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

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, H₂O stable

Prior work: Thermal Barrier Coatings
- durable
- oxidation resistant
- low T conductivity

CMC = Ceramic Matrix Composite, UHT = ultra high temperature
Beyond SiC

Past, Present & Future: ORNL Contributions to CMCs

ORNL: Vapor coating of ceramic fuel particles

1960
1970
1980
1990
2000
2010
2020
2030

ORNL: Forced-flow, thermal-gradient, Chemical Vapor Infiltration (CVI) process

1980 - 2000's

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

1992-2002

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

CFCC begins
2000
CFCC ends

Gen-1: Si-MI SiC matrices

SiC/SiC to engine market >25 yr

2016 LEAP engine

Si-free SiC/SiC

Gen-2

UHT

New ceramics

ORNL future

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

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

CVI: 1980s – 2000's

Pyrolytic C Interlayer
Ceramic Fiber

CVD SiC Matrix

CVI : 1980s – 2000's

ORNL Recent: SiC/SiC

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

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Ceramic Fiber

CVD SiC Matrix

ORNL Recent: SiC/SiC

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% H₂O at 1250°-1450°C
  - Coatings made at Stony Brook Univ. CTSR
    - With and without Si bond coating (Tₘ = 1414°C)

- **Objective**
  - **Develop a lifetime model for CMCs in land-based turbines**
    - Failure criteria
      - Cyclic testing in air+H₂O
    - 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$_2$Si$_2$O$_7$

Current “commercial” EBC

Next generation EBC (thinner YbDS: adhesion issue)

Single layer YbDS
No Si bond coating
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 SiO₂ 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

Thermal (cooling) stress: \( \sigma_{ox} = - E_{ox} \Delta T \cdot (\alpha_{\text{alloy}} - \alpha_{\text{oxide}})/(1-\nu) \)

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

SiO\(_2\) and SiC specimens:

Made Yb\(_2\)Si\(_2\)O\(_7\) and Yb\(_2\)SiO\(_5\) samples in collaboration with UVa (Opila’s group)

Task complete
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%H₂O 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 \( \text{H}_2\text{O} \) in several rigs at 1300°-1425°C

Nuclear Severe Accident Test Station

1-h cycles: automated cyclic rigs
Air + 90% \( \text{H}_2\text{O} \), 10 min cool in lab. air

1500°C maximum

1700°C maximum

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 SiO₂ phases

- New ORNL capability
  - Maps not point analysis
- Potential to detect amorphous/crystalline in thermally grown SiO₂ scale

Air Plasma Sprayed Yb₂Si₂O₇ top coating

Air Plasma Sprayed Si bond coating

CVD SiC substrate

- As-annealed coating
- No SiO₂ observed
- Black: amorphous YbSiO

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

Red = Yb₂SiO₅
Green = Yb₂Si₂O₇
Yellow = Cristobalite
Blue = Silicon
Raman shows cristobalite forms in all cases at 1350°C

- Tridymite formation (not observed) suggests contamination in system
Task 3: Methodology+software developed to measure kinetics

1350°C FCT in 90/10 H₂O/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:
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$_2$O ingress
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$_2$O acceleration
Enhancing SiC roughness improves coating adhesion without Si bond coating

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

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

Lifetimes of ~60µm YbDS

- 90vol%H₂O-10vol%air
  - v ~ 0.5-1.5 cm/s

- 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
  - β- 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

Log-Log plot can reveal kinetic transitions

\[ x^n = kt \]
Similar acceleration with a Si bond coating: edge failure?

BSE

Resin

YbDS

Silica TGO

Si

SiC

1000 1-h cycles 1350°C

OM

1350°C 500 1-h cycles

YbDS

BC lift-off

Substrate attack

SiC

Si

Si 100% consumed

Rapid increase:

\[ P_{H_2O} \sim 0.1 \text{ atm up to 500 h} \]

Loss of \( P_{H_2O} \) reduction above 500 h

Time in 1-h cycles at 1350°C (h)

\[ \begin{align*}
2.84 & \quad 4.71 & \quad 5.85 \\
\end{align*} \]

100 µm

1000 µm
Year 3 Milestone #7: compare 2 roughness levels

Initial result at 1350°C: 2nd ER iteration not as promising

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

Approximate thicknesses:
- ~60 µm YbDS on ER1
- ~200 µm YbDS on ER2

Materials:
- ER1-SiC
- ER2-SiC

Conditions:
- 1350°C
- 1-h FCT
- 90%H₂O
- 500 h

B&C adjusted for TGO visibility
Year 3 Milestone #8: compare YbDS to commercial mixed (Yb/Y)$_2$Si$_2$O$_7$ EBCs

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

- Cost
- Single Phase
- Low CTE
- Volatility
- CMAS Resist.

Y$_2$Si$_2$O$_7$

- Low cost
- Multi phase
- High CTE
- Volatility
- CMAS Resist.

(Yb/Y)$_2$Si$_2$O$_7$

- Lower cost
- Single Phase
- “medium” CTE
- Volatilization
- 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?

$3.4$/kg Y$_2$O$_3$

$16.4$/kg Yb$_2$O$_3$

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
1350°C 90%H₂O: silica growth slower on (Y/Yb)DS

1350°C
90vol%H₂O/10vol%air
500 1-h cycles

Resin
(Y/Yb)DS

(YbDS/YbMS)

Si TGO
CVD SiC

50 μm

Resin

Si TGO
CVD SiC

50 μm

TGO thickness (μm)

Time² (h²)

1350°C
1-h FCT
90vol%H₂O/10vol%air

~200 μm YbDS/YbMS
~140 μm (Y/Yb)DS

k_p = 5.8E-2 μm²/h

k_p = 3.6E-2 μm²/h
Task 3 model: 1\textsuperscript{st} iteration suggested 25 kh life is challenging

- Based on measured reaction kinetics
  - With and without Si bond coating
- Assume a critical SiO\textsubscript{2} thickness
  - Thermally grown oxide under silicate layer
  - Effective EBC will reduce kinetics (inhibit H\textsubscript{2}O)

![Image of YbDS, Silica TGO, Silicon, and CVD SiC micrograph with dimensions 50 µm]
2nd model iteration: “best case” scenario EBC stops all H$_2$O effects (using rates from test in dry air)

Unlike TBC, H$_2$O 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:


