Next Generation Environmental Barrier Coatings

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Field Work Proposal: FEAA300

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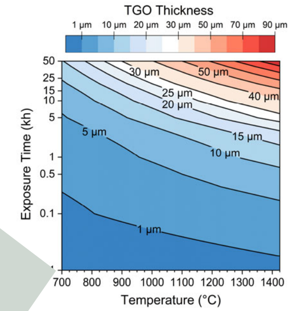
Past, Present & Future:
ORNL Contributions to Advanced Coatings

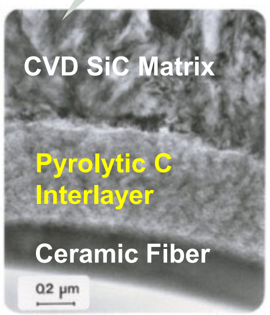


ORNL SiC Legacy:

-Vapor coating of SiC fuel particles

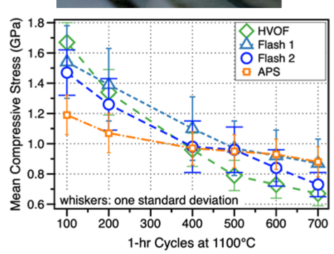
- Forced Flow CVI

- DOE Continuous Fiber Ceramic Composite (*CFCC*) Program



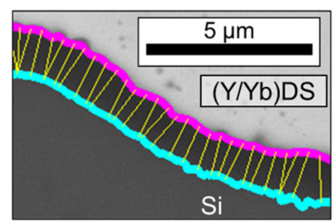
'09-'18

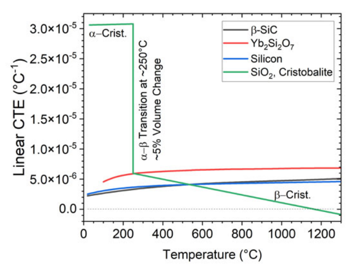
- TBC oxidation & durability



'19-'23 FWP FEAA149

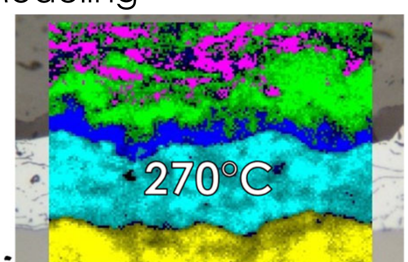
- Thermal expansion
- Thermal stability
- Oxidation
- Analysis Methodology

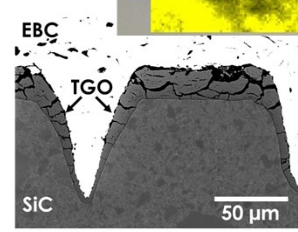




'24-'26 FWP FEAA300

- EBC durability
- Stress/Phase analysis
- Oxidation
- Lifetime prediction
- Combination of separate effects
- Modeling

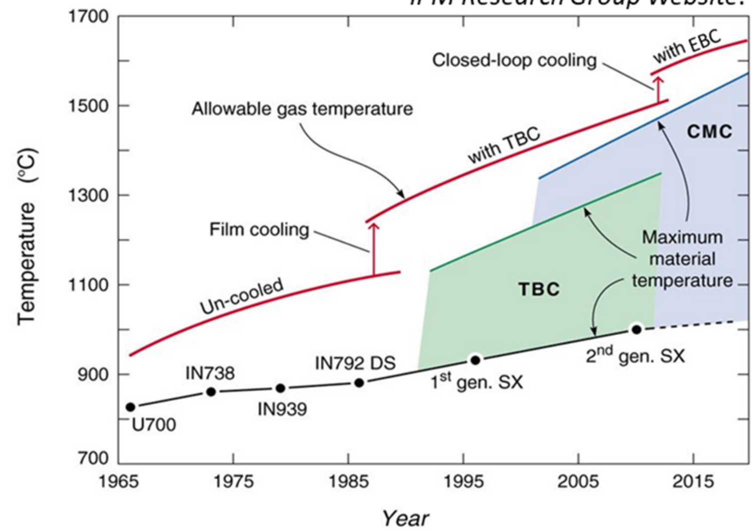




There is great interest in using ceramic matrix composites (CMCs) in combustion environments

- CMC components entered commercial aircraft service in 2016 (GE/Safran LEAP engine)
  - 1/3rd the density of traditional superalloys
  - Higher temperature stability of CMCs in combustion gases can allow for increased operating temperatures
- Interest in CMCs as hot section components for land-based turbines
  - In the future, Industrial Gas Turbines (IGT) will be fired using H_2 which will be at even higher temperatures
- Enabling CMCs for combustion environments requires protective Environmental Barrier Coatings (EBCs)
  - Si bond coating oxidation is a major failure mode

IPM Research Group Website.

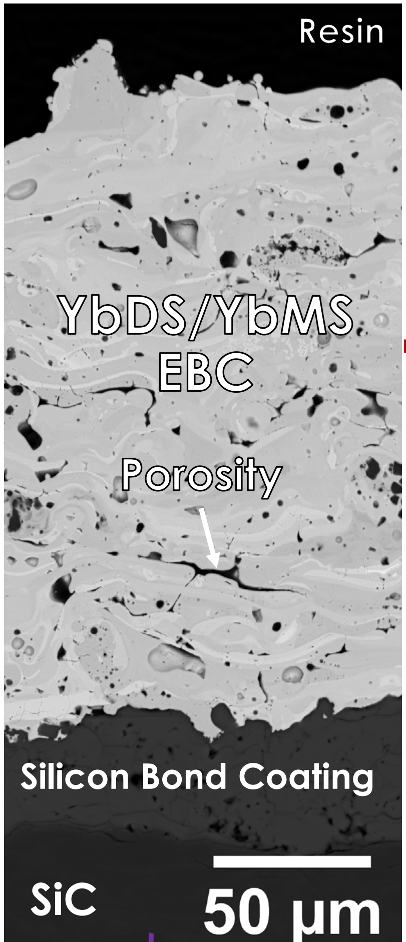


www.siemens-energy.com

https://github.com/TriplePointCat/SOFIA-CV

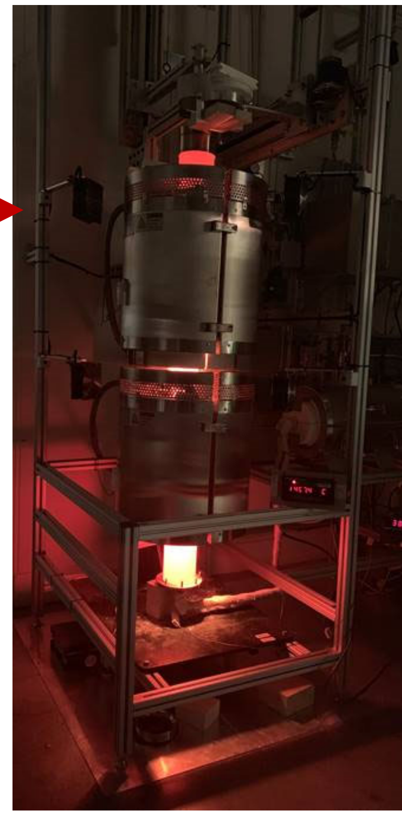
Open Source!

