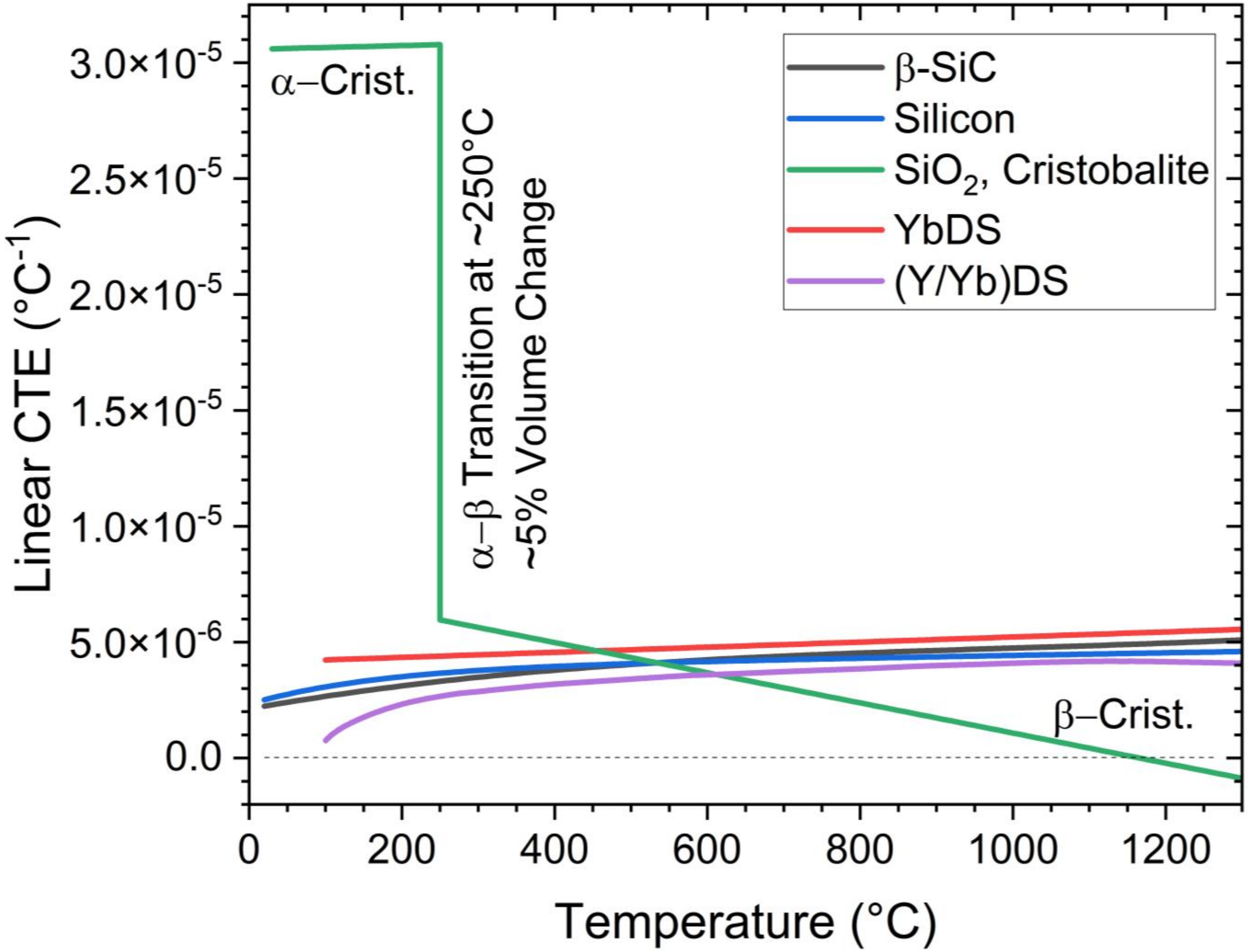
Delamination occurs at TGO – EBC interface



Understanding coating failure: largest stress may be from SiO_2 TGO phase transformation

Factors:
- Geometry Effects
- TGO Formation
- Material Properties

Needs:
- Better characterization of phase transformation
- Finite element modeling



SiO_2 Data From:
Swainson IP, Dove MT. Phys Chem Miner. (1995).
Peacor, D. Zeitschrift Fur Kristallographie - Z KRISTALLOGR. (1972).

