FEAA149: Next Generation Environmental Barrier Coatings

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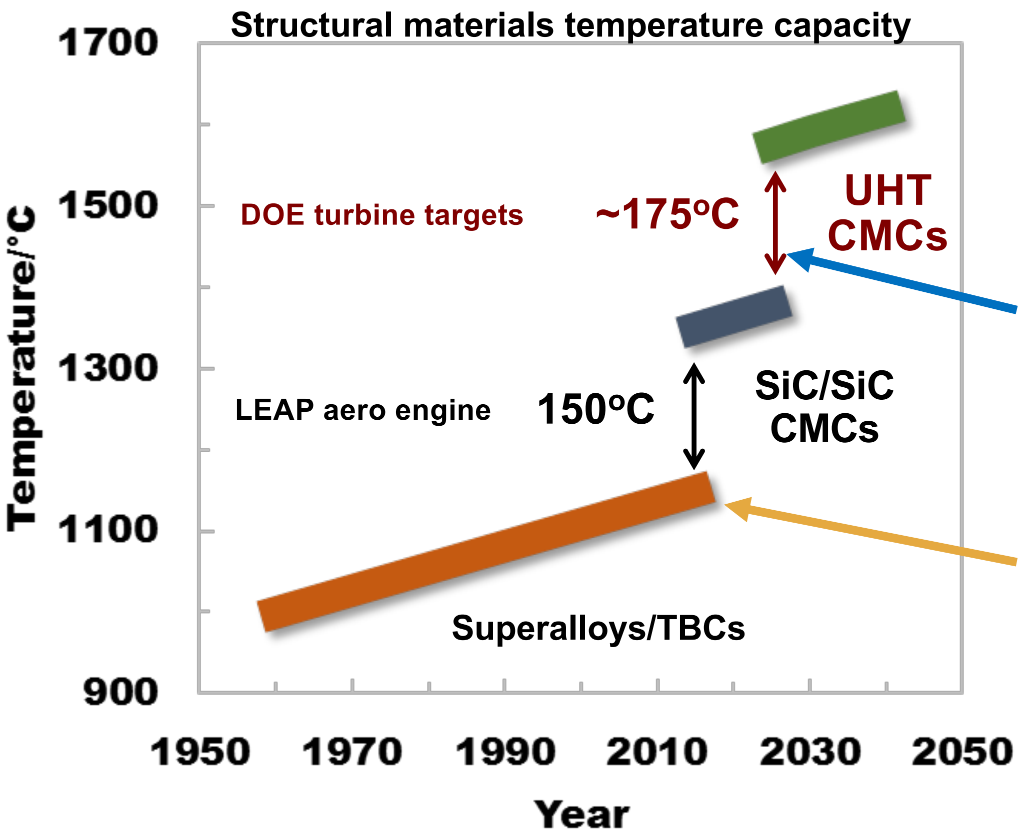
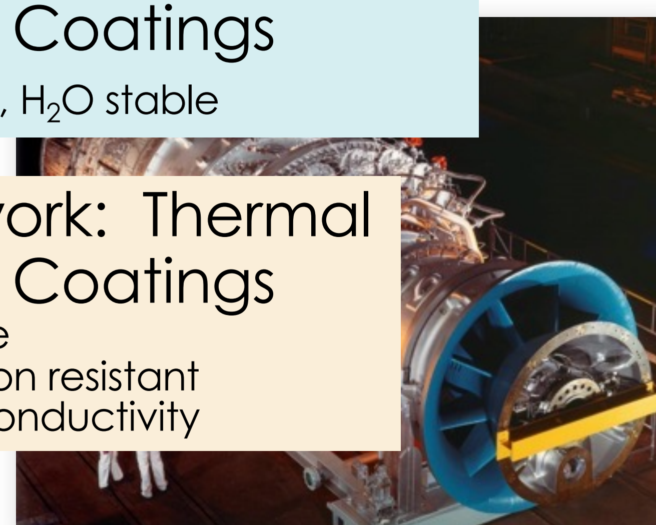
ORNL project exploring the next generation of EBCs to protect SiC/SiC CMCs for IGT duty cycle



CMC = Ceramic Matrix Composite, UHT = ultra high temperature

DOE Impact: Next generation, ultra high efficiency, utility turbines may require ~1500°C structural materials capability AND 25,000 h lifetime (~10X increase vs. aero applications)



Now: Environmental Barrier Coatings

- durable, H_2O stable

Prior work: Thermal Barrier Coatings

- durable
- oxidation resistant
- low T conductivity

Past, Present & Future: ORNL Contributions to CMCs

Malden Mills CMC liner for CHP (1999)
- -Solar Turbines
- -ORNL
- -Pratt & Whitney
- -BF Goodrich
- -Honeywell
- -ANL

After CFCC, GE invested 15 yr & ~$1.5B in CMCs

Gen-1: Si-MI SiC matrices

SiC/SiC to engine market >25 yr

CVI matrices → Gen-2

Si-free SiC/SiC

New ceramics → UHT

Beyond SiC

ORNL future

CFCC begins

CFCC ends

2016 LEAP engine

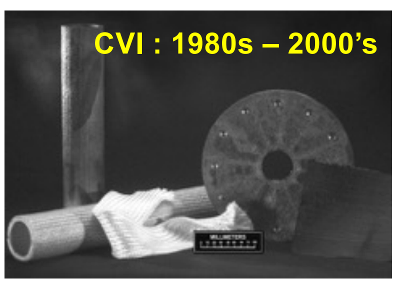
1960 | 1970 | 1980 | 1990 | BAP arrives | 2000 | 2010 | 2020 | 2030

ORNL: Vapor coating of ceramic fuel particles

ORNL Developed forced-flow, thermal-gradient, Chemical Vapor Infiltration (CVI) process

(1992-2002) DOE Continuous Fiber Ceramic Composite (CFCC) Program led by ORNL in close collaboration w/ industry (e.g., GE).
- Advanced CVI
- Interfaces & coatings
- Characterization
- Oxidation testing

ORNL Recent: SiC/SiC for accident tolerant nuclear fuels, CVD ZrC for Space Power.

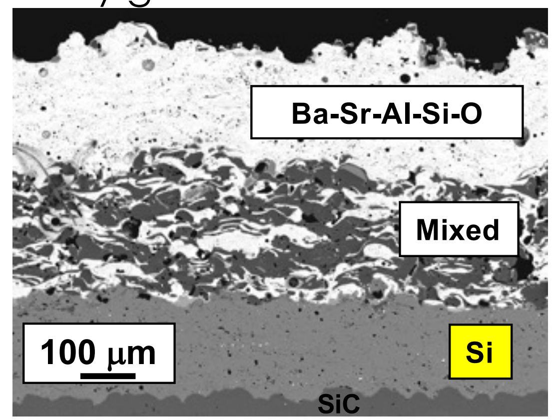


(1994-2001) DOE Advanced Turbine Systems (ATS) Program transferred aero-engine technology to power generation
- Thermal barrier coatings
- Single crystal superalloys

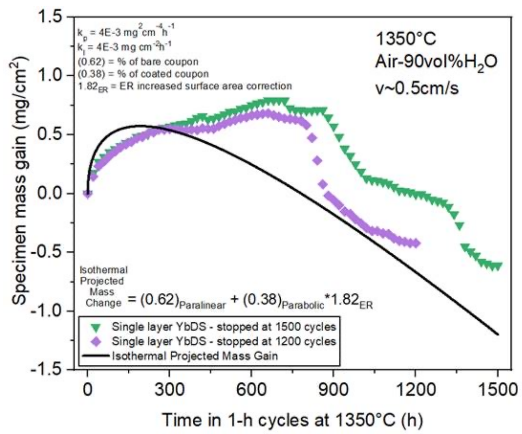
Maintained project structure since starting EBC work in 2018

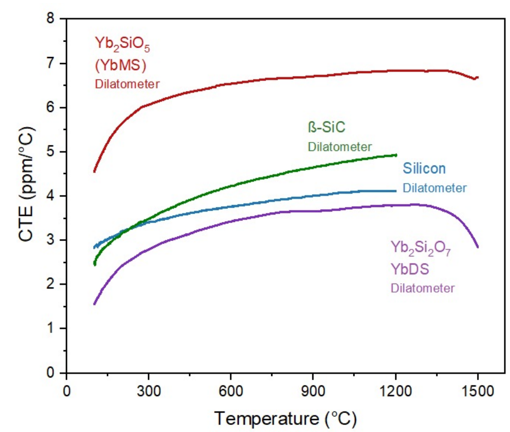
- Parameters
  - Coat high-purity CVD SiC (CMCs hard to find)
  - Experiments in 90-100% H_2O at 1250°-1450°C
  - Coatings made at Stony Brook Univ. CTSR
    - **With and without Si bond coating (T_m = 1414°C)**

Early generation EBC:



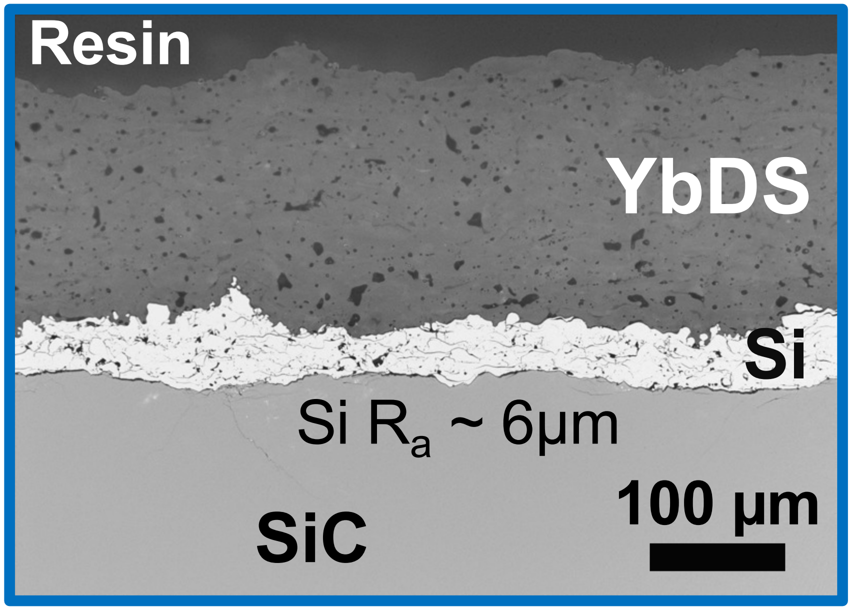
- Objective
  - **Develop a lifetime model for CMCs in land-based turbines**
    - Failure criteria
      - Cyclic testing in air+H_2O
    - Physical properties
      - Thermal expansion
      - Thermal conductivity
      - Mechanical properties
    - Microstructure analysis