Coating durability related to oxidation resistance

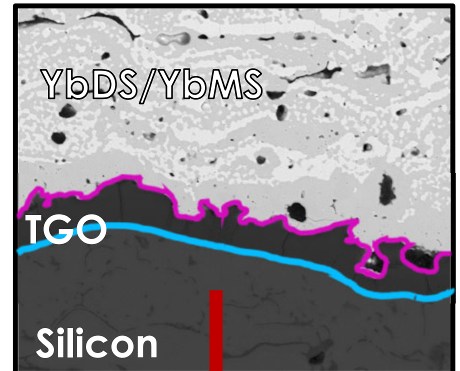


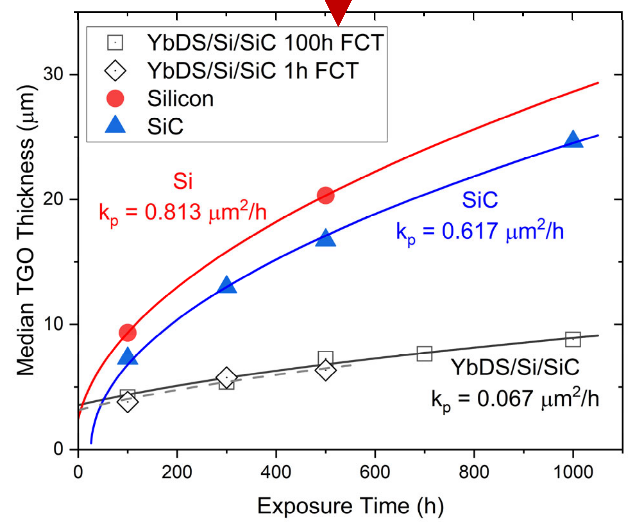
Specimens on sample hangers

Automated Cyclic Rigs
Steam/Air mixtures up to 1500°C



Automated Thickness Measurement Software





CVD SiC used to represent seal coat on CMCs

J Am Ceram Soc. 2023; 106: 613–620. https://doi.org/10.1111/jace.18769

FY24 Tasks

Task 1 (100%)

1.1: Compile industrial survey on the primary research obstacles for EBC/CMC systems in gas turbines, **Q2**

Task 2 (100%)

1.2: Submit a journal publication on the measured SiO_2 crack density during 100-h furnace cycle testing at 1350°C up to 1500h, **Q3**

Task 3 (100%)

- 2.1: Perform O^{18} (g) tracer diffusion experiments at 1300°C to measure oxidant diffusivity through EBCs to support EBC oxidation lifetime model, **Q4**

Task 4 (95%)

- 3.1: Submit a journal publication on utilization of Raman spectroscopy to measure layer stresses in an EBC/SiO_2/Si/SiC system in cross-section upon heating through the SiO_2 phase transformation temperature, **Q4**
  - **Paper in review**

Output for Ceramic Coatings R&D Community: Publications

- 15 publications on EBCs since 2019
- >250 total citations
- 2024 Publications:

1. Aguirre T, Lin L, Ridley M, Kane K, Pint B. Finite Element Modeling of the Phase Change in Thermally-Grown SiO2 in SiC Systems for Gas Turbines. *JOM - Journal of the Minerals, Metals and Materials Society*. 2024. https://doi.org/10.1007/s11837-024-06507-4

2. Ridley, M., Kane, K. & Pint, B. Environmental barrier coatings on SiC without a silicon bond coating: oxidation resistance, failure modes, and future improvements. *J. Korean Ceram. Soc.* (2024). https://doi.org/10.1007/s43207-024-00386-w

3. Ridley MJ, Lance MJ, Aguirre TG, Kane KA, Pint BA. Understanding EBC Lifetimes and Performance for Industrial Gas Turbines. J. Eng. Gas Turbines Power. 2024. https://doi.org/10.1115/1.4066349

Output for Ceramic Coatings R&D Community: Conferences

- 2023
  - The Minerals, Metals & Materials Society
  - 47th International Conference on Advanced Ceramics and Composites
  - 49th International Conference on Metallurgical Coatings and Thin Films
  - Center for Thermal Spray Research Consortium
  - High Temperature Corrosion Gordon Research Conference
  - 11th International Conference on High Temperature Ceramic Matrix Composites (session chair)
- 2024
  - Composites, Materials & Structures Conference
  - Pacific Operational Science and Technology (POST)
  - 50th International Conference on Metallurgical Coatings and Thin Films
  - Center for Thermal Spray Research Consortium
  - ASME Turbomachinery Technical Conference & Exposition

Task 1: Industry EBC Panel

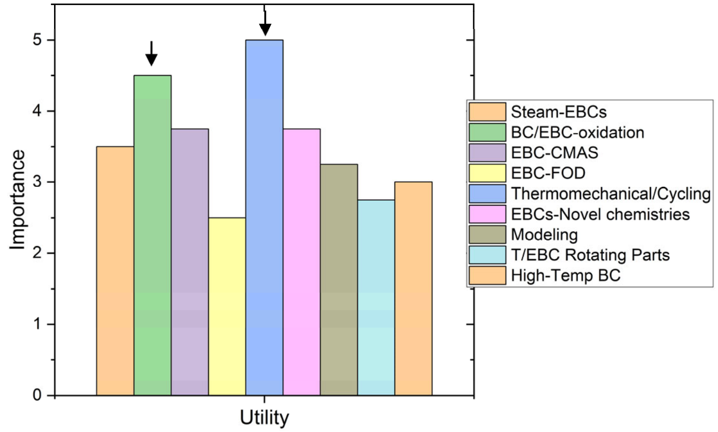
- Establish connections with industry
- Understand industry needs regarding EBC/CMC research
- Redirect ORNL EBC work scope to be most impactful
  - Emphasis on Industry Perspective*

10 Total Contributors

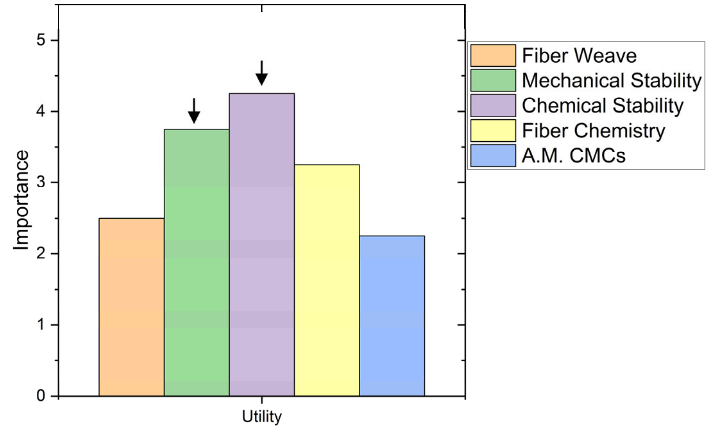
Industry	R&D
General Electric Aerospace	UES Inc., AFRL
General Electric Global Research	ORNL (x2)
Siemens Corporation (*R&D stage*)	Stony Brook University (x2)
Rolls-Royce	
Oerlikon Metco (*Supplier*)	

EBC Survey Outcomes
(Industry Perspective Only)

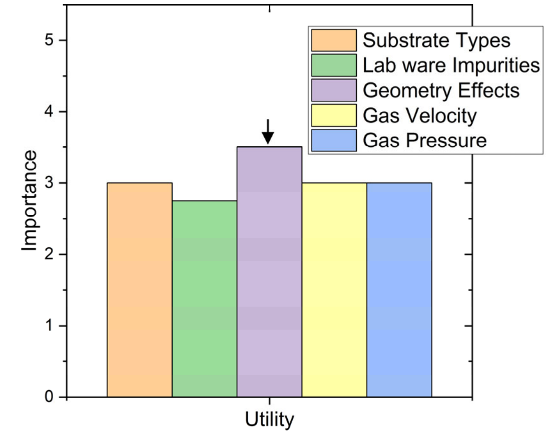
Environmental Barrier Coatings



SiC/SiC Composites



Laboratory Testing



Highest ranked interests from industry are:

1. Thermal cycle stability of EBCs
2. Bond coating oxidation
3. SiC/SiC mechanical/chemical stability

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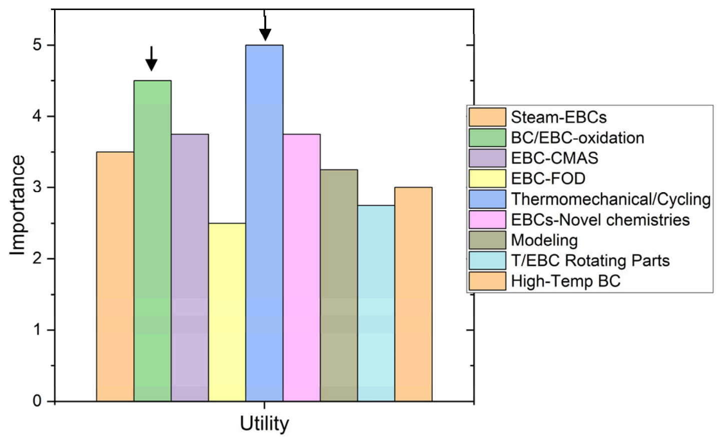
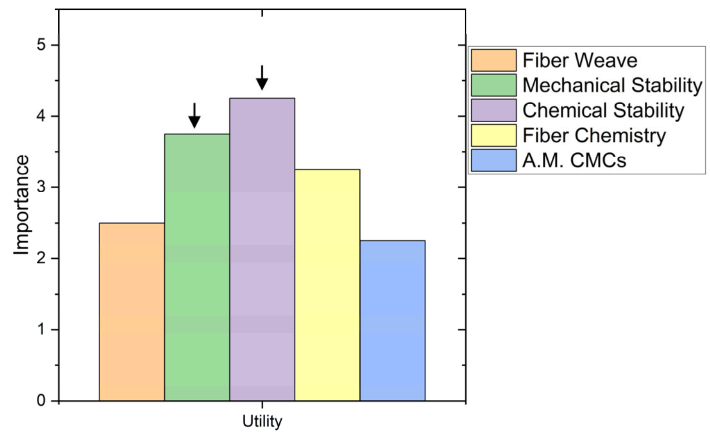
EBC Survey Outcomes
(Industry Perspective Only)

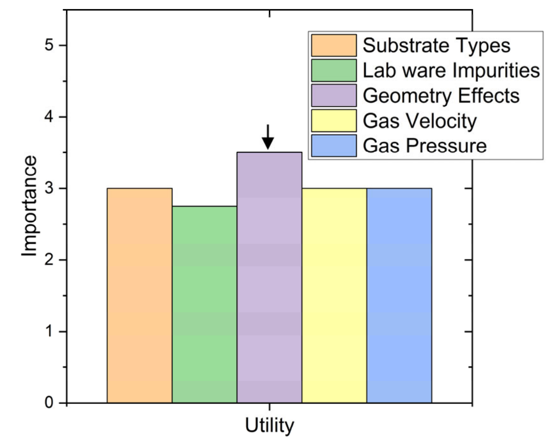
Environmental Barrier Coatings



SiC/SiC Composites



Laboratory Testing



Industry Statements (ORNL Active in These Areas)

- Oxidation mechanisms & EBC lifetime modeling are top priority
- **Low-temperature oxidation testing (<1200°C)**
- Thermal gradient testing needed to better simulate real world environment
- P_{Total} and P_{H2O} effects on oxidation needed for OEMs

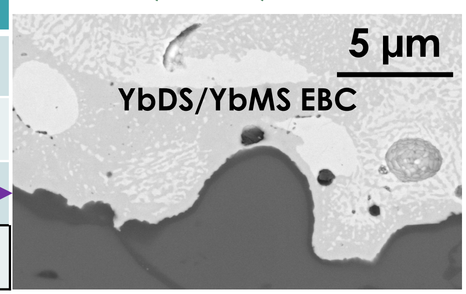
Oxidation kinetics can be visualized for simple lifetime prediction based on critical SiO_2 thickness

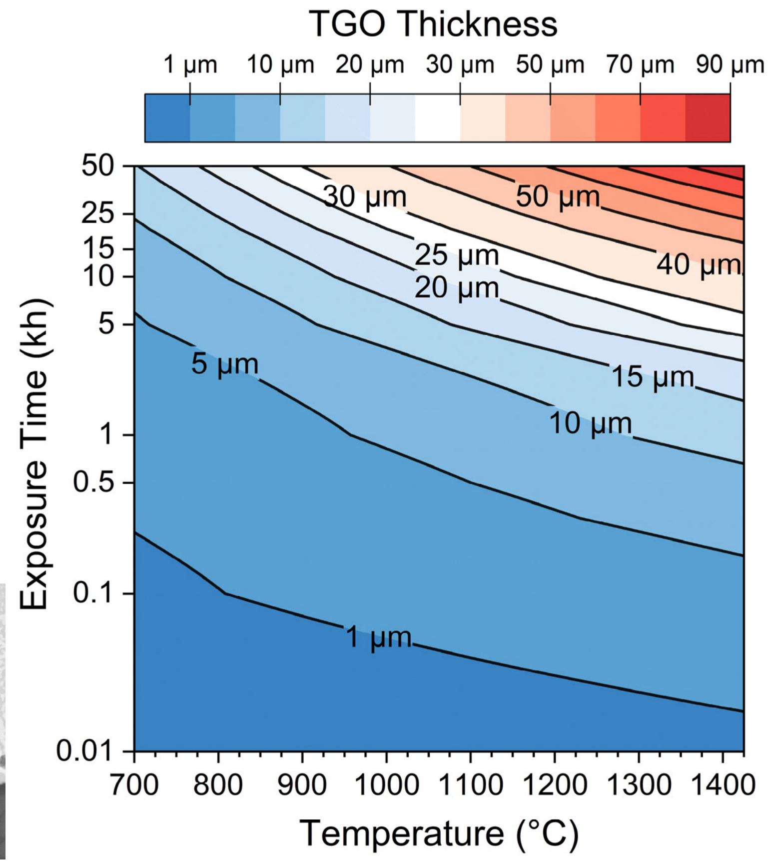
- 1350°C oxidation data used to extrapolate in *y-axis space*
- Temperature dependence for Si oxidation used to extrapolate in *x-axis space*
- **Model validates test data at 700, 1250, 1300°C (ex. 700°C, <u>OEM interest</u>)**

SiO_2 Thickness

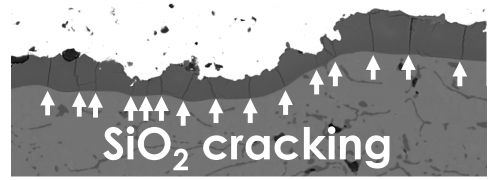
Time (h)	Model (µm)	Measured (µm)
100	0.66	0.73
300	1.14	1.13
500	1.47	1.31
Rate	4.3E-3 µm²/h	3E-3 µm²/h

500h, 700°C,1-h FCT



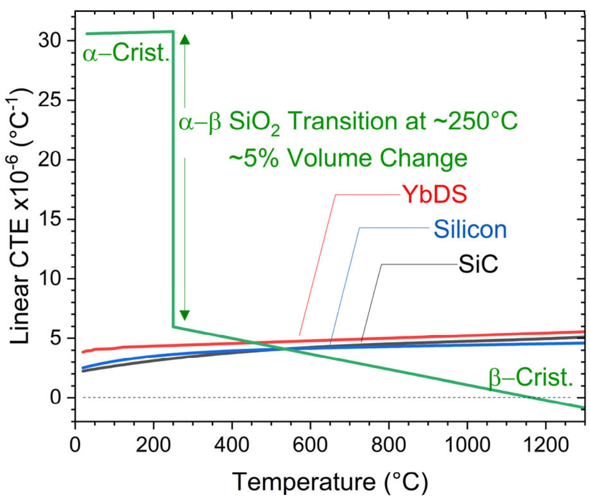


Task 2: SiO_2 Cracking

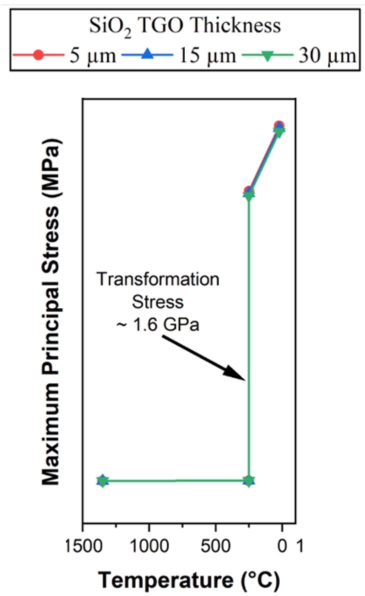


- Cracking in the SiO_2 TGO promotes delamination/spallation of EBC
- Caused by SiO_2 phase transformation below 300°C upon thermal cycling
- Crack density change as a function of exposure can inform EBC Lifetime Model