How do we develop a lifetime model for EBCs?

Lifetime Modelling of EBCs

- Kinetics/Thermo, FEM

Material Changes

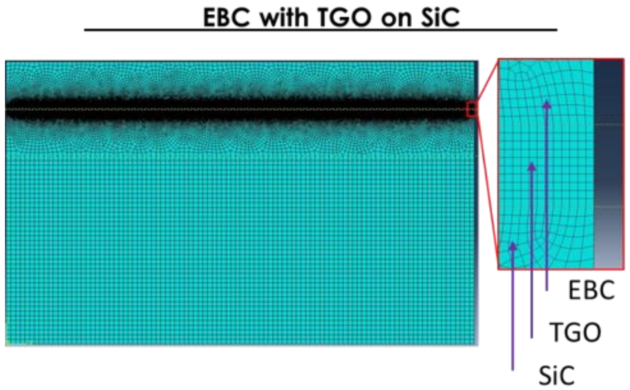
- EBC/Si/SiC
  (chemistry, thickness, roughness, density)

Laboratory Testing

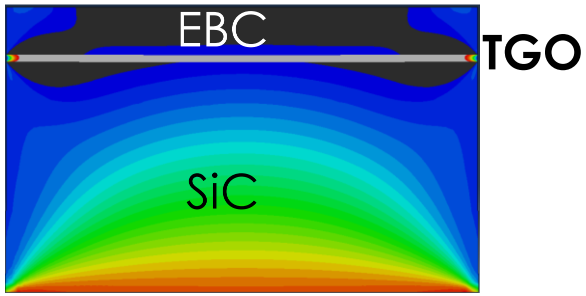
- Experimental (Methodology, geometry, cycling)
- Environmental
  (T, P, v, atm)

FE stress modelling with respect to SiO_2 TGO thickness

- SiO_2 undergoes ~5% vol. change and major CTE change at cristobalite transition (~200°C)
- <u>Step 1</u>: Measure thermal stress, cooling from 1300°C
- <u>Step 2</u>: Measure SiO_2 transformation stress at 200°C
- FEM with/without bond coat, roughened interfaces

