Environmental Barrier Coatings for Ceramic Matrix Composites – An Overview

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Progression of High Temperature Materials Capability

- Improving efficiency and reducing emissions are main driving forces behind ever increasing demands for higher gas turbine inlet temperatures (TIT).
- CMCs can provide a step change in materials capability.
CMC is a game changer

**Higher temperature capability**
- Mechanical properties (Creep rupture, Fatigue)
- Oxidation resistance
  - Reduced cooling and/or higher turbine firing temperature

**Light weight**
- 1/3 of Ni-base superalloys
  - Reduced fuel consumption
  - Higher thrust
  - Reduced NOx and CO emissions

CMC’s are the most promising material option for significant fuel and pollution reductions

K. N. Lee, 3rd EBC Workshop
Commercialization Challenges

Design of Components
- Adequate attachment compliance to account for thermal expansion mismatch
- Adequate part sealing to realize cooling air flow and leakage goals

Life of MI-CMC Components
- Industrial applications require tens of thousands of hours
- Damage propagation after initial damage
- Requires minimization of processing defects in components

Coating Life
- Required minimum of 24,000 hours
- Damage propagation after FOD or otherwise localized damage

Component Cost
- Target is 1 - 2 times the metallic component cost

K. L. Luthra, Ceramic Leadership Summit 2011
Outline

- CMC and EBC Background
- Gen 1 EBC & Gen 2 EBC
- Engine Test Experience
- Summary & Conclusion

Acknowledgements

This presentation is based on the EBC section of CMH-17 (Composite Materials Handbook)
CMH-17 Mission

The Composite Materials Handbook organization creates, publishes and maintains proven, reliable engineering information and standards, subjected to thorough technical review, to support the development and use of composite materials and structures.

CMH-17 Vision

The Composite Materials Handbook will be the authoritative worldwide focal point for technical information on composite materials and structures.
Moving Forward

- **FAA CLEEN Program** accelerating commercial CMC technology development
  - Aircraft component certification beginning in 2016
- **FAA is exploring potential CMC certification issues with industry**
- **CMH-17 Handbook** is a resource
  - Lessons learned in PMC certification apply
  - All stakeholders may contribute
- **Building consensus for key tasks/timeframes**
### Representative Non-oxide CMC Systems with Constituents

<table>
<thead>
<tr>
<th>Fabrication Process</th>
<th>Fiber</th>
<th>Matrix</th>
<th>Interface</th>
<th>Compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVI</td>
<td>SiC (~40%)</td>
<td>SiC (60%)</td>
<td>Pyrocarbon (PyC) Boron Nitride (BN)</td>
<td>SiC/PyC/SiC, SiC/BN/SiC, SiC/PyC,BN/SiC</td>
</tr>
<tr>
<td>MI (prepreg)</td>
<td>SiC(20-25%)</td>
<td>SiC(70-63%)</td>
<td>BN,(\text{Si}_3\text{N}_4) (8-10%)</td>
<td>SiC/BN/SiC</td>
</tr>
<tr>
<td>MI (slurry cast)</td>
<td>SiC(35%)</td>
<td>CVD SiC(25%), SiC slurry cast (16%), Si(12%)</td>
<td>BN,(\text{Si}_3\text{N}_4) (6%)</td>
<td>SiC/BN,\text{SiC}/SiC</td>
</tr>
<tr>
<td>PIP</td>
<td>C(_2\text{SiC})(40%)</td>
<td>SiNC(_2\text{SiC}), SiC+ (\text{Si}_3\text{N}_4)</td>
<td>\text{PyC, BN}</td>
<td>SiC/BN/\text{SiC, C}/\text{SiC}</td>
</tr>
</tbody>
</table>

CVI: Chemical Vapor Infiltration, MI: Melt Infiltration, PIP: Polymer Impregnation and Pyrolysis, 2D/3D: 2/3-dimensional.