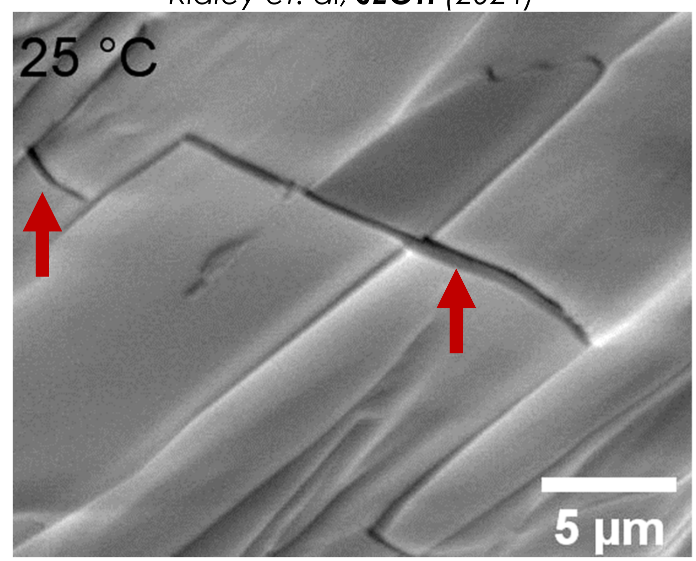
M. Lance et. al, ***JACerS*** *(2023).*



T. Aguirre et. al, ***JOM*** (2024).

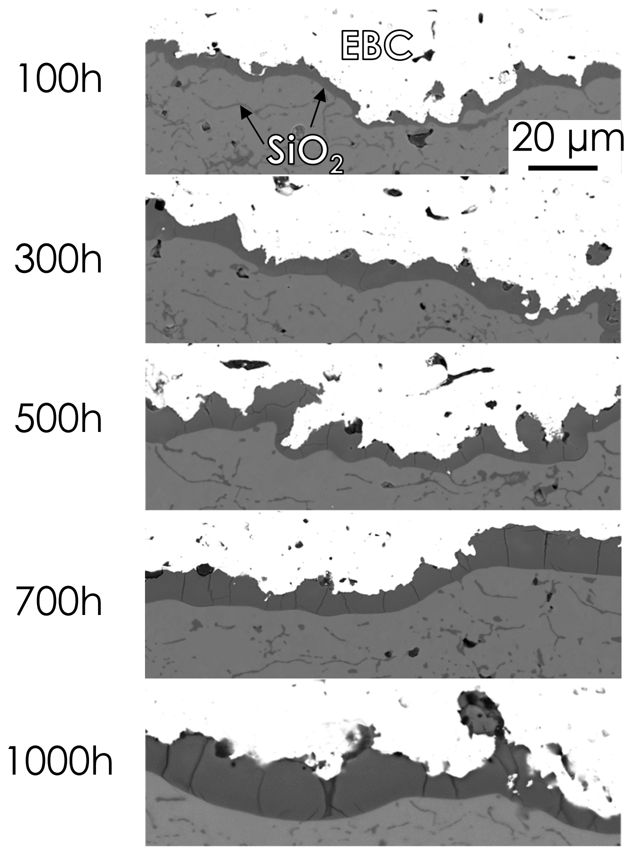


SiO_2 TGO on Si,
100h 1350°C steam exposure
Ridley et. al, ***JEGTP****(2024)*

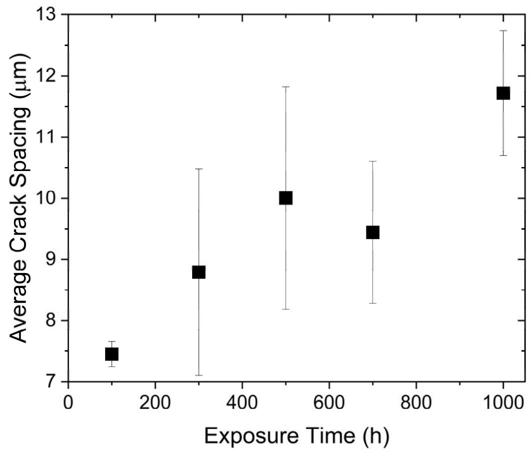


100-h Cycling of YbDS EBCs at 1350°C in 90% H_2O (g)

Ridley et. al, JACerS (2024) Submitted for Review



- 100-h cycle is more relevant to gas turbine duty cycle compared to typical aero 1-h cycle testing
- Crack density decreased as a function of exposure time???
  - Crack healing mechanism likely SiO_2 creep



Exposure Time (h)	Number of channel cracks measured	Cracks/ mm
100	139	188
300	121	110
500	215	179
700	152	109
1000	238	85

Task 3: Oxidant Diffusivities through EBCs

- Extremely limited data available on oxidant diffusivities
  - Lit. data focuses on dry air
- Diffusivity directly relates to oxidation rate
  - Needed for modeling efforts
- *Test 1: Furnace Injection*
  - Rapid, multiple samples tested at once (rapid consumption of tracer)
- *Test 2: Capsule (in progress)*
  - Controlled variables, improved quality, single specimen test

Dry air oxidant diffusivities

D_{Bulk}<1x10^{-11} cm^2/s EBC requirement for steam

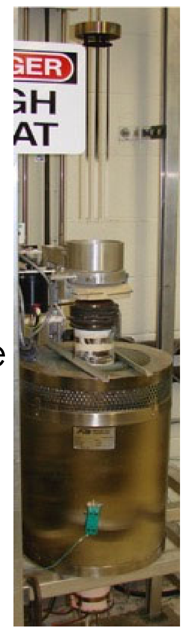
Thermo-chemical	SiO_2	Yb_2O_3	Yb_2SiO_5	$Yb_2Si_2O_7$
O_2 (g) Self diffusion D_{Bulk} in EBC, 1400 °C, cm^2/s	2.3x10^{-10}	8.0x10^{-12}	8.3x10^{-14}	1.3x10^{-14}

Ridley et. al, JACerS Feature Review Article (2024).

Test 1: $H_2{}^{18}O$ Furnace Injection

lid

furnace



Test 2: $H_2{}^{18}O$ Capsule

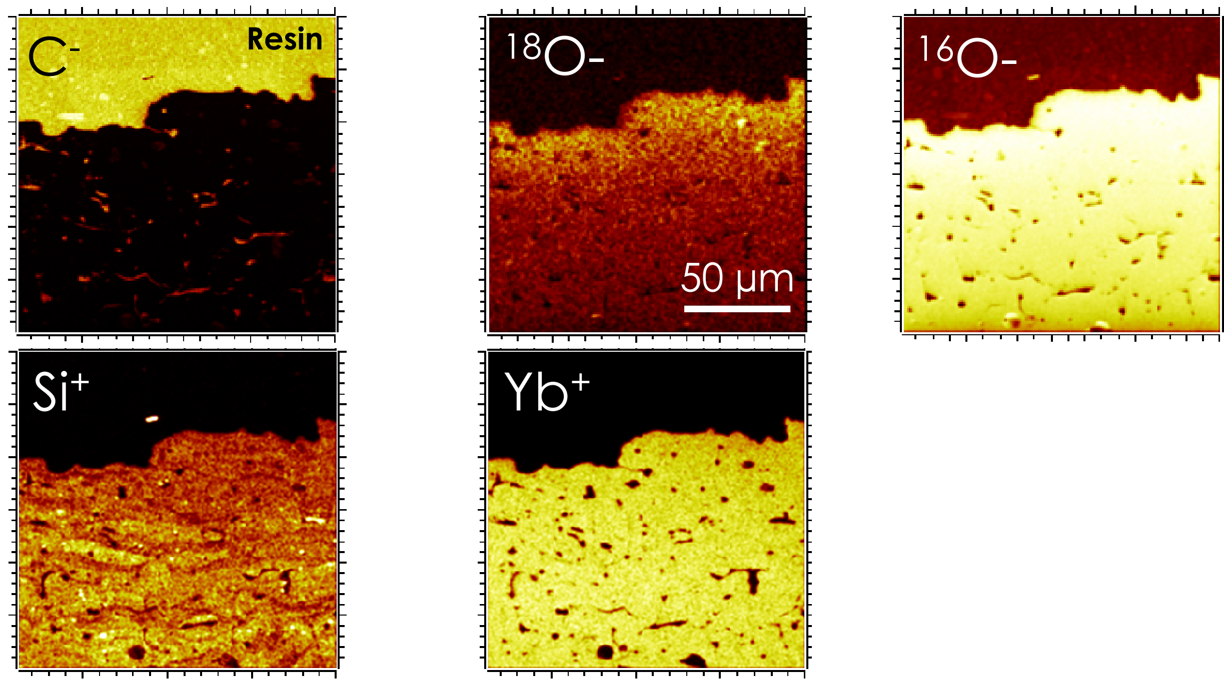
Test 1: $H_2{}^{18}O$ and $H_2O/{}^{18}O_2$ exchanges to understand diffusion pathways and diffusivities