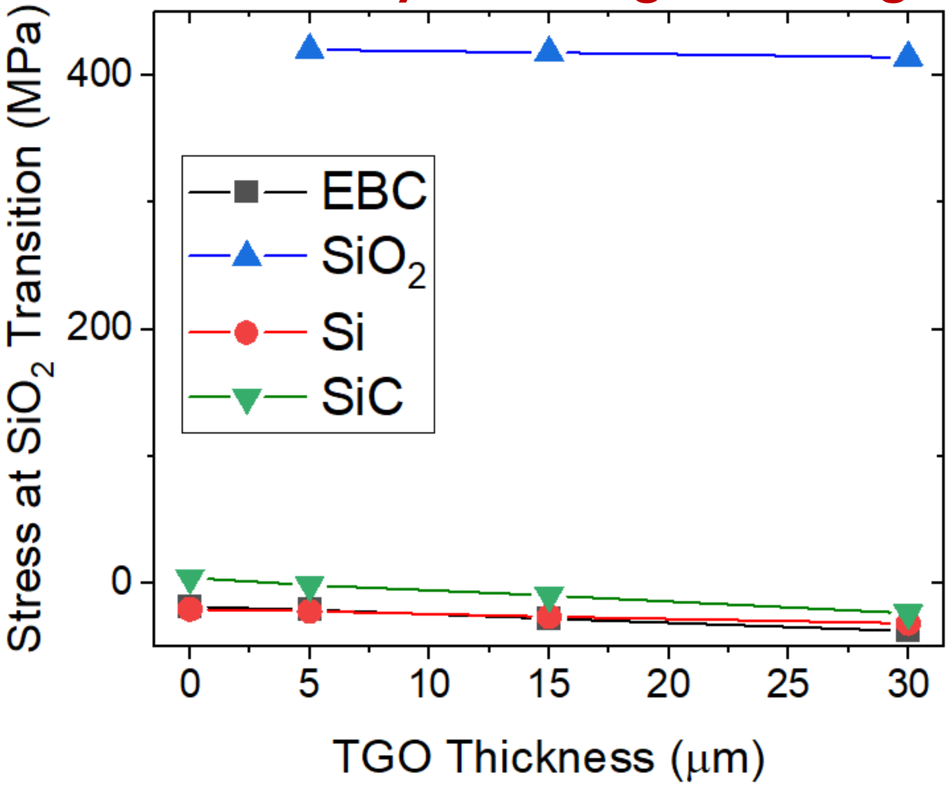


Freeze Frame of 2D EBC system on cooling

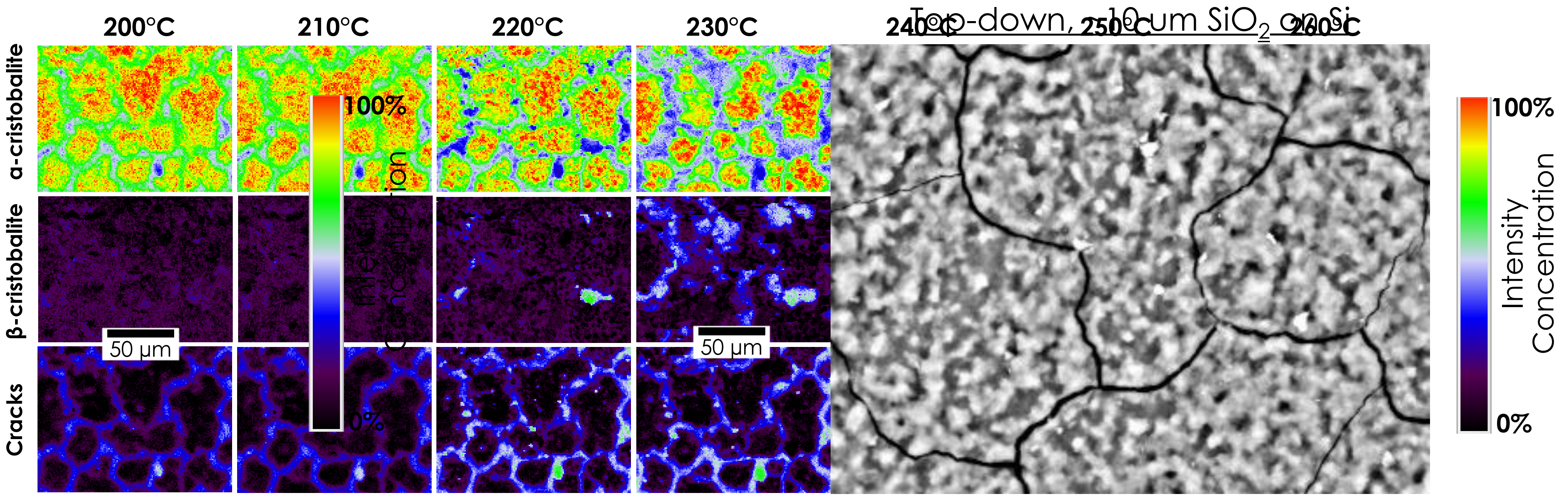


In progress!

SiO_2 undergoes rapid stress change during the phase transformation, likely inducing cracking