GE’s Melt Infiltrated, Prepreg CMC Process

- Fiber
- CVD Fiber Coating
- Prepregging
- Matrix slurry impregnation
- Wet drum winding
- Lay-Up and laminate
  - Preform fabrication

Additional CMC process steps
- Burn-out
  - >500°C to pyrolyze binders
  - coated fiber binder + C and/or SiC powder
- Si melt infiltration
  - 1400-1450°C to melt silicon and infiltrate body (Si + C → SiC)
  - coated fiber porous preform containing carbon and/or SiC
  - coated fiber dense SiC + Si matrix

K. L. Luthra, Ceramic Leadership Summit 2011
Standard Slurry Cast Melt-Infiltrated (MI) 2D&3D Woven Composites

Fiber

Weaving

Fabric

Low Temp. CVI
BN Interphase Infiltration

Reactor

CVI SiC Matrix Infiltration

Reactor

SiC/SiC preform

Slurry Cast SiC Matrix

CVI Preform

Silicon Melt Infiltration

Furnace

MI SiC/SiC

G. N. Morscher et al., Composites at Lake Louise, Canada 2007
CMC Microstructure

Microstructure of Prepreg MI Composites

- Fibers Homogeneously Distributed; Vf = ~25%
- Separated Fibers and Fiber Coatings
- ~1-3% Matrix Porosity

K. L. Luthra, Ceramic Leadership Summit 2011
Degradation of SiC/SiC CMCs

- Major application: Hot section components of advanced gas turbines
  - Combustor liners, nozzles, shrouds, rotors, blades, etc.
- Water vapor degradation in hot section – NASA Model

**Maximum SiC/SiC CMC combustor liner life at ~1200°C: ~ 5,000h**

Based on “E. J. Opila et al., 197-205 (1997)”

\[
\text{SiO}_2 + 2\text{H}_2\text{O}(g) = \text{Si(OH)}_4(g)
\]

\[
\text{Si}_3\text{N}_4 + 6\text{H}_2\text{O}(g) = 3\text{SiO}_2 + 6\text{H}_2(g) + 2\text{N}_2(g)
\]

\[
R = \text{rate (µm/h)} = 465 \exp(-111 \text{ kJ/mole/RT}) \sqrt[2]{P_{\text{H}_2\text{O}}^2 P_{\text{total}}^{-1/2}}
\]

SiC/SiC CMC combustor liner after 1048h of Solar engine testing

Effect of Water Vapor on SiC Degradation

Stagnant water vapor – Oxidation of Si

High velocity water vapor – Recession of SiC

- High oxidation rate in water vapor is due to high permeability of water vapor in SiO\textsubscript{2} (~10 times larger than that of oxygen)

- Several mils of recession per 100h is projected at 1400°C and 7 atm


Environmental Barrier Coating (EBC)

- An external coating to isolate CMC from water vapor
- EBC is an enabling technology for CMC

\[
\text{SiO}_2 (s) + 2\text{H}_2\text{O} (g) = \text{Si(OH)}_4 (g)
\]

Requirements

- Environmental durability
  - \(-\text{H}_2\text{O}\)
  - \(-\text{CMAS}\)
- Chemical compatibility
- Slow TGO growth
- Low stress
- CTE match
- Phase stability
- Low modulus
- Sinter resistance

# EBC Test Rigs

<table>
<thead>
<tr>
<th>Rig</th>
<th>Typical Test Condition</th>
<th>Capability</th>
</tr>
</thead>
</table>
| Steam thermal cycle rig (NASA Glenn)             | $P(H_2O) = \text{up to 1 atm}$  
$v = \text{a few cm/s}$  
$P_{\text{total}} = 1 \text{ atm}$           | Steam oxidation test         |
| High steam burner rig (Fraunhofer, Dresden)      | $P(H_2O) \sim 0.3 \text{ atm}$,  
$v \sim 100 \text{ m/s}$  
$P_{\text{total}} = 1 \text{ atm}$           | Recession test               |
| High pressure burner rig (NASA Glenn)            | $P(H_2O) \sim 0.6 \text{ atm}$  
$v \sim 24 \text{ m/s}$  
$P_{\text{total}} \sim 6 \text{ atm}$         | Steam oxidation test  
Recession test                                     |
| Steam Jet Rig (Teledyne)                         | $P(H_2O) = 1 \text{ atm}$,  
$v = \text{up to} \sim 300 \text{ m/s}$  
$P_{\text{total}} = 1 \text{ atm}$           | Recession test               |
| High heat flux laser rig (NASA Glenn)            | $P(H_2O) = \text{ambient air}$,  
$v = \text{zero}$  
$P_{\text{total}} = 1 \text{ atm}$           | Thermal fatigue test         |

The only test vehicle that includes all the variables is an engine or an expensive combustor test rig, which means real validation can only occur in an engine or an expensive combustor rig

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Developed at NASA Glenn in collaboration with GE and P&W – 1990s