EBCs from:
Stony Brook University

- 1300°C exchange, 2h
- Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) performed at ORNL
  - Mapping positive and negative ions
- Capsule testing underway (Test 2)

Collaboration with visiting scientist, Juho Lehmusto, Åbo Akademi University, Finland

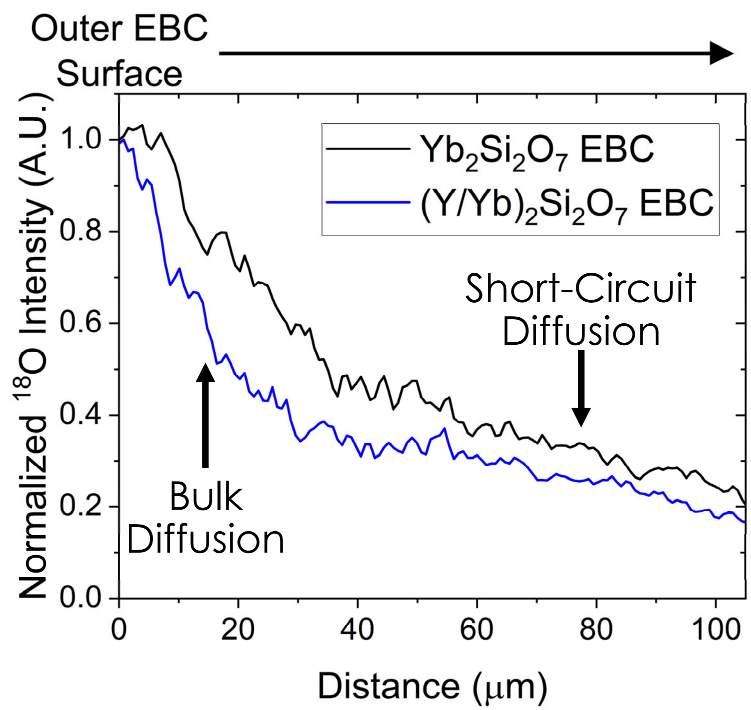
$Yb_2Si_2O_7/Yb_2SiO_5$ EBC
Furnace Testing, 90% H_2O / 10% ${}^{18}O_2$, ToF-SIMS maps



Center for Nanophase Materials Sciences (CNMS) proposal was awarded for use of ToF-SIMS at ORNL (FY24-FY25)

Decreased bulk diffusion in Y/Yb EBCs was measured

- Initial results show decreased bulk ^{18}O diffusion into (Y/Yb) EBC, in agreement with oxidation studies
  - Short circuit diffusion (controlled by microstructure/defects) similar for both EBC chemistries
- Capsule testing underway (Test 2)
  - Multiple exchange times/temperatures
  - FY25 Activity



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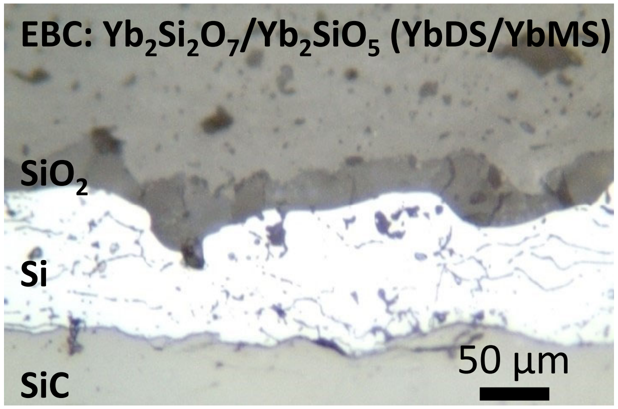
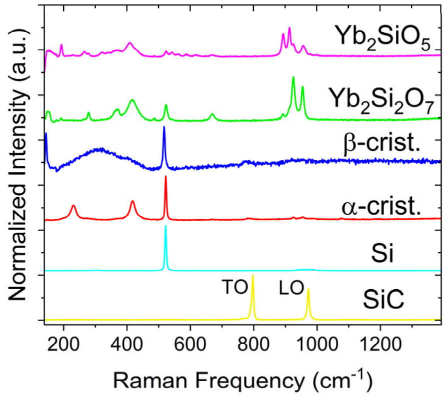
Task 4: Raman stress analysis in EBCs
High-temperature mapping of phases

- YbDS/YbMS Sample:
  - 90% H_2O/10% air
  - 1350°C
  - 10 100-h cycles
- Raman performed up to 300°C
- Principle component analysis used for phase correlation

25°C Optical Image

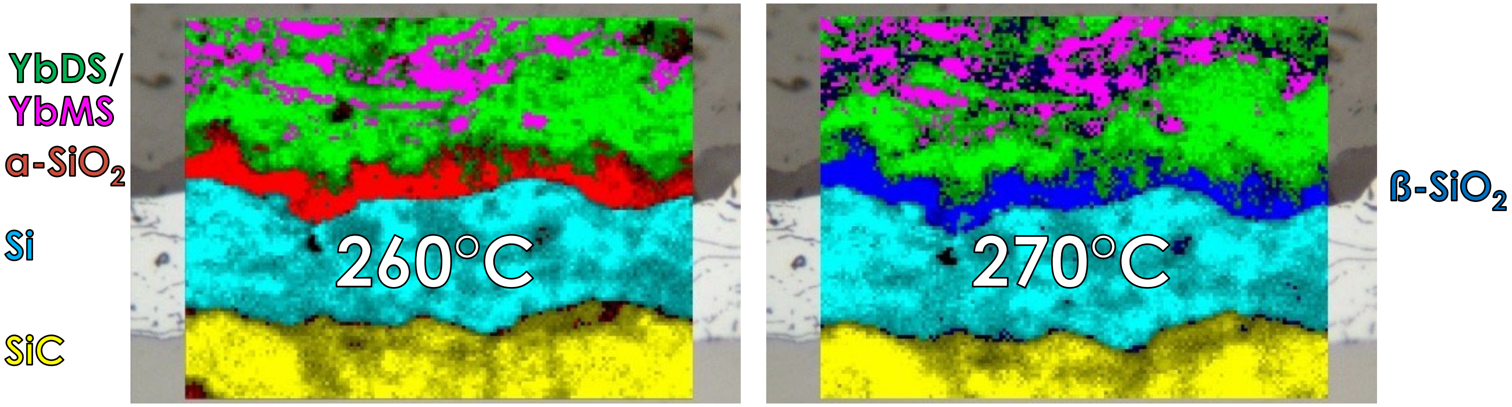


Raman Spectra



Ridley et. al, ***JEGTP****(2024)*

260°C Raman Spectra Map ***270°C Raman Spectra Map***



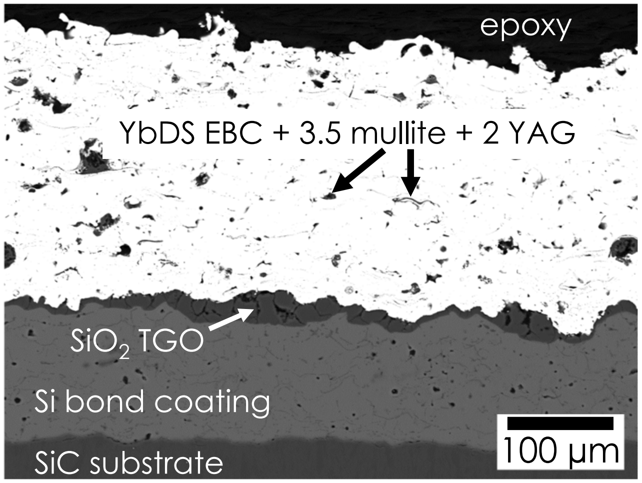
EBCs from:
Stony Brook University

Oak Ridge National Laboratory

EBCs doped with Al-containing phases were studied

- CVD SiC substrates were coated by air plasma spray with silicon and a $Yb_2Si_2O_7$ EBC modified with and without 3.5 wt% mullite and 2 wt% YAG (**from NASA GRC**).
- All samples were annealed at 1300°C for 4 hours in air prior to exposure.
- Samples were heated in steam at 1350°C for 1-h cycles in a SiC vertical tube furnace.
- During each cycle, the samples were cooled in laboratory air for 10 minutes which ensured the SiO_2 underwent the β↔a phase transformation around 250°C.