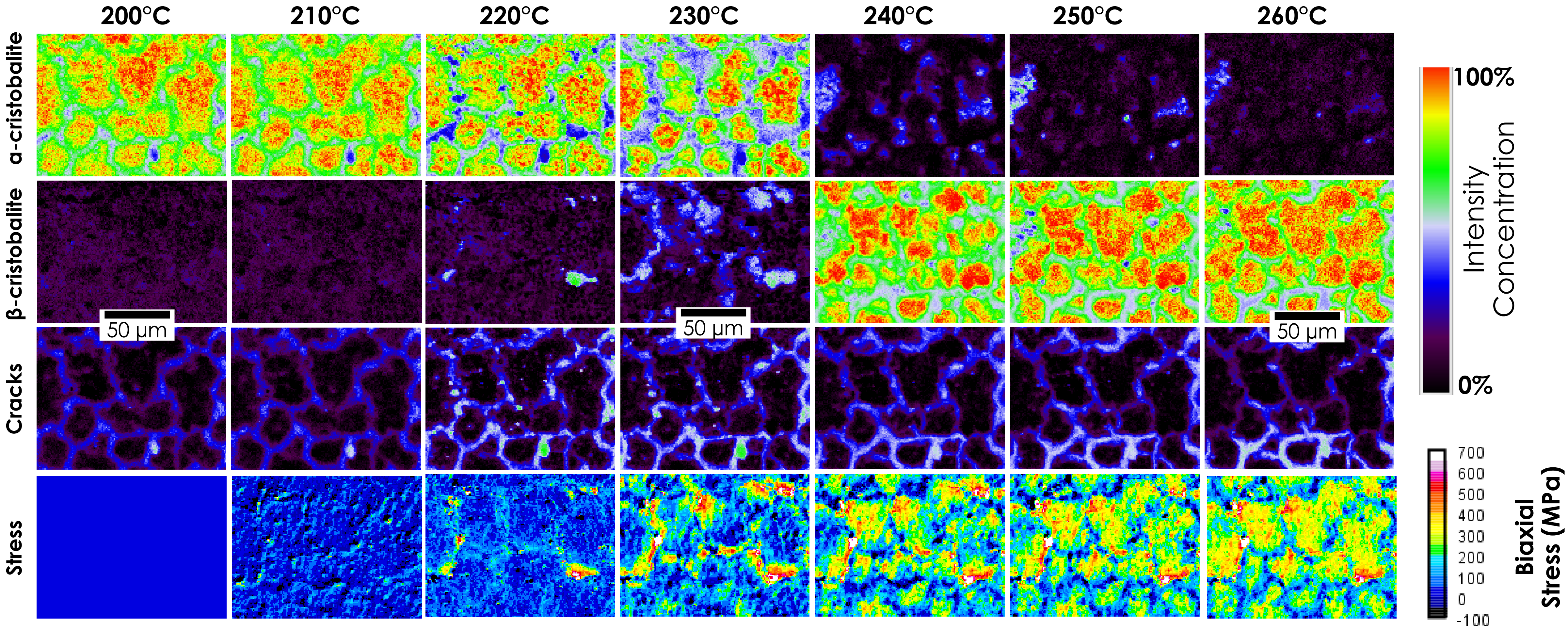


Raman Mapping: The α→β cristobalite phase transformation occurred at 240°C



- Each map took 30 minutes to acquire and was collected from the same location at each temperature.
- **Principal component analysis** of the Raman maps identified three unique components (phases); α, β cristobalite, and "cracks".
- The phase transformations starts at the cracks in the TGO and moves inward.
- **Peak shifting can be correlated independently to Temperature and Stress**

Stress in the Si substrate increased 300–500 MPa due to the α→β cristobalite phase transformation during heating