- From early work on mullite coatings on SiC (Solar, GTE, NASA) – 1980s/1990s
- Si/mullite+BSAS/BSAS standard Gen 1 EBC – deposited by plasma spraying
  - BSAS: \((1-x)\text{BaO}\cdot x\text{SrO}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\), \(0 \leq x \leq 1\): barium-strontium-aluminosilicate
    - High stability in water vapor, CTE match with SiC/SiC, low modulus
  - Si: Bond coat: Improve oxidation life of EBC by forming slow growing \(\text{SiO}_2\) TGO
  - Mullite: intermediate coat that separates BSAS from \(\text{SiO}_2\) TGO
    - \(\text{SiO}_2\) reacts with BSAS to form eutectic melt at \(T \sim 1300\,^\circ\text{C}\)
    - BSAS addition reduces thermal stress: 20 wt% ~ 50 wt%


Upper Temperature Limit of Gen 1 EBC

- Long-term durability at >~1300°C is an issue
- Glass formation due to BSAS-silica eutectic reaction
- Glass-silica TGO reaction accelerates oxidation rate

1000-1h Cycles @1316°C, 90% H₂O-Bal. O₂

Gen 2 EBCs

- NASA Ultra Efficient Energy Technology (UEET) program - Early 2000’s
- EBC surface temperature goal: 1482°C (2700°F)
- EBC/CMC interface temperature goal: 1316°C (2400°F)
- Candidate materials: Low CTE Rare Earth silicates
  - Monosilicates: $\text{RE}_2\text{SiO}_5$ and Disilicates: $\text{RE}_2\text{Si}_2\text{O}_7$
  - RE = yttrium (Y), ytterbium (Yb), scandium (Sc), lutetium (Lu), etc.
- higher $\text{H}_2\text{O}$ stability and m.p. compared to BSAS, CTE match with CMC

Cross section of Si/mullite/$\text{Yb}_2\text{SiO}_5$-coated CMC after 1000h with 1h cycles at $T=1380°C$ (2516°F), $p_{\text{H}_2\text{O}} = 0.9$ atm, $P_{\text{TOTAL}} = 1$ atm, and $v = 2.2$ cm/s

Gen 2 EBC-coated SiC/SiC CMC and superalloy vanes after 5 h with 2 min cycles at $T=\sim1260°C$ - $\sim1316°C$, $P_{\text{TOTAL}} = 6$ atm, and $v = 24$ m/s

Silica Activity of Rare Earth Silicates at 1377C

- Consistent with experimental volatility

<table>
<thead>
<tr>
<th></th>
<th>RE = Y</th>
<th>RE = Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a(\text{SiO}<em>2)</em>{RE_2\text{Si}_2\text{O}_7} )</td>
<td>0.281</td>
<td>0.194</td>
</tr>
<tr>
<td>( a(\text{SiO}<em>2)</em>{RE_2\text{Si}_2\text{O}_5} )</td>
<td>0.000804</td>
<td>0.00298</td>
</tr>
<tr>
<td>( \frac{a(\text{SiO}<em>2)</em>{RE_2\text{Si}_2\text{O}_7}}{a(\text{SiO}<em>2)</em>{RE_2\text{Si}_2\text{O}_5}} )</td>
<td>350</td>
<td>65</td>
</tr>
</tbody>
</table>

G. Costa and N.S. Jacobson, ICACC, Daytona Beach, Jan 2015

Recession of RE disilicates

\[ \text{RE}_2\text{Si}_2\text{O}_7 + 2\text{H}_2\text{O} \, (\text{g}) \rightarrow \text{RE}_2\text{SiO}_5 + \text{Si(OH)}_4 \, (\text{g}) \]

\[ \text{RE}_2\text{SiO}_5 + 2\text{H}_2\text{O} \, (\text{g}) \rightarrow \text{RE}_2\text{O}_3 + \text{Si(OH)}_4 \, (\text{g}) \]

- High velocity burner rig test: 1450°C, 100 m/s, P(H\text{}_2\text{O})=0.27 atm, P(total)=1 atm
  - Volatilization of Yb\text{}_2\text{Si}_2\text{O}_7 results in Yb\text{}_2\text{SiO}_5 surface layer (~224h test)
  - Monosilicate layer slows down volatility

Klemm et al., Fraunhofer Institute, Proc. 2004 Cocoa Beach Meeting
Summary of EBC Coated SiC/SiC CMC Engine Field Tests