BSE image of EBC after 500h in wet air at 1350°C



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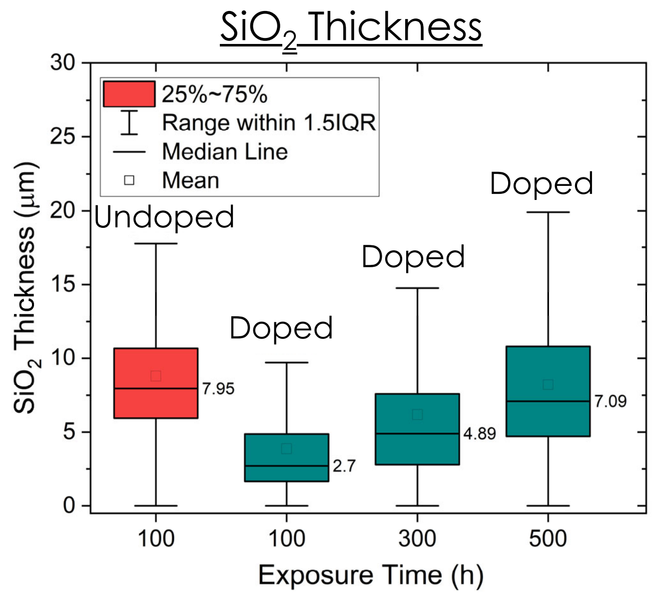
Yb2Si2O7 EBC + 3.5 mullite + 2 YAG EBC had a longer lifetime and slower TGO growth rate than the undoped Yb2Si2O7 EBC

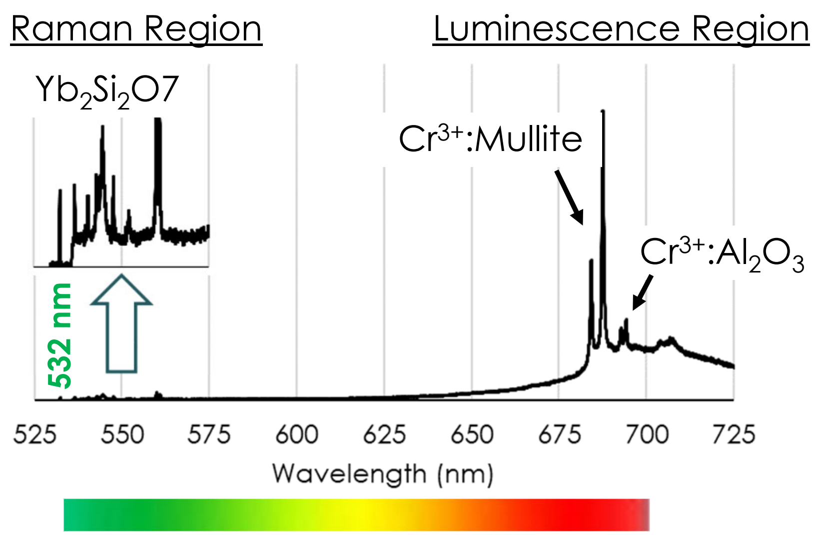


1-h cycles at 1350°C in steam

- Doping the YbDS with mullite and YAG slowed the TGO growth rate.
  - Slower TGO growth rate may be due to lower porosity.
- The undoped EBC failed at 260 ± 53 h and was 11.8% porous.
- The doped EBC failed at 1000 h and was 7.5% porous.

Photo-Stimulated Luminescence Spectroscopy (PSLS) was used to identify phases and measure stress within Al-containing oxides

$Yb_2Si_2O_7$ with 3.5 wt% Mullite and 2 wt% YAG



- A Raman Microprobe is used to acquire both Raman and PSLS spectra.
- The spot size is ~1 μm and acquisition time is <1 second.

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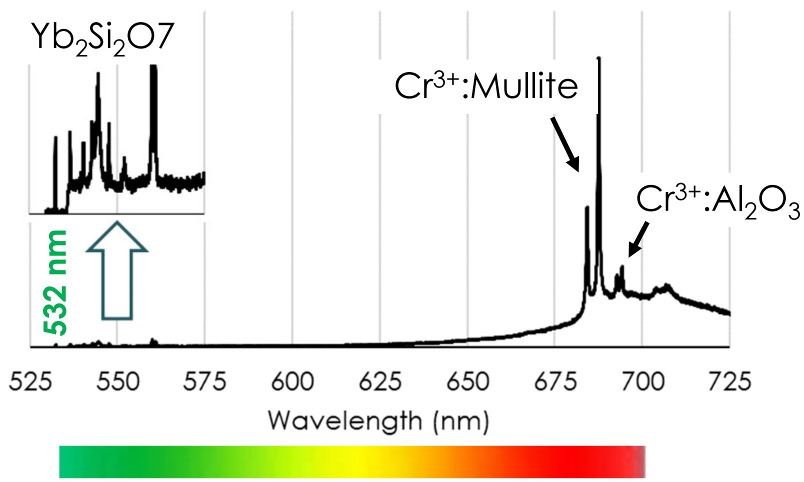
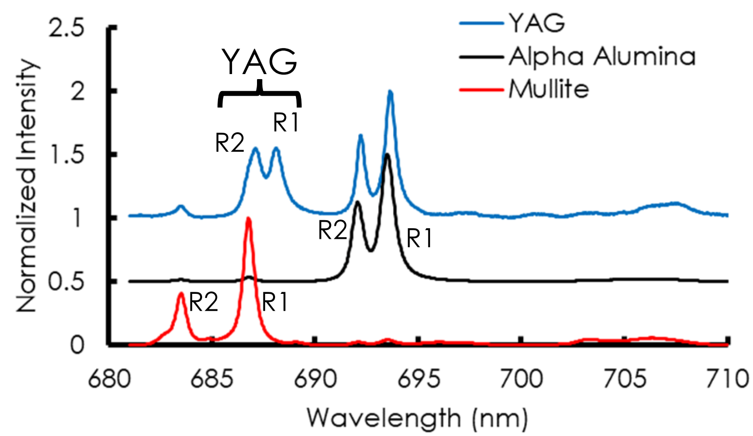
Raman Region   Luminescence Region



Luminescence Region



- A Raman Microprobe is used to acquire both Raman and PSLS spectra.
- The spot size is ~1 µm and acquisition time is <1 second.
- Trace Cr^{3+} substitutes for Al and absorbs green laser light and emits 2 R(Red)-lines.
- YAG, mullite and a-Al_2O_3 luminesce at different wavelengths.