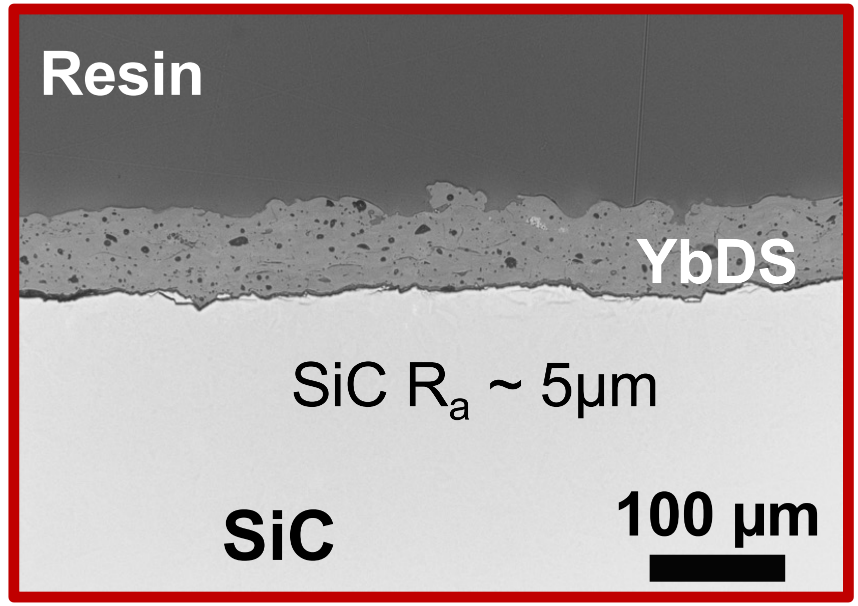
Current EBC limited by Si melting point ~1410°C; How does EBC perform without Si bond coating?

YbDS: $Yb_2Si_2O_7$



Current "commercial" EBC

Single layer YbDS
No Si bond coating

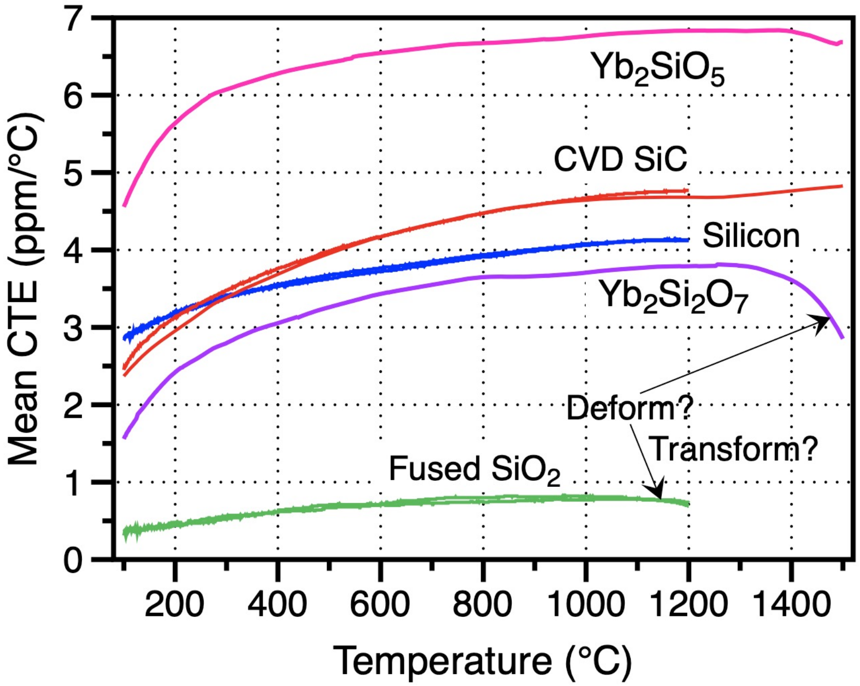


Next generation EBC
(thinner YbDS: adhesion issue)

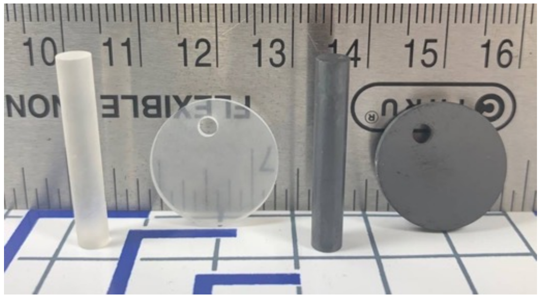
Year 2 milestones complete: built on Year 1 milestones

- Task 1. Define Reaction Kinetics and Failure Criteria
  - Milestone #1: measure oxidation kinetics at 3 temps. ±Si bond coating
  - Milestone #4: complete at least 1,500 cycles at 1350°C (complete)
    - Hoping to achieve failure ±SI bond coating to develop EBC failure criteria
    - Is there a critical SiO_2 thickness at failure?
- Task 2. Measure thermal expansion coefficients
  - Milestone #2: measure CTE of 2+ EBC components
  - Milestone #5: measure CTE of 2+ EBC ceramic components (complete)
    - Task complete with full set of CTE data to ~1500°C for model (new ORNL dilatometer)
- Task 3. Advanced Characterization and Modeling
  - Milestone #3: initial estimate of critical temperature for 25,000 h lifetime
  - Milestone #6: refine lifetime predictions using Task 1 and Task 2 input
    - Idealized "best case" scenario in completed 2nd iteration

Task 2 milestone: 1500°C CTE measured for model



SiO_2 and SiC specimens:



Made $Yb_2Si_2O_7$ and Yb_2SiO_5 samples in collaboration with UVa (Opila's group)

Task complete

Thermal (cooling) stress: $\sigma_{ox} = - E_{ox} \bullet \Delta T \bullet (\alpha_{alloy} - \alpha_{oxide})/(1-\upsilon)$

Strain Energy: $W = f(\delta_{oxide})$: $\delta_{spall} = f(\Delta T \bullet \Delta\alpha)^{-2}$ (critical scale thickness for spallation)

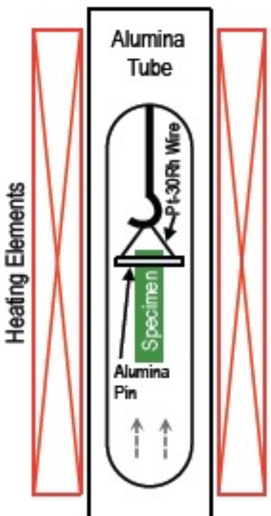
Year 3 (FY21-22) milestones to continue this progression

- **Improving on current EBC performance at ≥1350°C**
  - Milestone #7: Compare the cyclic oxidation performance in air-90%H_2O of two EBC-coated SiC substrate roughnesses at two temperatures including the effect on the scale growth rate
    - ORNL filed provisional patent on surface roughening strategy in 2020
- **Need to be industry relevant**
  - Milestone #8: Compare the silica growth rate and cyclic oxidation durability of Yb disilicate and mixed Y-Yb disilicate EBC coatings on SiC substrates with and without a Si bond coating
    - Y-Yb is less expensive industry standard EBC
- **Advanced characterization is key to progress**
  - Milestone #9: Submit a journal publication on the use of Raman spectroscopy to study the evolution of the phase composition of the EBC and the thermally grown silica scale at multiple temperatures

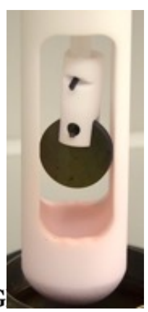
Exposures to H_2O in several rigs at 1300°-1425°C