GE CMC Shroud Engine Tests
Solar Turbines Inc. CMC Combustor liner Engine Tests

<table>
<thead>
<tr>
<th>Start Test - End Test</th>
<th>CMC</th>
<th>EBC</th>
<th>Hours/Starts</th>
</tr>
</thead>
<tbody>
<tr>
<td>GE/7FA engine/stage 1 inner shrouds</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dec. 19, 2002-Aug. 17, 2003 rainbow test, S.Florida (9 CMC shrouds)</td>
<td>HiPerComp® MI prepreg, slurry cast (GRC, HACI, BFG)</td>
<td>Si/mullite+BSAS/BSAS (GRC)</td>
<td>5,366/14</td>
</tr>
<tr>
<td>April 17, 2006-End Sept. 2010a JEA test, Jacksonville, Florida (96 shrouds)</td>
<td>HiPerComp® MI prepreg (CCP,GRC)</td>
<td>Si/mullite+BSAS/BSAS, Rare Earth silicates (GRC,MP&amp;E)</td>
<td>1,537/497</td>
</tr>
</tbody>
</table>

Solar/Centaur 50S engine/inner (top) and outer (bottom) annular combuster liners

<table>
<thead>
<tr>
<th>Start Test - End Test</th>
<th>CMC</th>
<th>EBC</th>
<th>Hours/Starts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apr 1999-Nov. 2000, Texaco, Baskerville, California</td>
<td>HiNi SiC/BN/SiC MI (ACI)</td>
<td>Si/mullite/BSAS (URTC)</td>
<td>13,937/61</td>
</tr>
<tr>
<td>Aug. 1999-Oct. 2000, Malden Mills, Lawrence, Massachusetts</td>
<td>HiNi SiC/BN/SiC MI (BFG)</td>
<td>Si/mullite+BSAS/BSAS (URTC)</td>
<td>7,238/159</td>
</tr>
<tr>
<td>Nov. 2001-May 2002, Texaco, Bakersfield, California</td>
<td>HiNi SiC/BN/SiC MI (BFG)</td>
<td>Si/mullite+BSAS/BSAS (URTC)</td>
<td>7,238/159</td>
</tr>
<tr>
<td>Aug. 2000-July 2002, Malden Mills, Lawrence, Massachusetts</td>
<td>TiZM/BN/SiC MI (ACI)</td>
<td>Si/mullite+BSAS/BSAS (URTC)</td>
<td>15,144/92</td>
</tr>
<tr>
<td>July 2002-July 2003, Malden Mills, Lawrence, Massachusetts</td>
<td>TyZM/BN/SiC MI (ACI)</td>
<td>Si/mullite+BSAS/BSAS (URTC)</td>
<td>8,368/32</td>
</tr>
<tr>
<td>May 2003-Nov. 2004, Chevron Texaco, Bakersfield, California</td>
<td>HiNi/BN/SiC (DLC/ACI) N720/Al2O3 (COIC/SWPC)</td>
<td>Si/mullite/BSAS (URTC)</td>
<td>12,582/63</td>
</tr>
<tr>
<td>June 2006-May 2007, Tipton, California</td>
<td>TyZM/BN/SiC MI (CCP)</td>
<td>Si/mullite/SAS (URTC)</td>
<td>7,784/43</td>
</tr>
</tbody>
</table>

a Marks end of the govt. program; testing was continued under GE in-house effort.

Two Variants of Gen 1EBCs

GE Shroud
Total: 6,903h


Solar Combustor Liner Set
Total: 83,010h


Limit of Gen1 Standard EBC @~1200C: ~ 15,000h
Degradation of Gen 1 EBC Coated SiC/SiC CMCs

15,144-h Solar Combustor Liner Engine Test
- Pathway for ingress of water vapor (e.g. cracks in EBC)
- Bond coat oxidation: $\text{SiO}_2$ TGO formation
  - TGO has different CTE from EBC layers
- Horizontal cracks at Si-$\text{SiO}_2$/mullite+BSAS interface
  - Hypothesis: transient thermal stresses+bond coat oxidation
  - Many thermal cycles aggravate crack formation
  - Cracks may also go vertically into the Si bond coat

5,366-h GE “rainbow” test – progression of degradation
- Edge EBC is more porous, cracks form at surface
- Pathway for ingress of water vapor
- Bond coat oxidation, $\text{SiO}_2$ TGO formation
- Lateral crack formation -> debonding, spallation


Degradation of Gen 1 EBC Coated SiC/SiC CMCs

13,937-h Solar Combustor Liner Engine Test
- Pinhole formation from CMC fabrication tooling bumps – Slurry cast CMC
- Tooling bumps cause EBC processing defects
- Pathway for ingress of water vapor in EBC and CMC
- Pinholes extend 1.25-1.50 mm (i.e. into EBC)