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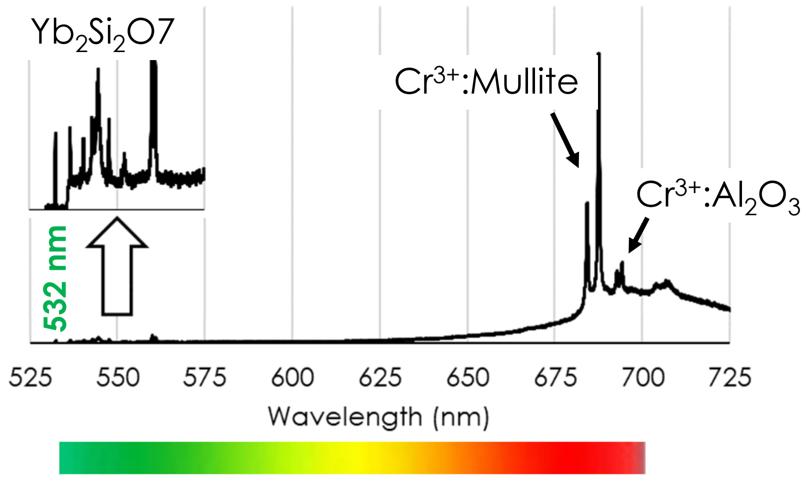
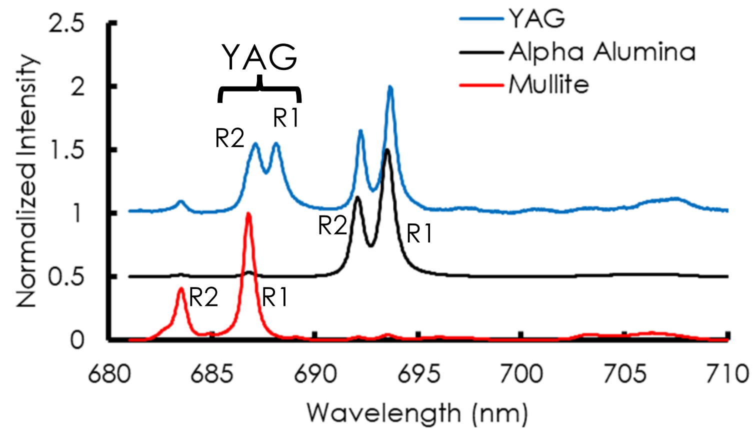
Raman Region | Luminescence Region



Luminescence Region



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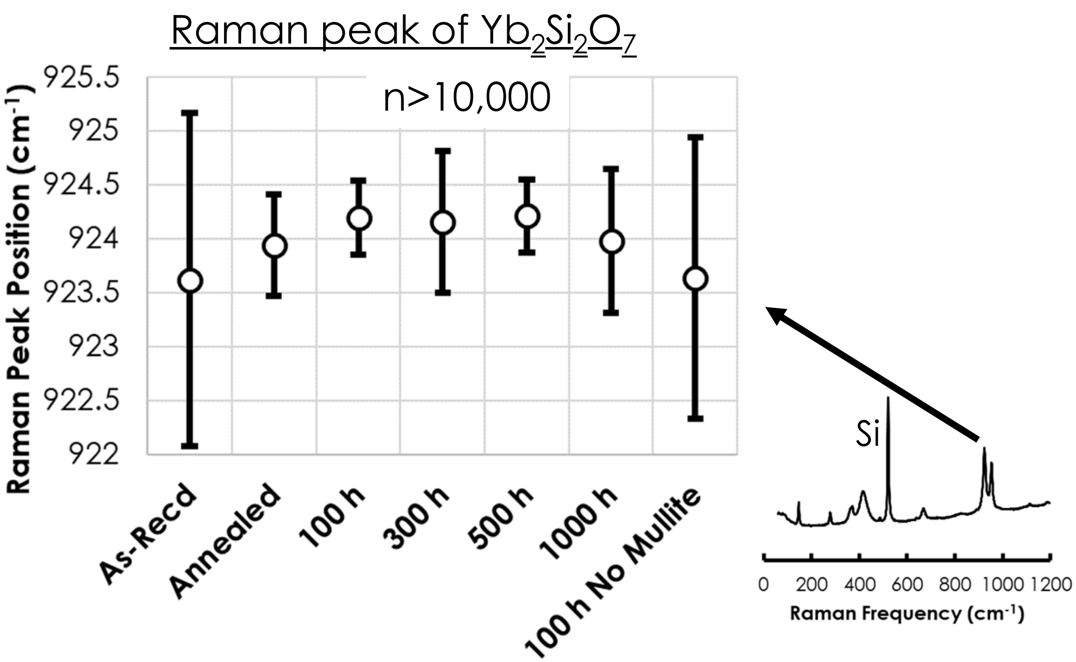
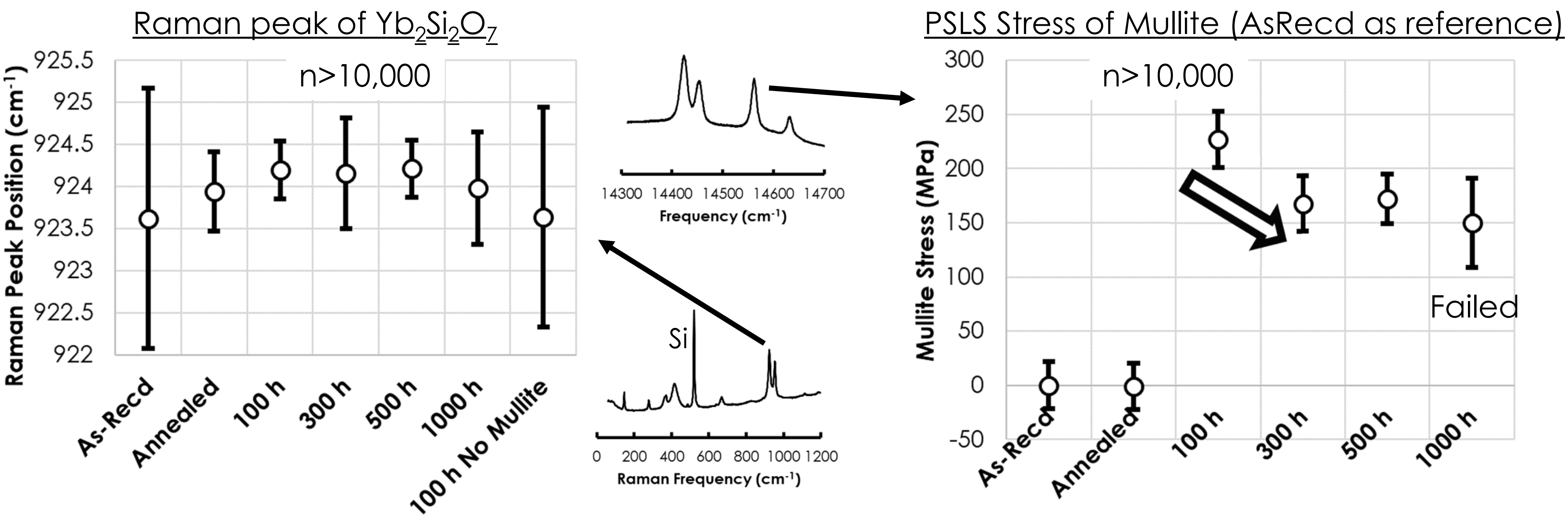
- Trace Cr^{3+} substitutes for Al and absorbs green laser light and emits 2 R(Red)-lines.
- YAG, mullite and a-Al_2O_3 luminesce at different wavelengths.
- Both Raman and PSLS spectra shift linearly with stress.
- The stress shift and intensity of the R-lines are both much larger than that of the Raman YbDS peaks.

PSLS peak shifts are statistically significant, not Raman



- The low EBC stiffness and cracking between the Si and the EBC prevents stresses from thermal cycling and the SiO_2 phase transformation from being detected.