Nuclear Severe Accident Test Station

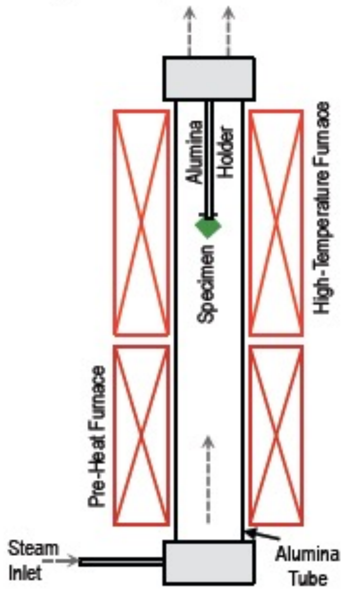
Rubotherm TGA



1500°C maximum



High Temperature Furnace



1700°C maximum

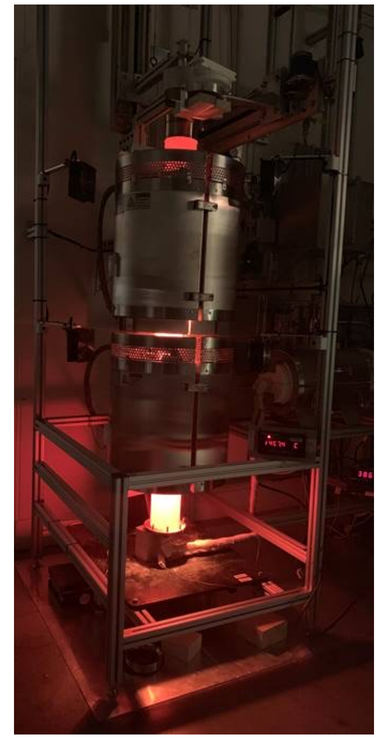
1-h cycles: automated cyclic rigs

Air + 90%H_2O, 10 min cool in lab. air

lid

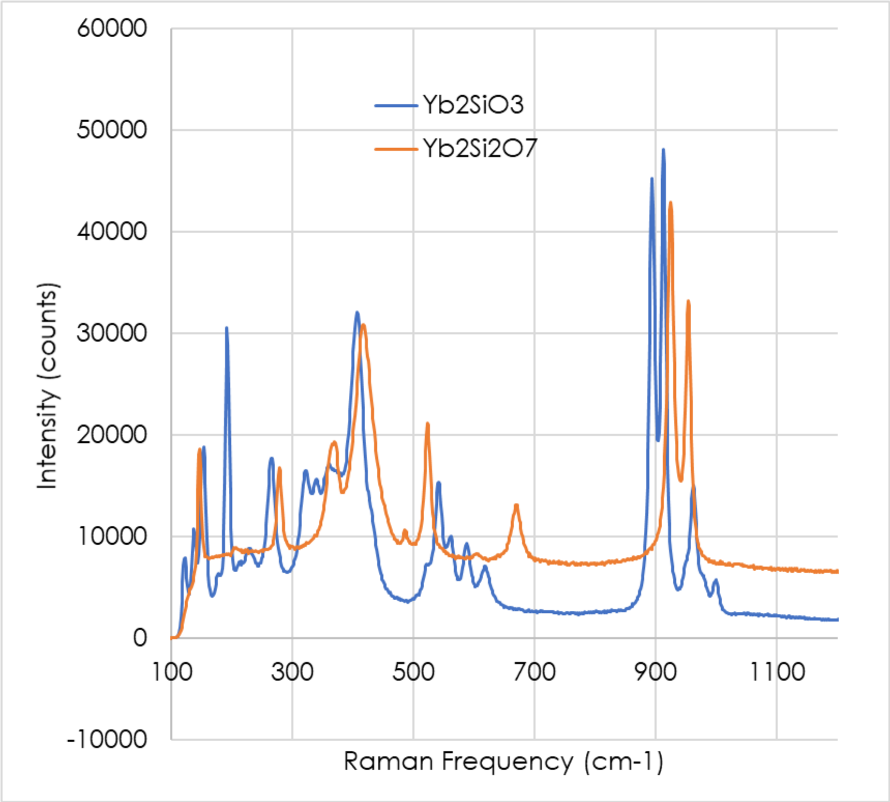
furnace

Current: maximum 1350°C



New rig: >1400°C

Task 3: Advanced characterization
Yb mono- and di-silicates have unique Raman spectra



Year 3 Milestone #9: Educating community about new Raman technique that can detect silicate and SiO_2 phases

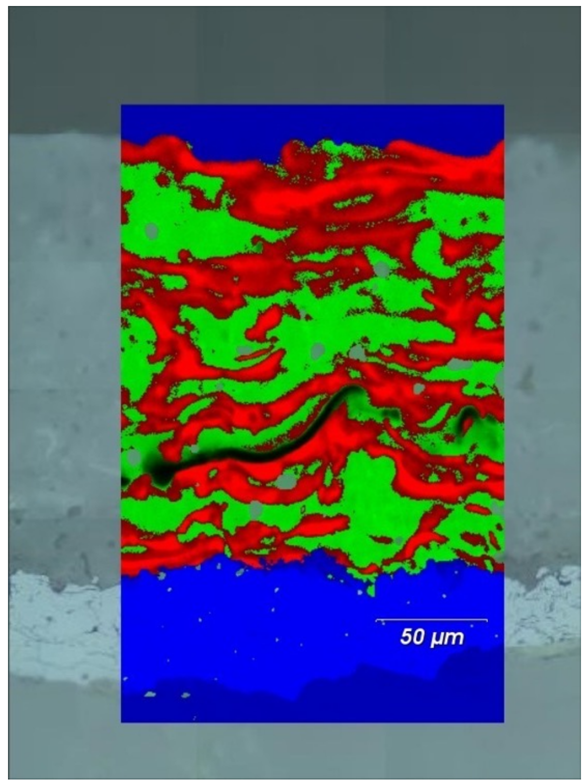
- New ORNL capability
  - Maps not point analysis
- Potential to detect amorphous/crystalline in thermally grown SiO_2 scale

Air Plasma Sprayed $Yb_2Si_2O_7$ top coating

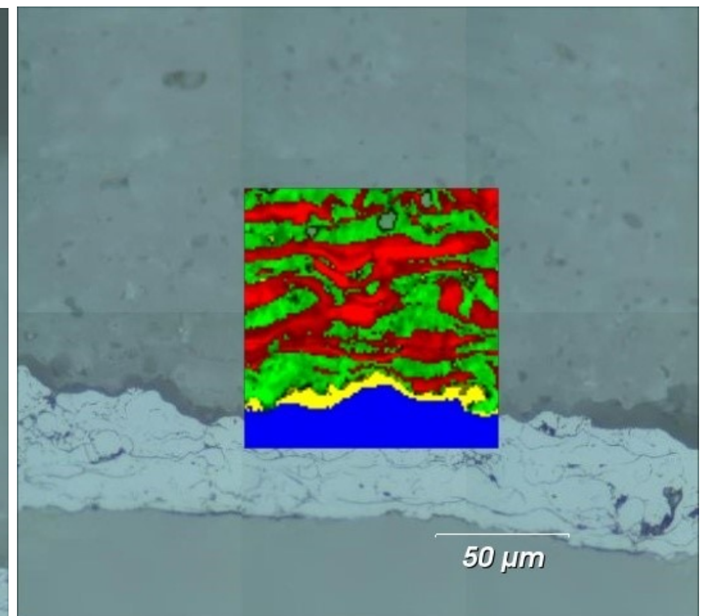
Air Plasma Sprayed Si bond coating

CVD SiC substrate

- As-annealed coating
- No SiO_2 observed
- Black: amorphous YbSiO



- 500 1-h cycles 1250°C
- No amorphous phase



Red = Yb_2SiO_5
Green = $Yb_2Si_2O_7$
Yellow = Cristobalite
Blue = Silicon

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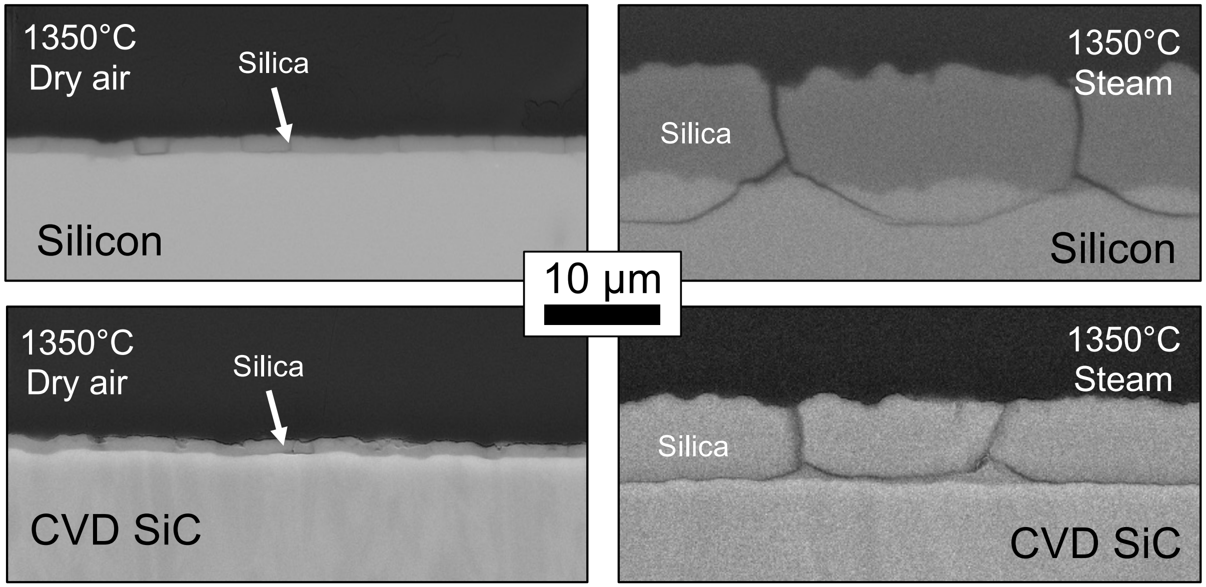
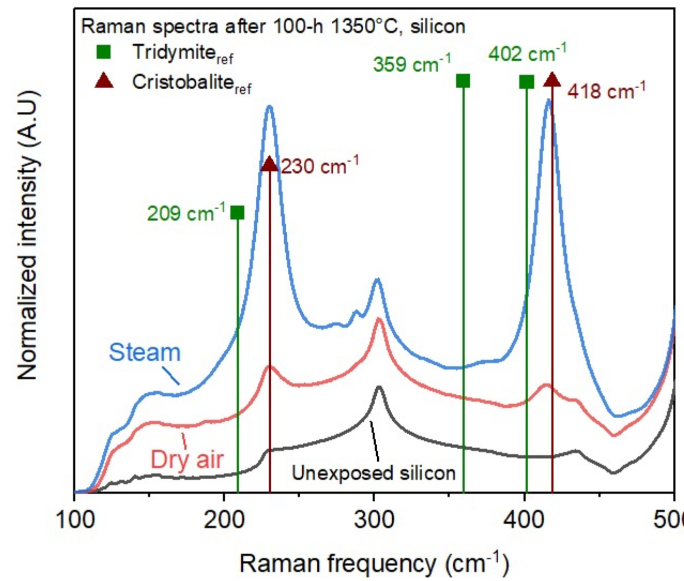
Raman shows cristobalite forms in all cases at 1350°C





- Tridymite formation (not observed) suggests contamination in system

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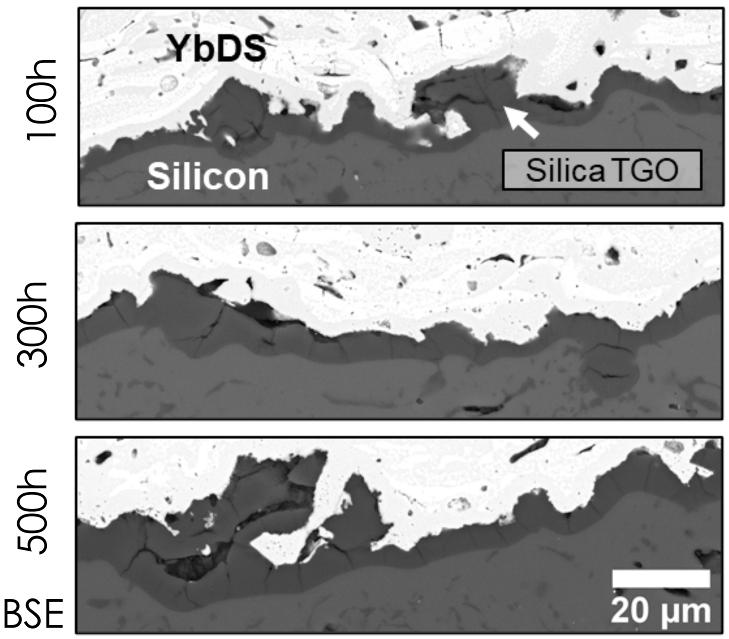
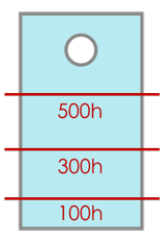
Task 3: Methodology+software developed to measure kinetics

1350°C FCT in 90/10 H_2O/air

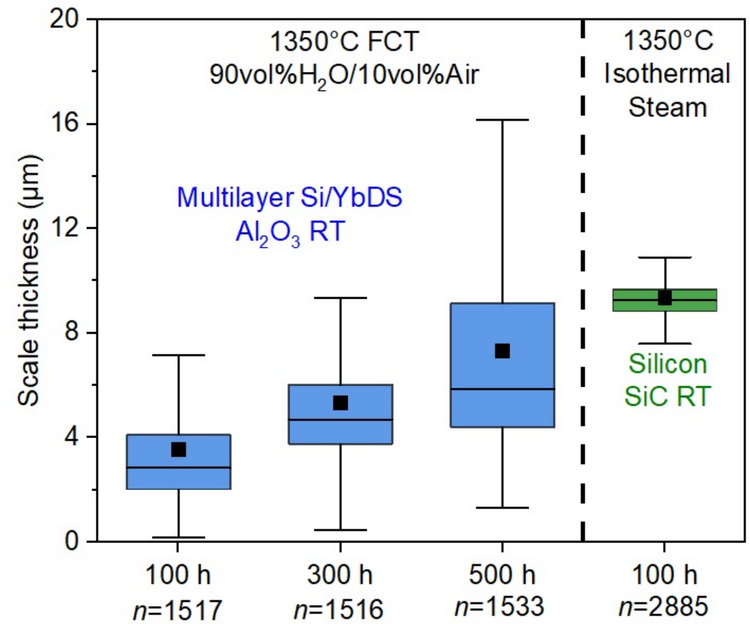




Non-uniform TGO in multilayer EBC

1. Undulating interface
2. APS Si microstructure defects

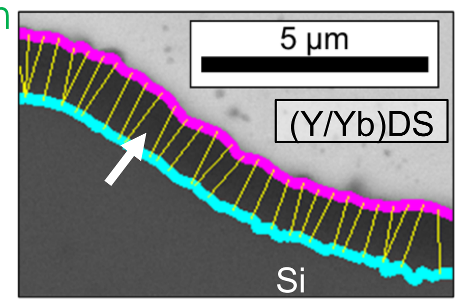
EBC: median better, distribution not normal



~900 µm span

~1800 µm span

Based on 1500-3000 automated measurements:



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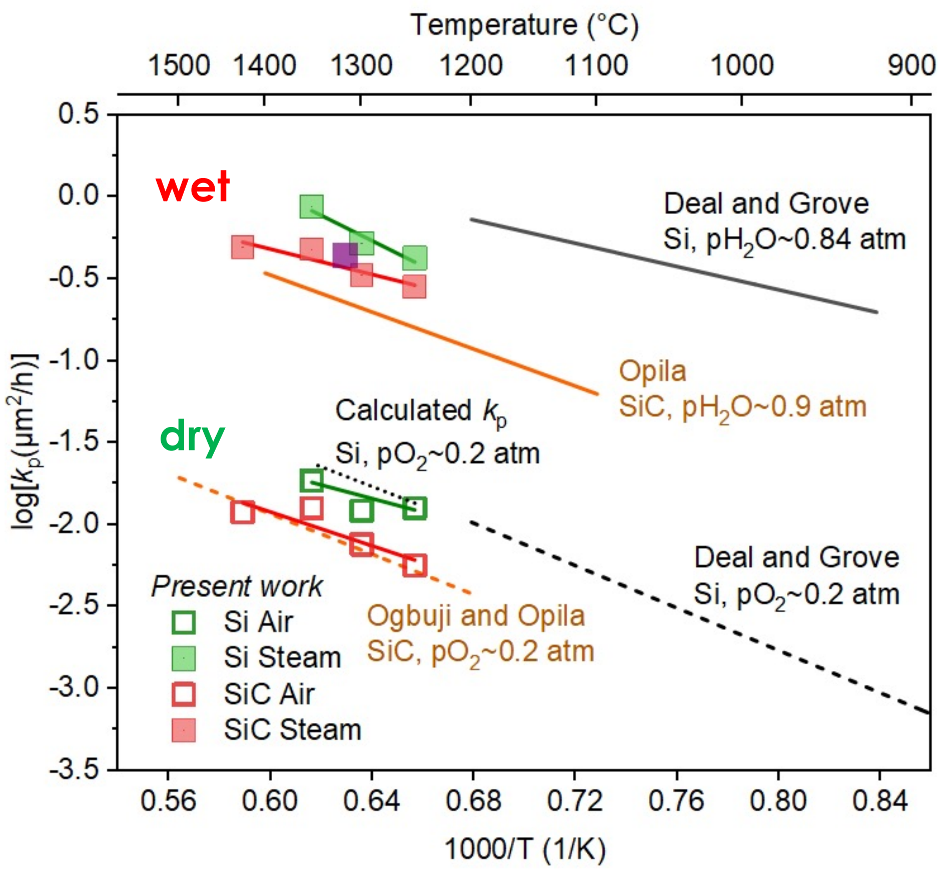
Task 1 Key accomplishments: established oxidation baseline

- Utilized SiC reaction tube to mitigate specimen volatilization

- Bare coupon steam rate
  = Max. possible oxidation rate
- Bare coupon air rate
  = Min. possible oxidation rate

- Baseline kinetics allow qualitative evaluation of EBC effectiveness in reducing H_2O ingress



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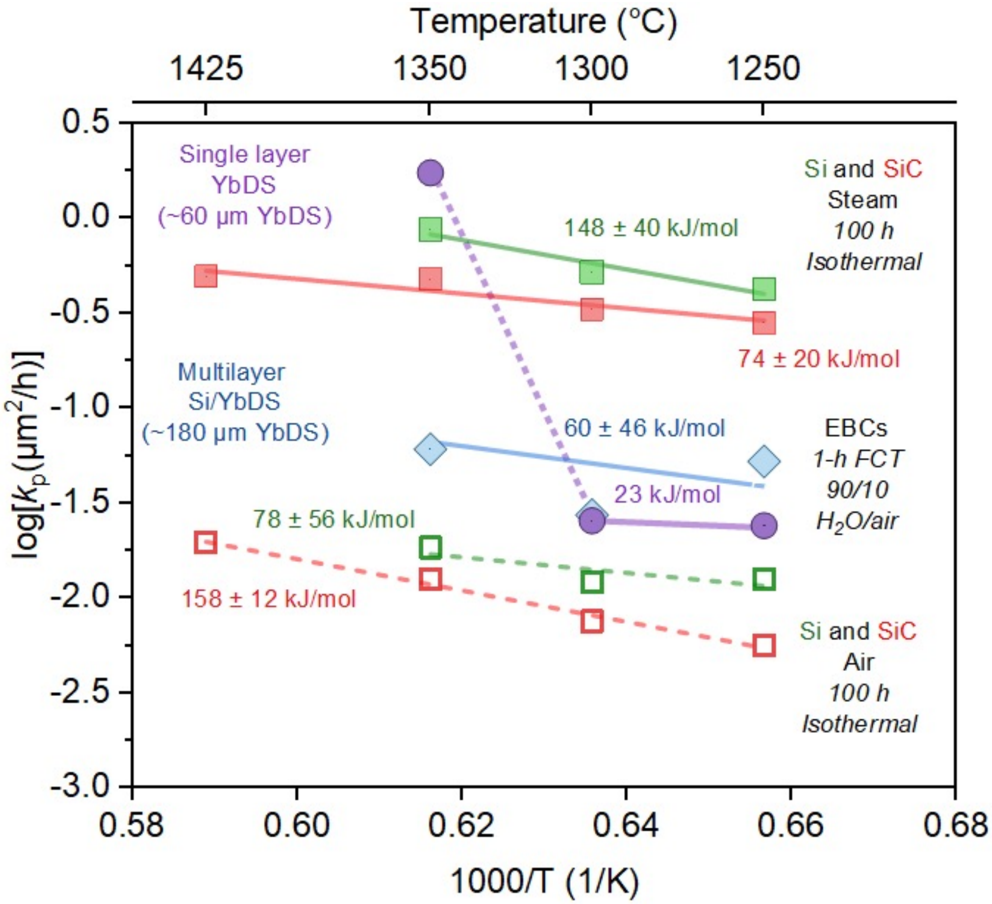
Methodology for assessing EBC performance

- All based on measured SiO_2 growth rate
- Based on Harder (NASA)

- Si and SiC in steam
  - No EBC protection

- EBC behavior

- Si and SiC in air
  - No H_2O acceleration



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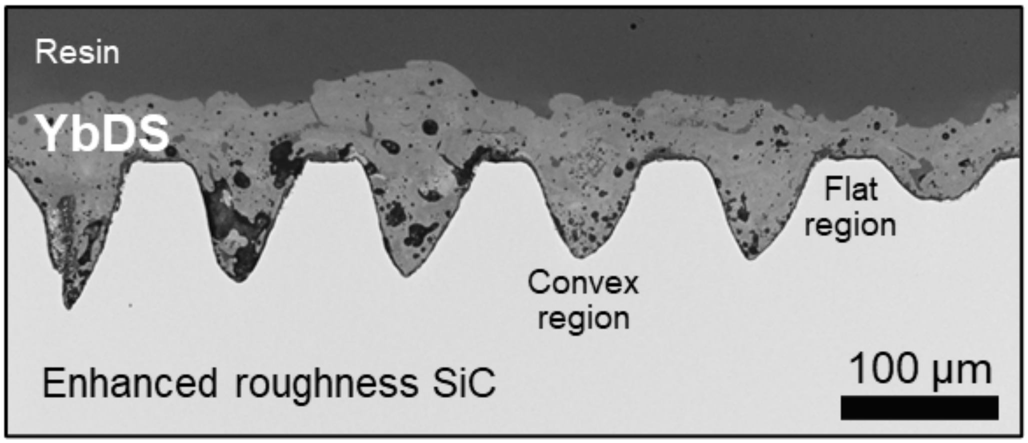
Enhancing SiC roughness improves coating adhesion without Si bond coating