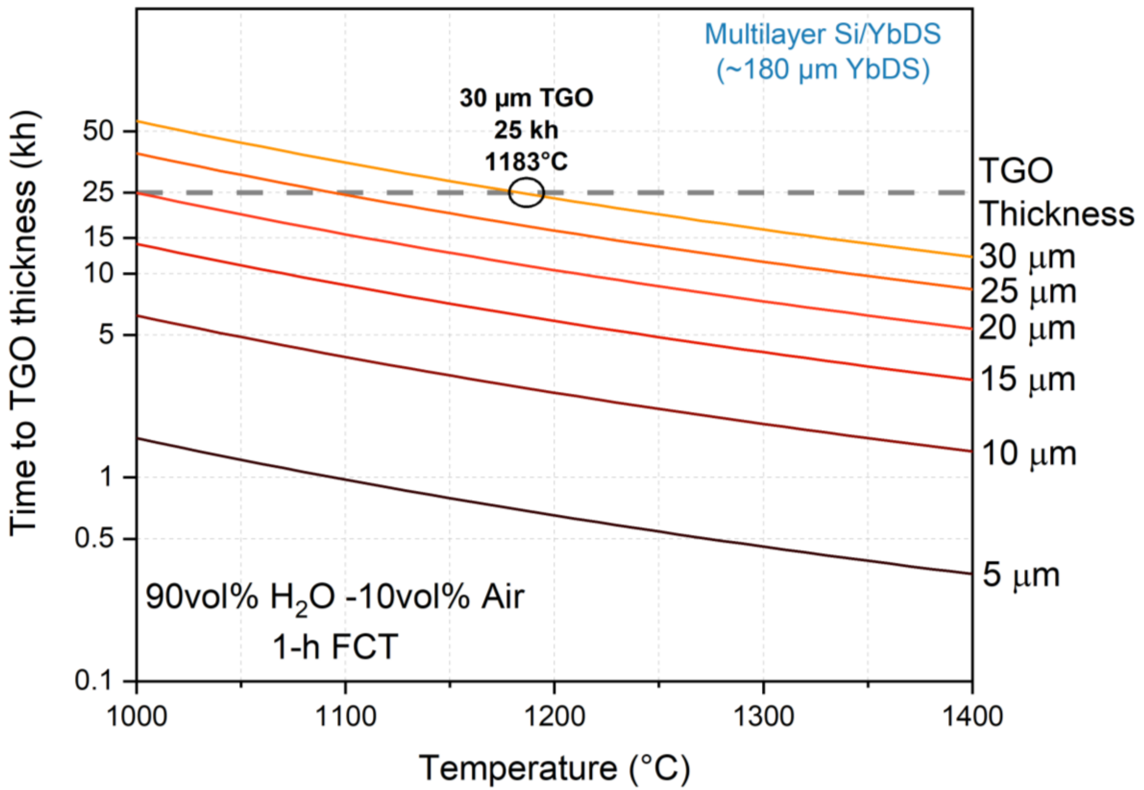


- The map at 200°C was used as the zero-stress reference
- Temperature shift of Si peak removed based on literature data
- Resulting peak shift correlated to stress at each pixel

Steam oxidation kinetics can be extrapolated to predict upper temperature limit for expected lifetime in IGTs

- Assuming: extrapolation + 30µm SiO_2 reaction product is adherent
- Used Deal & Grove Si oxidation temperature dependence (68 kJ/mol) with 1350°C wet air rates
- Rates for additional temperatures coming soon to improve model