5,366-h GE “rainbow” test
- Pinhole formation from CMC fabrication tooling bumps - Slurry cast CMC
- Pathway for ingress of water vapor
- EBC degradation – undercutting of EBC
- Rapid degradation of CMC when EBC is breached

Degradation of Gen.1 EBC Coated SiC/SiC CMCs

13,937-h Solar Combustor Liner Engine Test

- Edge defect, present in thermal diffusivity NDE
- Present after CMC fab., increased after EBC deposition
- Defect pattern duplicated in NDE after test
- Defect pattern also in post-test digital photograph

13,937-h Solar Combustor Liner Engine Test

- Recession of BSAS top layer
- Recession more severe in hot middle section
- Recession less severe in cool aft section


**GE 1,537-h shroud engine test**

- Boroscope inspection: 1122h/169 start/stops
- Complete edge-to-edge spall
- Post coating heat treat at 1300°C gives desired C-polymorph
- At op. temperature of 1200°C: conversion to D-polymorph
  - Grain growth, expansion anisotropy -> cracking EBC and EBC spallation
- Remedy: composition modification to prevent D-phase formation
  - Verified by steam rig test

**Solar 7,784-h combustor engine test**

- Some discoloration at aft edge, minor edge spallation at fore edge—otherwise effective

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Published engine data on Gen 2 EBCs very limited

Next Gen EBCs under development –1480-1650°C (2700-3000°F) mostly proprietary
CMAS Attack on EBCs

- Particulates (sand, volcanic ash, other silicate) ingested by air-breathing turbine engines
- \( T \sim 1200^\circ C \): forms glassy deposits of calcium-magnesium-aluminosilicate (CMAS) with other minor oxides
- Molten CMAS deposits adhere to EBC-coated CMC components, cause compositional and property degradation
- Gen 1 EBC – BSAS is not CMAS resistant
- Model CMAS system: \( 33\text{CaO-9MgO-13AlO}_{1.5}-45\text{SiO}_2 + \text{BSAS} \) -> dissolves both hexacelsian and celsian phases and reprecipitates thermodynamically stable celsian phase
- Penetrates the BSAS layer at 1300\(^\circ\)C
- CMAS reacted with BSAS also affects the EBC residual stress state negatively
- Gen 2 EBCs (Yttrium silicates, ytterbium silicates) - insufficiently resistant to CMAS penetration
- CMAS mitigation needs to be developed – Pyrochlore (e.g. \( \text{Gd}_2\text{Zr}_2\text{O}_7 \)) shows promise, but mechanical properties are inferior to RE-silicates and large CTE mismatch
- Research for CMAS mitigation is ongoing

B. Harder et al., J. Am. Ceram. Soc. 94 (2011)
EBC Failure Modes

- Cyclic Steam Oxidation
- Recession by Water Vapor
- Stress Cracking
- CMAS Degradation
- Erosion
- Foreign Object Damage (FOD)

Synergies between failure modes are likely to lead to the ultimate EBC failure

Summary

- SiC/SiC CMCs for advanced power generation hot section components ~5,000h life limit
  - Water vapor attacks CMC to form volatile components
  - CMC consumption by water vapor recession leads to component thinning, property degradation. Component loses functionality and becomes life-limited
- Gen 1 EBCs: Si/mullite+BSAS/BSAS increase SiC/SiC CMC life to ~15,000h
- A number of EBC issues have surfaced in CMC/EBC component field testing by GE and Solar Turbines Inc. under US government programs: EBC degradation through various mechanisms leads to pathways for water vapor ingress, bond coat oxidation, cracking at the bond coat/intermediate layer interface, EBC debonding and spallation. BSAS recession is additionally life-limiting
- Gen 2 EBCs focuses on Rare Earth monosilicates and disilicates which have lower volatilities under water vapor conditions. Lab and rig data and limited engine test data indicate improved performance compared to Gen 1 EBCs, but more development and validation will be required.
- CMAS formation in air-breathing turbines results in degradation of EBC which lose their effectiveness. A fully CMAS-resistant EBC has yet to be demonstrated.
Conclusion

- CMCs are a game changer for next generation gas turbine engines due to high temperature capability
  - Improves SFC, thrust, and emission
  - EBC is an enabling technology for CMCs

- The first and second Gen EBCs developed in mid 1990s- early 2000s laid the foundations for current EBCs
  - A number of rig and engine tests have been successfully completed

- The introduction of CMCs represents a significant challenges as failure of the EBC means significant reduction in component life
  - Development of a reliable EBC life model required