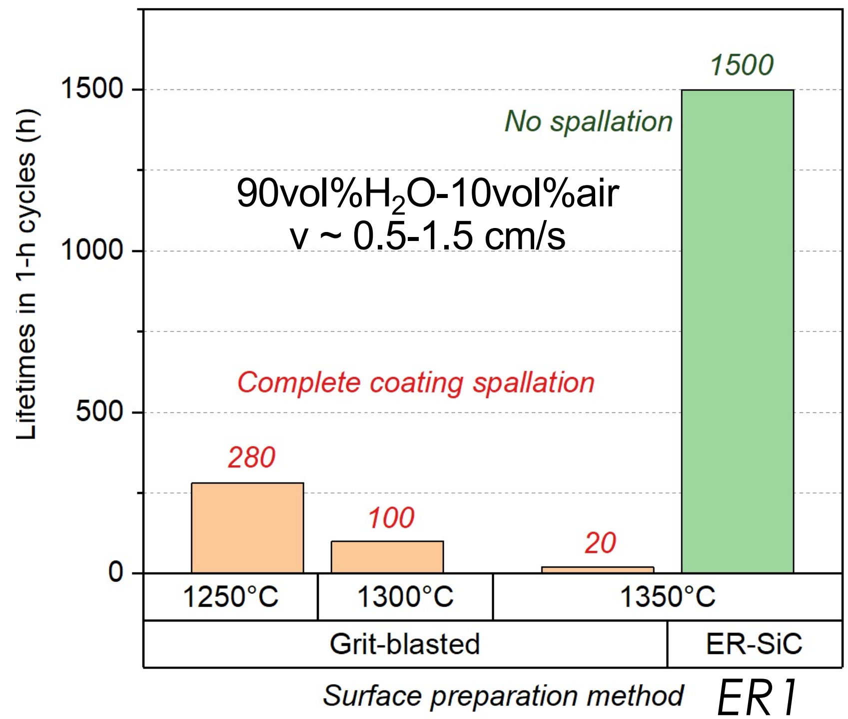
YbDS deposited onto ER1-SiC, "as-received" condition

LOM



- YbDS thickness kept consistent with grit blasted specimens
- Nominal ~60 µm YbDS thickness
- **2020: submitted provisional patent**

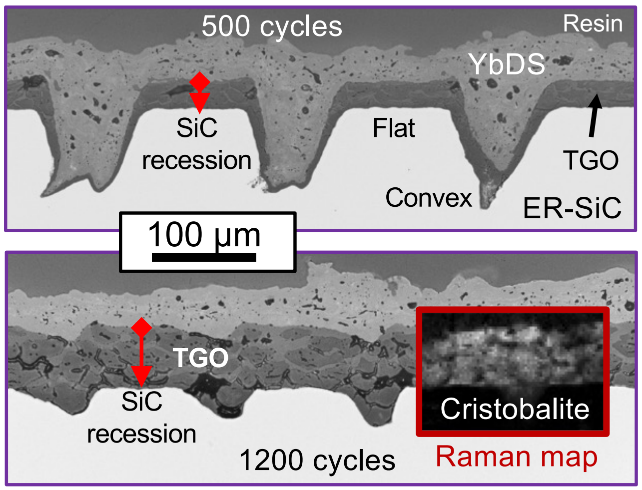
Lifetimes of ~60µm YbDS



ER1

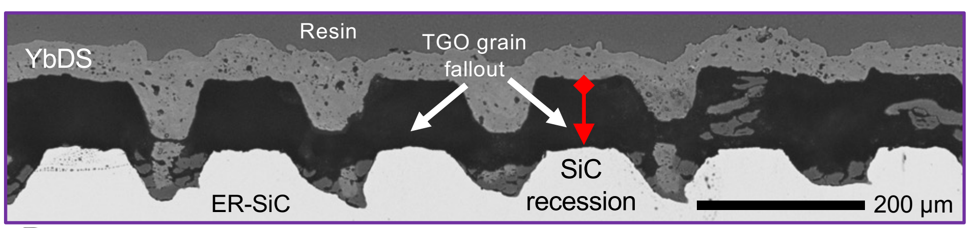
- FCT lifetime increased at 1350°C

>500 1-h cycles at 1350°C: transition to faster growth

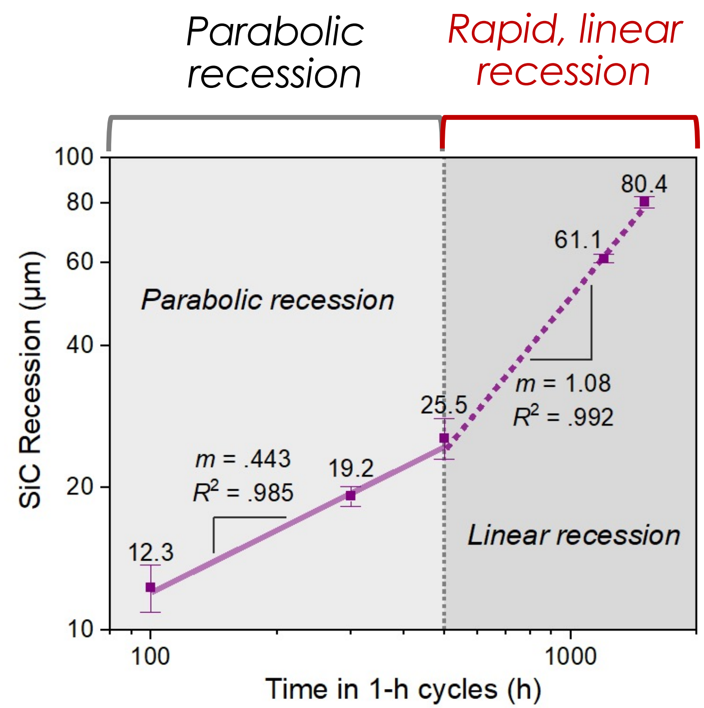


- Visibility of convex regions heavily dep. on polishing angle
- Measuring "SiC recession" at flat regions more objective
- Scales fully cristobalite
  - ß- to α-phase at ~270°C with 5vol% reduction ~10^1-10^2 GPa

- At 1500 1-h cycles, incomplete resin infiltration, TGO grain fall out during polishing; can still measure SiC recession



YbDS – 1500 cycles

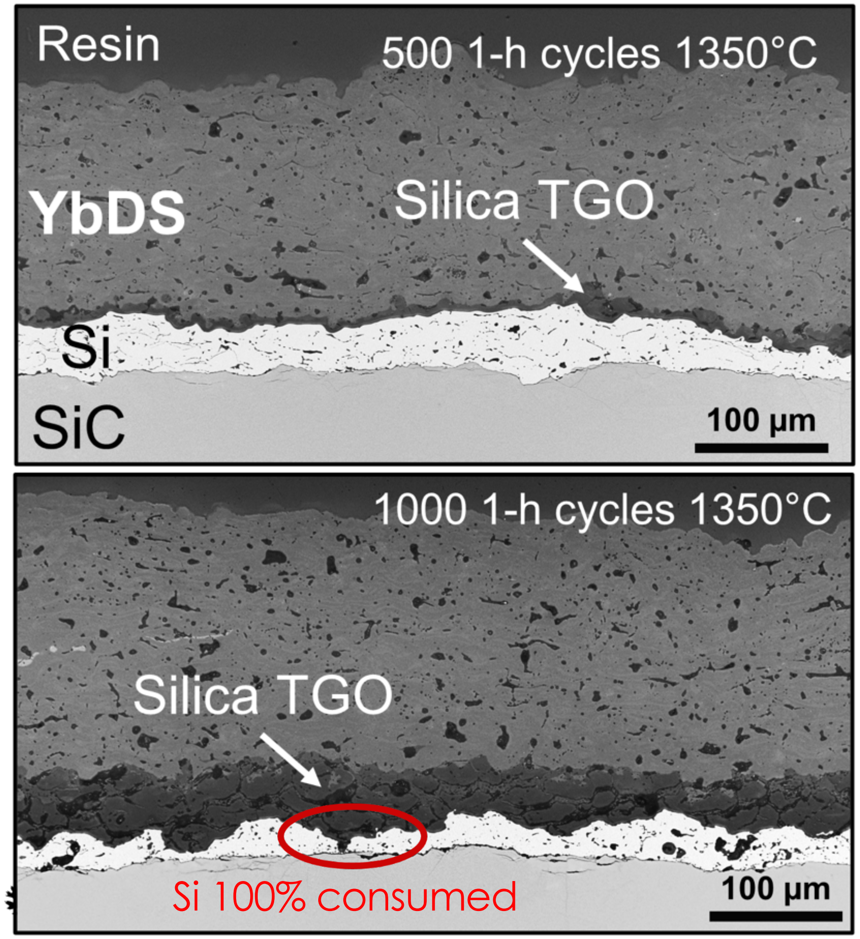


Log-Log plot can reveal kinetic transitions

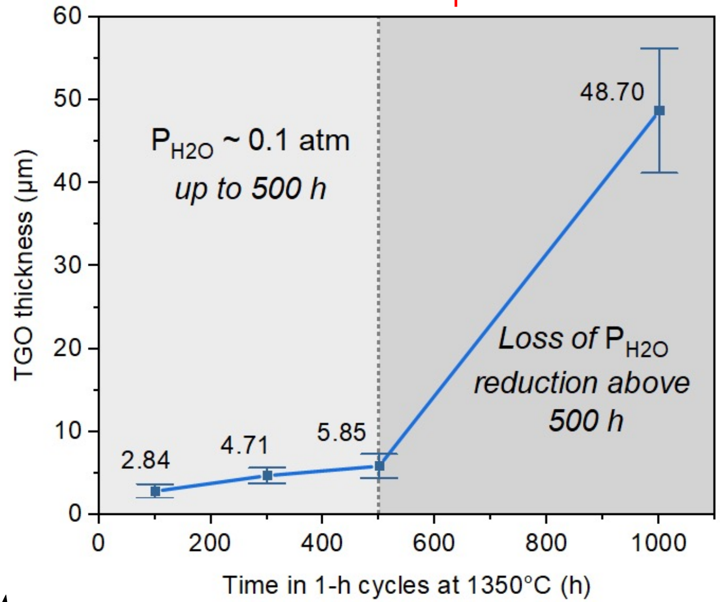
$$x^n = kt$$

Similar acceleration with a Si bond coating: edge failure?