Si/YbDS: limited to 1183°C

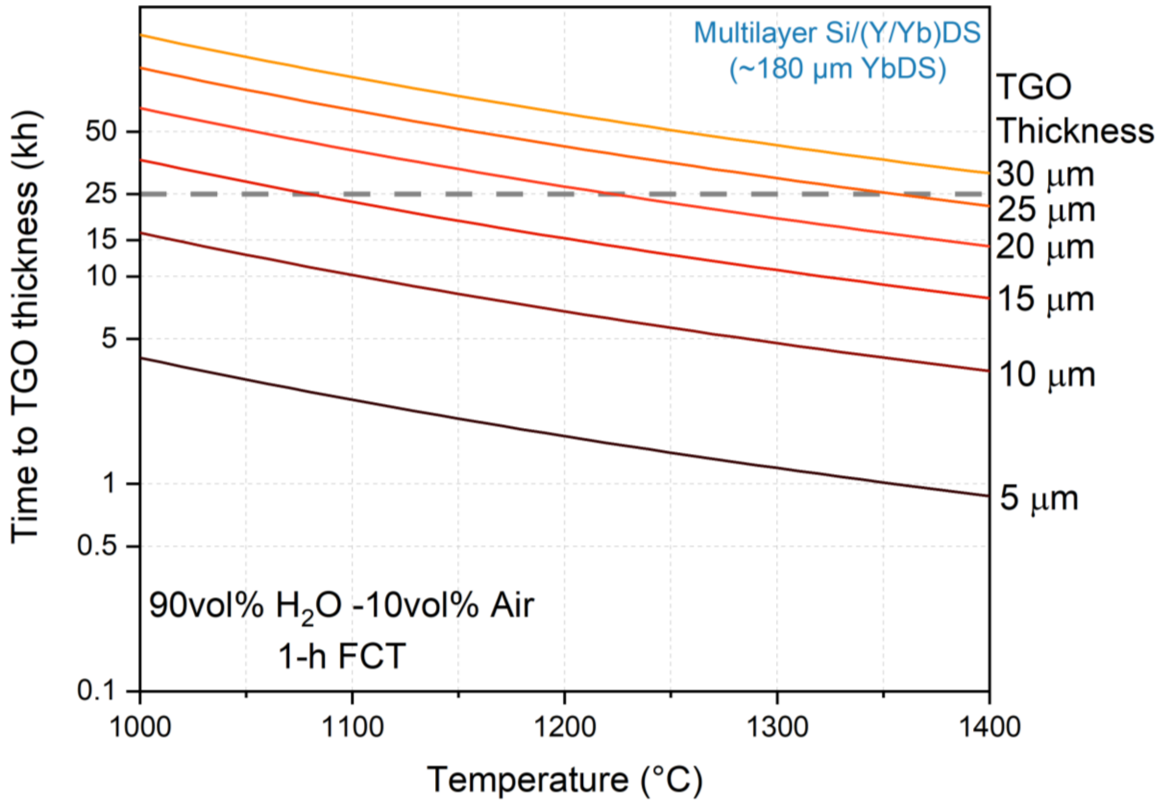


OAK RIDGE National Laboratory

EBC chemistry & microstructure modifications can greatly increase upper temperature limit for IGTs

- Assuming: extrapolation + 30μm SiO_2 reaction product is adherent
- Used Deal & Grove Si oxidation temperature dependence (68 kJ/mol) with 1350°C wet air rates
- Rates for additional temperatures coming soon to improve model

Slower (Y/Yb)DS rates: limited by Si melting



How do we develop a lifetime model for EBCs?

Lifetime Modelling of EBCs

- FEM, Kinetics, Thermodynamics

Material Changes

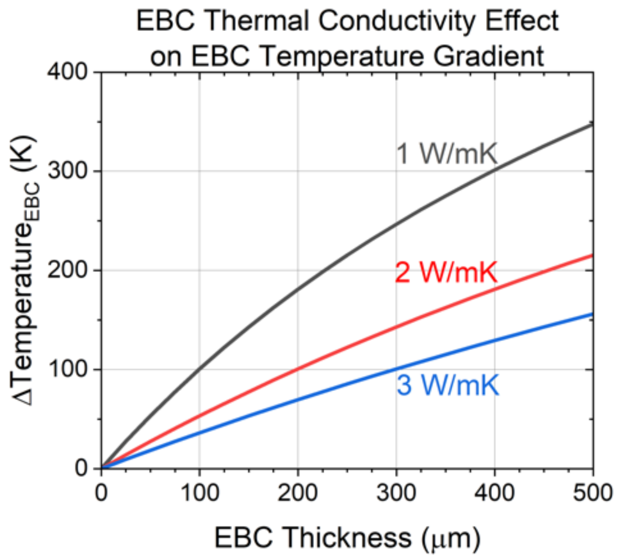
- EBC/Si/SiC (chemistry, thickness, roughness, density)

Laboratory Testing

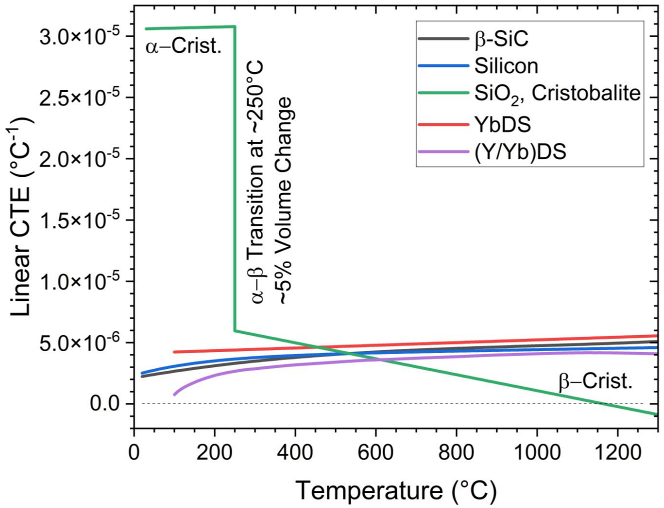
- Experimental (Methodology, geometry, cycling)
- Environmental (T, P, v, atm)