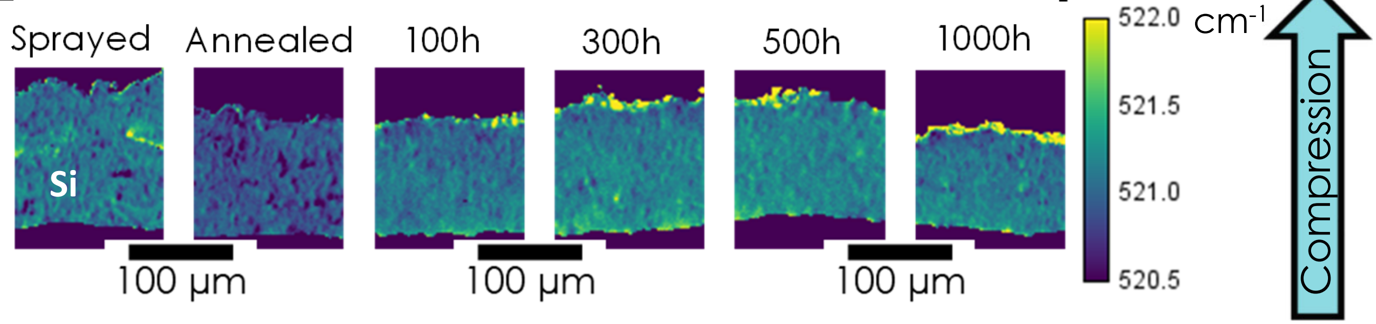
PSLS peak shifts are statistically significant, not Raman



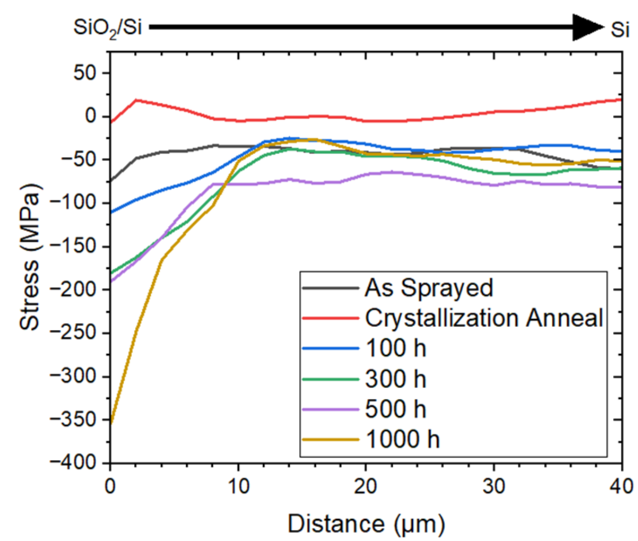
- The low EBC stiffness and cracking between the Si and the EBC prevents stresses from thermal cycling and the SiO_2 phase transformation from being detected.
- The decline in stress in the mullite with exposure time maybe caused by microcracking which reduces the CTE mismatch stress with the $Yb_2Si_2O_7$.
- **PSLS may be used as a stress sensor to predict remaining lifetime of Al-doped EBCs.**

Si peak position shifts from Raman Spectroscopy can be used to quantify critical scale thickness for EBC failure

<u>Room Temperature</u> Si Raman Peak Position Maps, 100h cycling in 90% H_2O / 10% air



- 1350°C, 90% H_2O (g) / 10% air
- -4 cm^{-1}/GPa stress relationship
- Capturing the total residual compressive stress retained from exposure
  - Thermal, *phase change*, growth stress impacts on Si

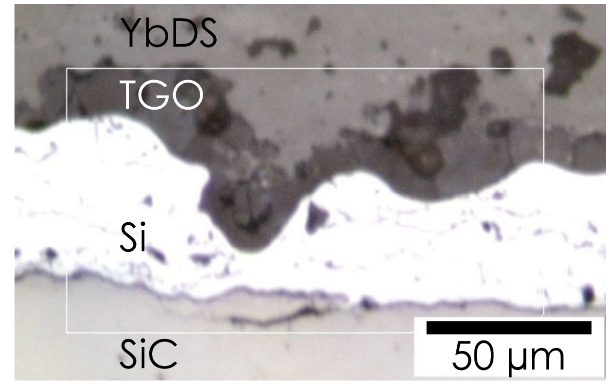


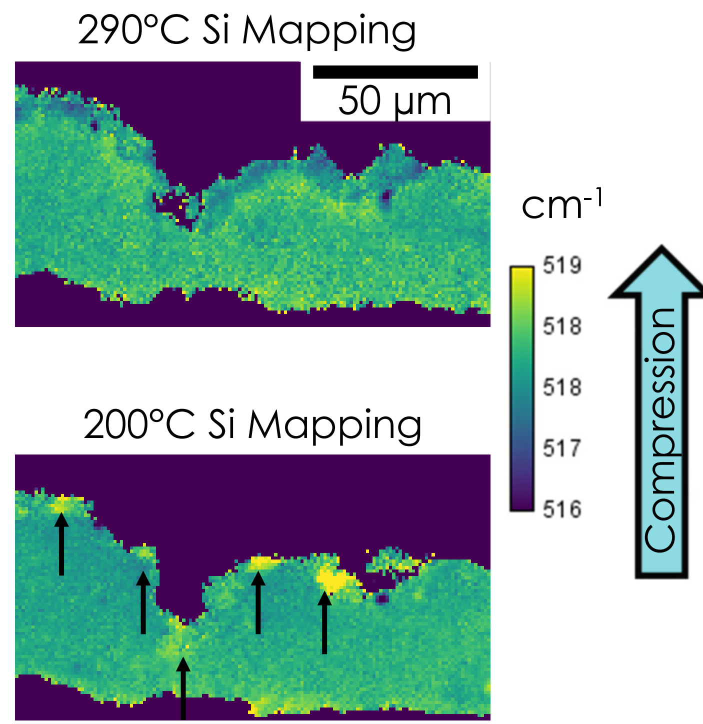
EBCs from: NASA GRC

OAK RIDGE National Laboratory

Stress analysis of Si bond coating after steam thermal cycling: High Temperature Stress Measurements

- Elevated stress was measured only in the first few microns of the Si upon cooling
  - Positive wavenumber shift corresponds to compressive stress in Si from SiO_2 phase change
  - Stress does not extend past splat boundaries in Si bond coating





**Publication in ORNL internal review*

OAK RIDGE National Laboratory

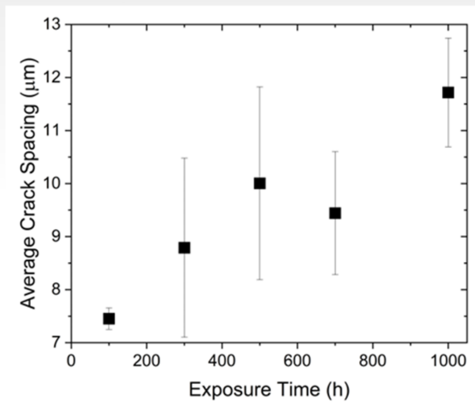
Summary

Industrial Survey

1. Oxidation mechanisms & EBC lifetime modeling
2. Low-temperature oxidation testing
3. Thermal gradient testing needed
4. Pressure effects on oxidation needed

SiO_2 crack density

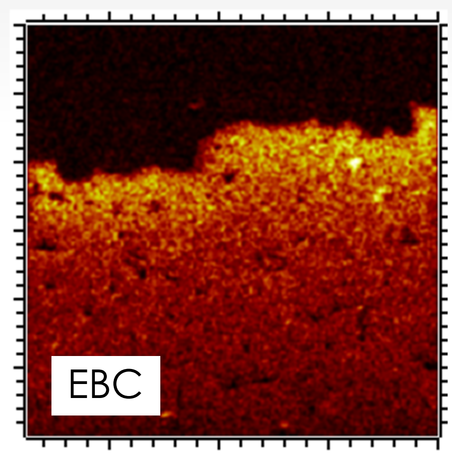
- Crack density decreased with 100 h cycles at 1350°C.



$^{18}O_2$ tracer diffusion

- Decreased bulk $^{18}O_2$ diffusion into EBC, in agreement with oxidation studies.

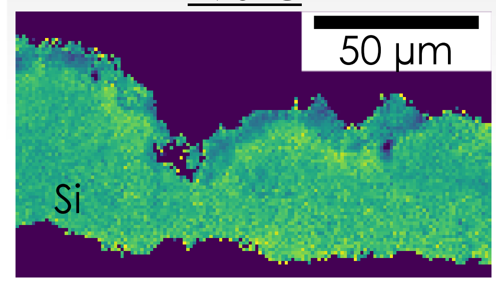
$^{18}O^-$



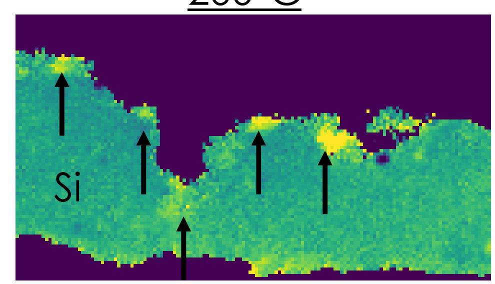
Raman stress in EBC

- SiO_2 transformation stress results in compressive stress in the Si adjacent to the TGO.

290°C



200°C



Thank you!
Any questions?

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