BSE



Rapid increase:



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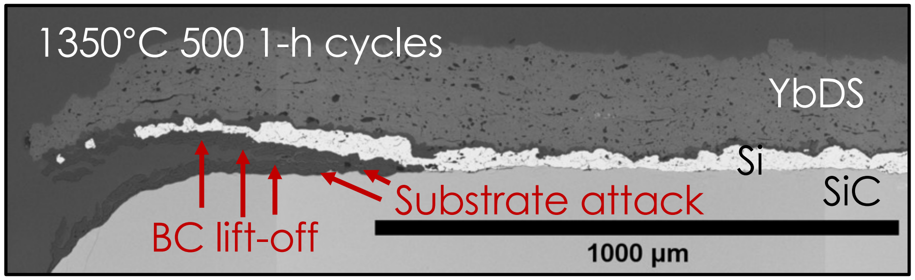
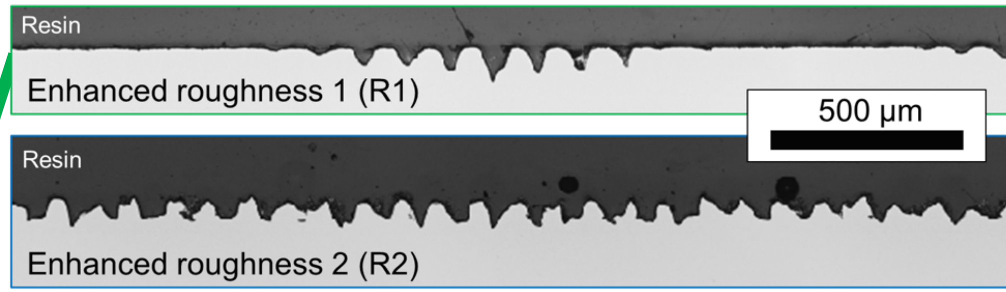
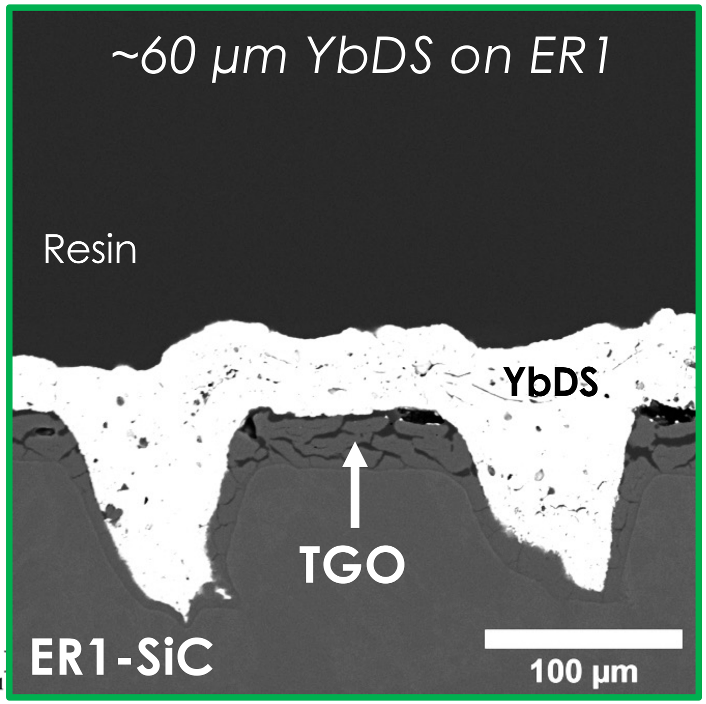


Year 3 Milestone #7: compare 2 roughness levels Initial result at 1350°C: 2^{nd} ER iteration not as promising

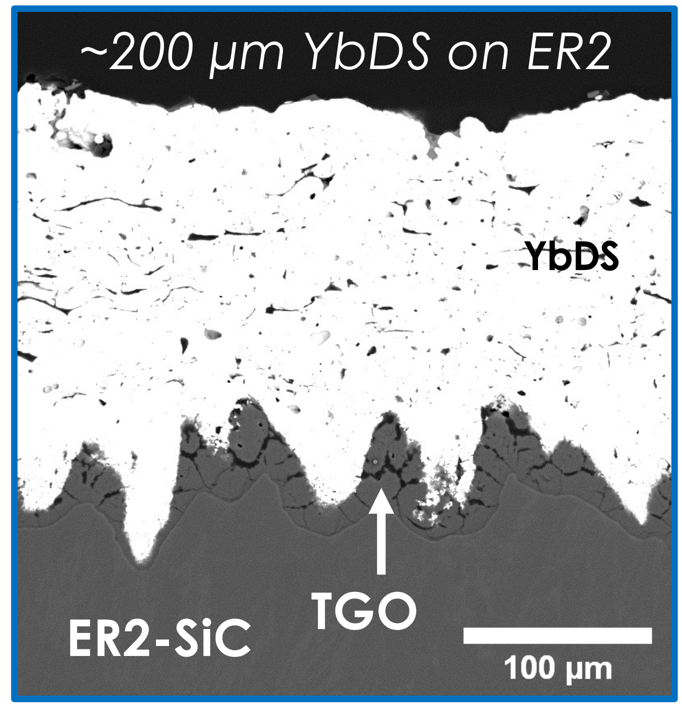


At increased roughness and ~200µm YbDS, TGO still thick and cracked

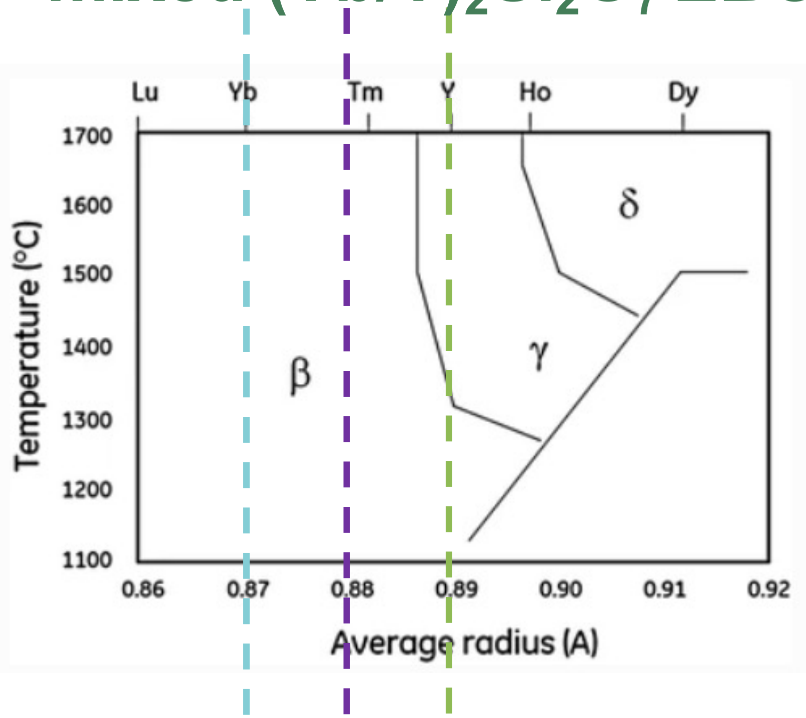


1350°C
1-h FCT
90%H_2O
500 h

B&C adjusted for TGO visibility



Year 3 Milestone #8: compare YbDS to commercial mixed $(Yb/Y)_2Si_2O_7$ EBCs



$3.4/kg Y_2O_3
$16.4/kg Yb_2O_3

https://en.institut-seltene-erden.de/aktuelle-preise-von-seltenen-erden/

$Yb_2Si_2O_7$		$Y_2Si_2O_7$		$(Yb/Y)_2Si_2O_7$
↑ Cost	+	↓ Low cost	=	↓ Lower cost
✓ Single Phase		× Multi phase		✓ Single Phase
✓ Low CTE		× High CTE		✓ "medium" CTE
↓ Volatility		↑ Volatility		↑ Volatilization
↓ CMAS Resist.		↑ CMAS Resist.		↑ CMAS

Is mixed REDS EBC phase stable through thermal cycling?

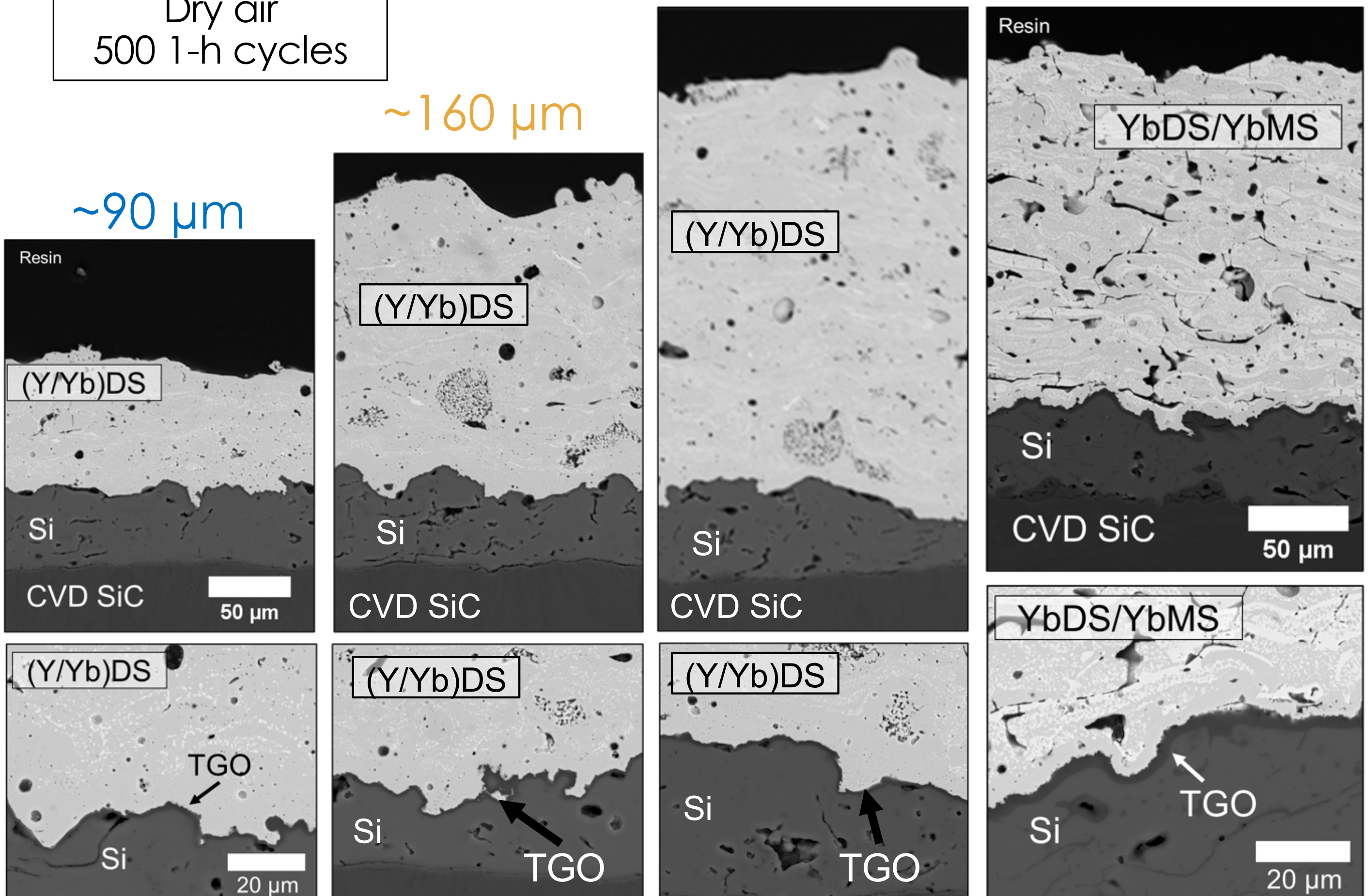
Does increased CTE of mixed REDS lead to premature spallation compared to YbDS?