ORNL EBC outlook: plenty of work to keep everyone busy

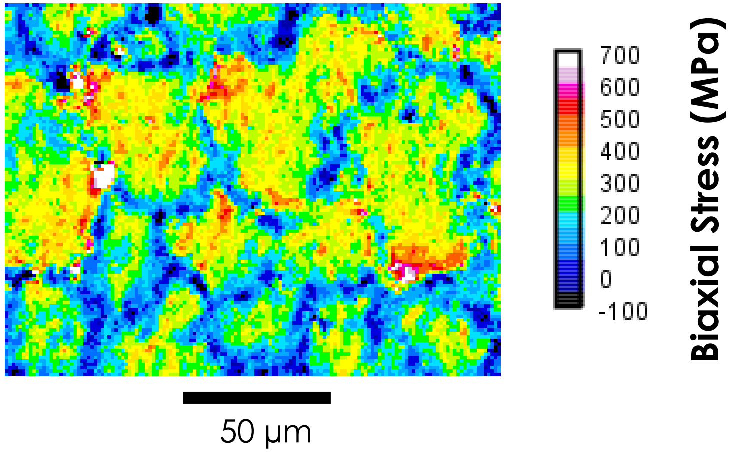
- We need better EBCs
  - Lower thermal conductivity
  - Increased chemical stability
  - Oxidant barrier
  - FCT baselines for SiC and Silicon



- Understand/mitigate the SiO_2 phase trans-formation might help
  - Phase stabilization?
  - Need basic SiO_2 data
  - Modeling for stress induced EBC failure



- Use Raman for further understanding
  - Calibrate Si stress measurements
  - Compare SiO_2 grown in dry and wet air
  - Quantify as function of thickness & oxidation temperature



Thank you for your attention!
EBC publications:

- K. A. Kane, E. Garcia-Granados, R. Uwanyuze, M. J. Lance, K. A. Unocic, S. Sampath, B. A. Pint, "Steam oxidation of atmospheric plasma sprayed ytterbium disilicate environmental barrier coatings with and without a silicon bond coat," **Journal of the American Ceramic Society** 104 (2021) 2285-2300.
- B. A. Pint, P. Stack and K. A. Kane, "Predicting EBC Temperature Limits for Industrial Gas Turbines" ASME Paper #GT2021-59408, for Turbo Expo 2021 Virtual Conference and Exhibition, June 11-15, 2021 & **Diesel and Gas Turbine Worldwide** Jan.-Mar. issue (2022) p.40-43.
- K. A. Kane, E. Garcia, P. Stack, M. Lance, C. Parker, S. Sampath, B. A. Pint, "Evaluating steam oxidation kinetics of environmental barrier coatings," **Journal of the American Ceramic Society**, 105 (2022) 590-605.
- K. A. Kane, E. Garcia, M. Lance, C. Parker, S. Sampath, B. A. Pint, "Accelerated oxidation during long-term cycling of ytterbium silicate environmental barrier coatings at 1350°C," **Journal of the American Ceramic Society**, 105 (2022) 2754-2763.
- P. Stack, K. Kane, M. Sweet, C. Parker, M. Lance, M. Ridley, B. A. Pint, "Dry air cyclic oxidation of mixed Yb/Y disilicate environmental barrier coatings and bare silica formers," **Journal of the European Ceramic Society** 42 (2022) 3345-3350.
- M. J. Ridley, K. A. Kane, M. J. Lance, C. G. Parker, Y.-F. Su, S. Sampath, E. Garcia, M. Sweet, M. O'Connor, B. A. Pint, "Steam Oxidation and Microstructural Evolution of Rare Earth Silicate Environmental Barrier Coatings," **Journal of the American Ceramic Society** (2022).