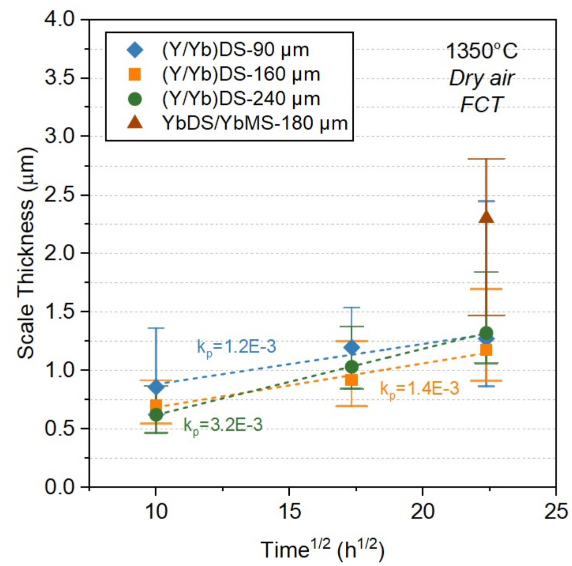
Does EBC composition or thickness influence TGO kinetics?

1350°C air: EBC thickness did not impact scale growth rate

1350°C
Dry air
500 1-h cycles

~90 µm ~160 µm ~240 µm ~200 µm Yb only





- All mixed (Y/Yb)DS EBCs form thinner scales than YbDS/YbMS EBC

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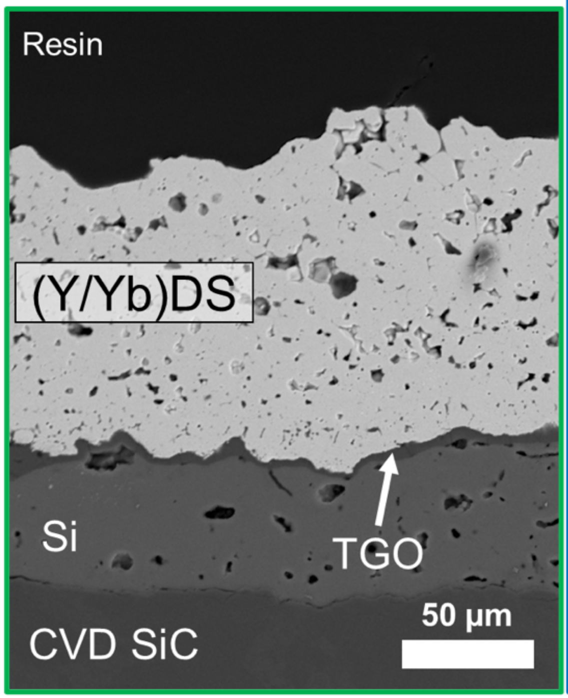
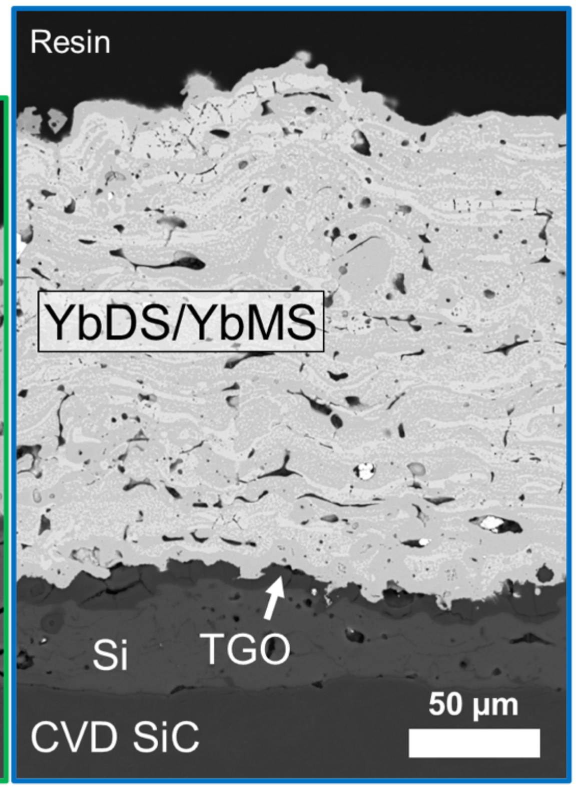
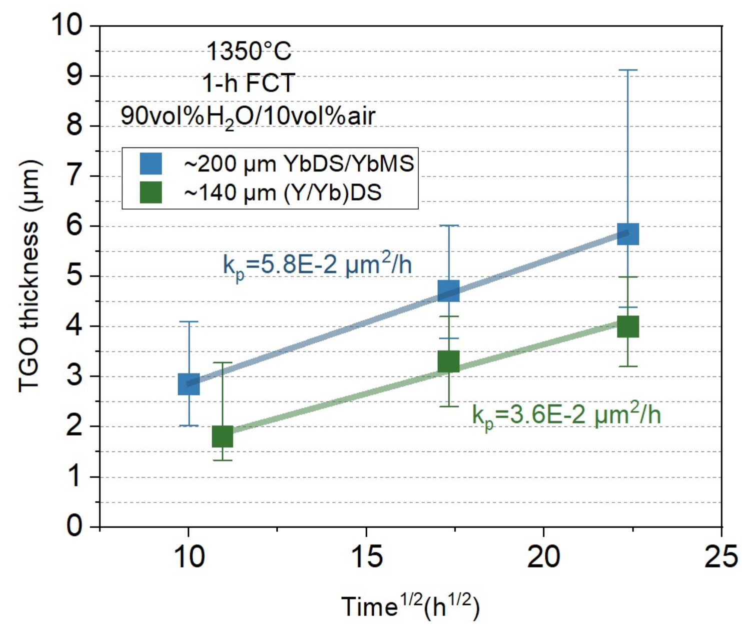
1350°C 90%H_2O: silica growth slower on (Y/Yb)DS

1350°C
90vol%H_2)/10vol%air
500 1-h cycles







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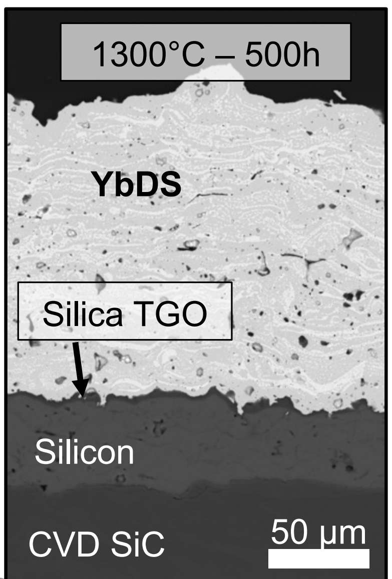
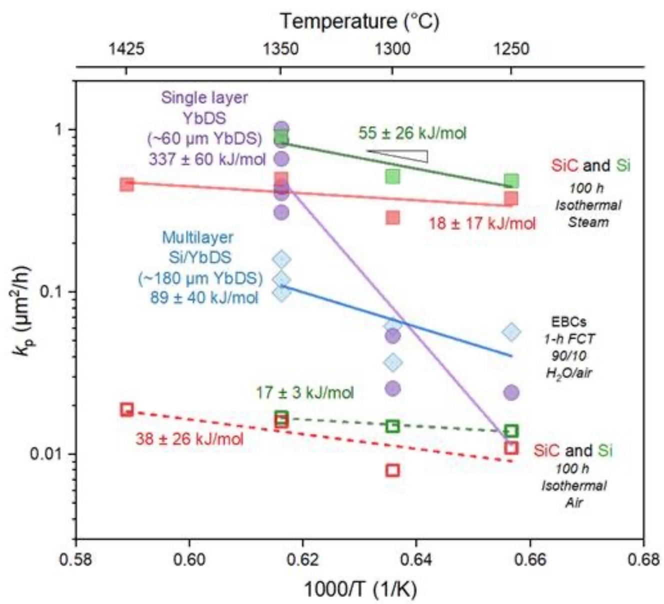
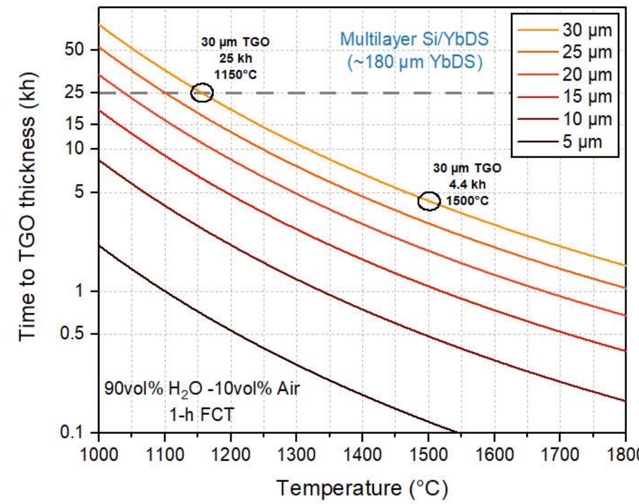
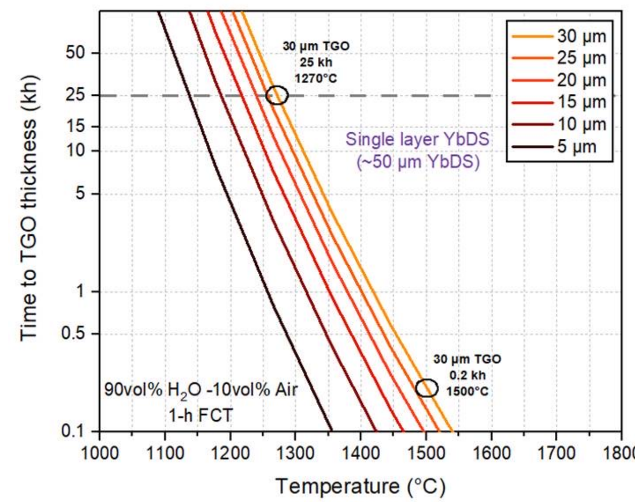
Task 3 model: 1st iteration suggested 25 kh life is challenging

- Based on measured reaction kinetics
  - With and without Si bond coating
- Assume a critical SiO_2 thickness
  - Thermally grown oxide under silicate layer
  - Effective EBC will reduce kinetics (inhibit H_2O)



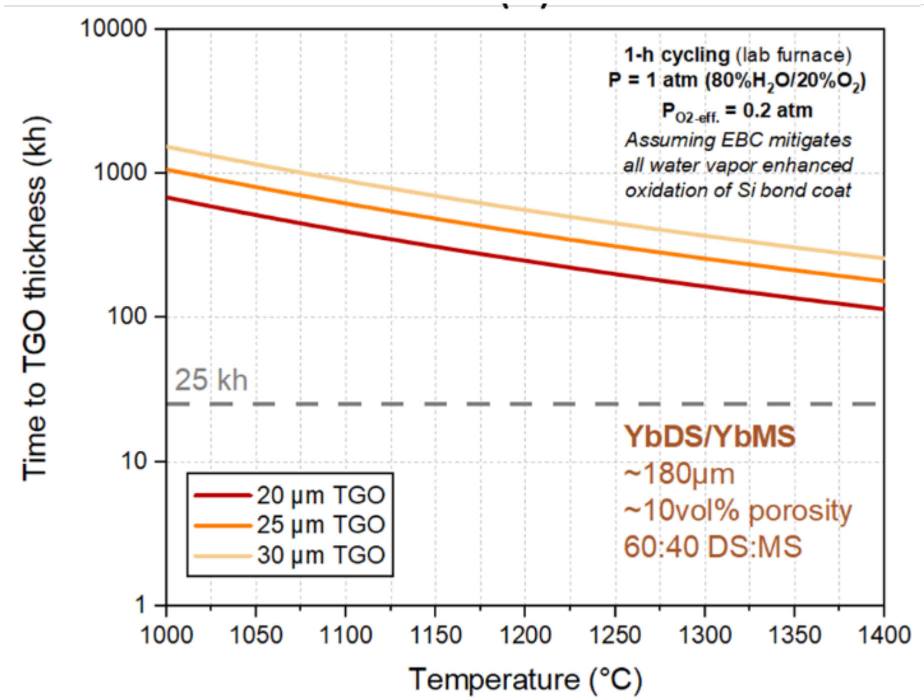




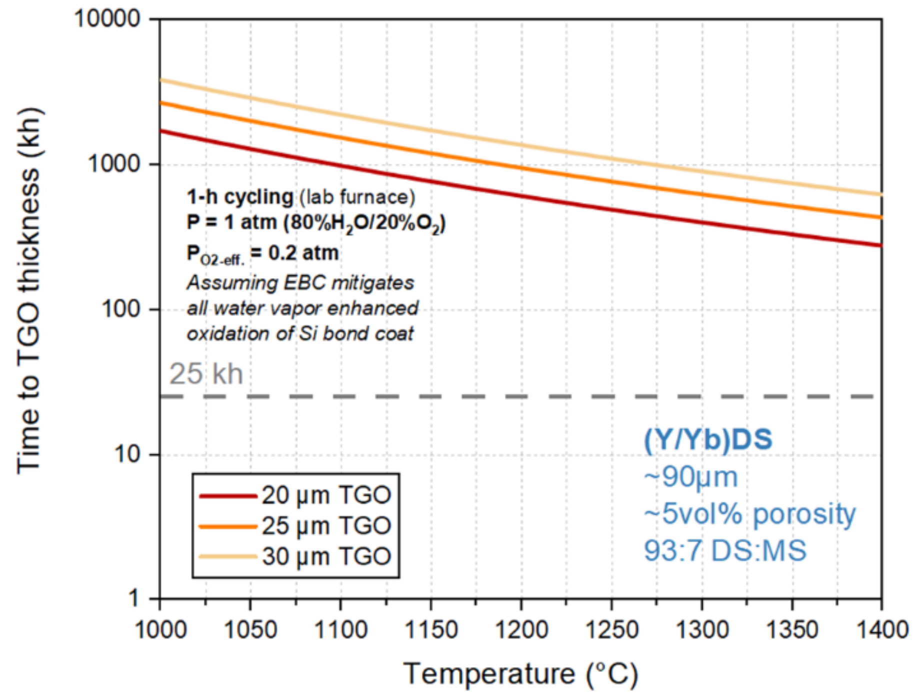


2^{nd} model iteration: "best case" scenario EBC stops all H_2O effects (using rates from test in dry air)

YbDS/YbMS with Si bond coating



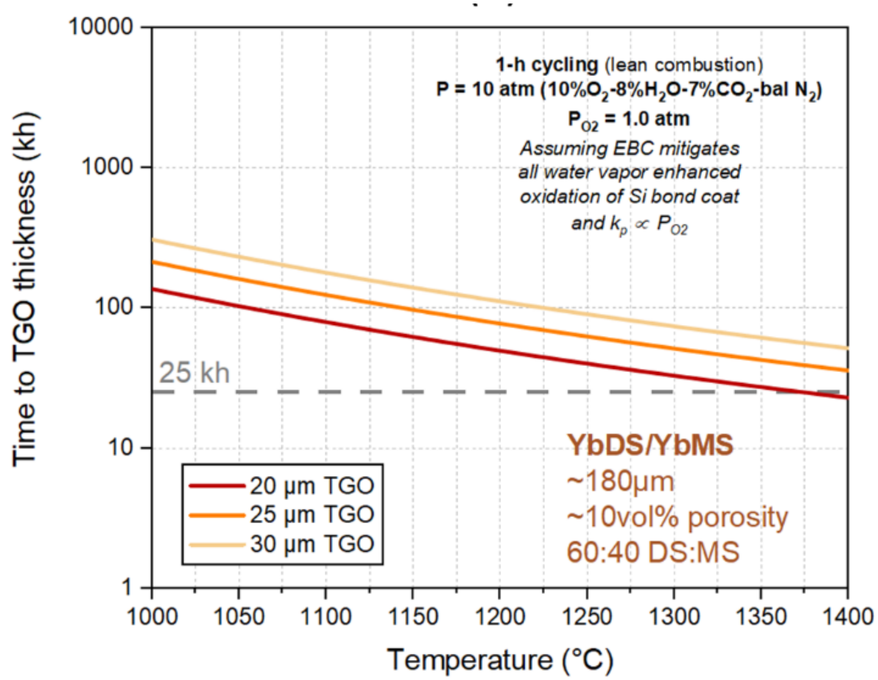
(Y/Yb)DS with Si bond coating



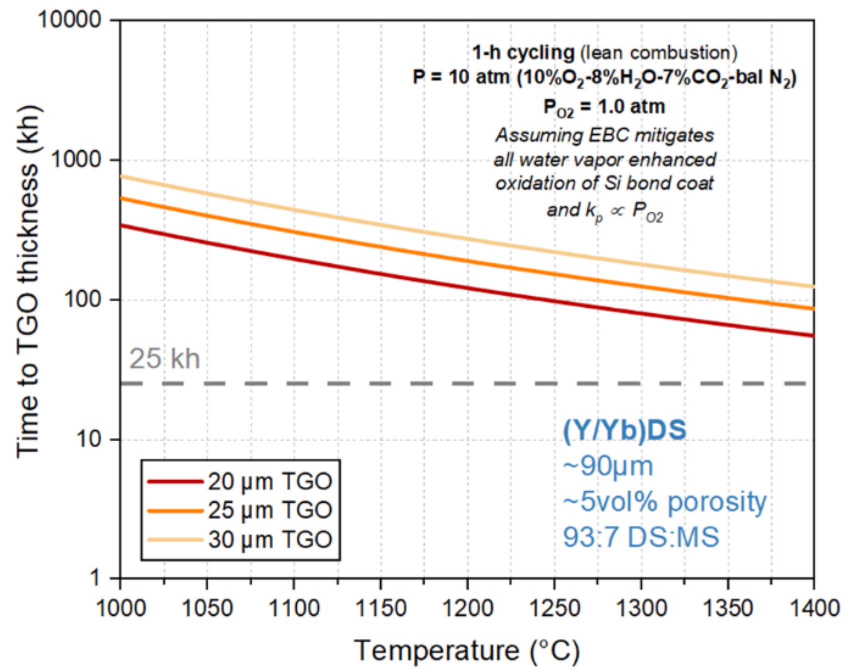
Unlike TBC, H_2O effect accelerating SiO_2 growth has a major effect on predicted life

2nd model iteration: rates recalculated for 10 atm combustion gas

YbDS/YbMS with Si bond coating



(Y/Yb)DS with Si bond coating



Still assuming EBC prevents H_2O effect for entire lifetime

Major accomplishments and more great things to come

- Accomplishments
  - Measured CTE values to 1500°C for model
  - Established framework for assessing EBC performance
  - Established procedure for measuring EBC reaction kinetics
    - New image analysis tool developed to measure TGO
  - 2nd iteration of EBC lifetime model complete (w/o Si bond coating)
- Year 3 milestones will continue progress on next generation EBCs for >1400°C operation
- Developing partnerships
  - NASA Glenn
    - Modifications to reduce scale growth, joint fabrication of specimens/testing
  - Industry
    - Commercial sprayed Yb/Y silicate EBCs for testing at ORNL

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.
- 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**, in press. https://doi.org/10.1111/jace.18093
- 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**, in press. (accepted 10/29/2021)