Calcium-Magnesium-Alumino-Silicates (CMAS) Reaction Mechanisms and Resistance of Advanced Turbine Environmental Barrier Coatings for SiC/SiC Ceramic Matrix Composites

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Advanced Ceramic Matrix Composites:
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Emphasize material temperature capability, performance and long-term durability - Highly loaded EBC-CMCs with temperature capability of 2700°F (1482°C)

- 2700-3000°F (1482-1650°C) turbine and CMC combustor coatings
- 2700°F (1482°C) EBC bond coat technology for supporting next generation
  - Recession: <5 mg/cm² per 1000 h
  - Coating and component strength requirements: 15-30 ksi, or 100-207 Mpa
  - Resistance to Calcium Magnesium Alumino-Silicate (CMAS)

Step increase in the material’s temperature capability

2700°F (1482°C) Gen III SiC/SiC CMCs

2400°F (1316°C) Gen I and Gen II SiC/SiC CMCs

2000°F (1093°C), PtAl and NiAl bond coats
Outline

• Environmental barrier coating (EBC) development: the CMAS relevance and importance

• Some generalized CMAS related failures

• CMAS degradation of environmental barrier coating (EBC) systems: rare earth silicates
  – Ytterbium silicate and yttrium silicate EBCs
  – Some reactions, kinetics and mechanisms

• Advanced EBCs, HfO$_2$- and Rare Earth - Silicon based 2700°F+ capable bond coats
  – Compositions, and testing results

• Summary
EBC-CMAS Degradation is of Concern with Increasing Operating Temperatures

- Emphasize improving temperature capability, performance and long-term durability of ceramic turbine airfoils
  
  • Increased gas inlet temperatures for net generation engines lead to significant CMAS-related coating durability issues – CMAS infiltration and reactions


Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests

- Synthetic CMAS compositions, in particular, NASA modified version (NASA CMAS), and the Air Force Powder Technology Incorporated PTI 02 CMAS currently being used for advanced coating developments
- CMAS SiO₂ content typically ranging from 43-49 mole%; such as NASA’s CMAS (with NiO and FeO)

ARFL PTI 11717A 02

Fully reacted CMAS EDS

AFRL02 particle size distribution
(34% Quartz, 30% Gypsum, 17% Aplite, 14% Dolomite, 5% Salt)
Percentile Size (μm)
10 2.5 +/- 1.0
50 8.5 +/- 2.0
90 40.5 +/- 3.0

As received

Fully reacted

Fig. 4. The 10% MgO plane of the system CaO–MgO–Al₂O₃–SiO₂ showing the isotherms and fields of primary crystallization. A.T. Prince, J. Amer. Ceram. Soc., 37(9)1954 p.402-408
Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests - Continued

- NASA modified version (NASA CMAS)
- CMAS SiO\(_2\) content typically ranging from 43-49 mole%; such as NASA’s CMAS (with NiO and FeO)

### NASA CMAS Compositions

<table>
<thead>
<tr>
<th>Method</th>
<th>Content (mol%)</th>
</tr>
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<tr>
<td>(Designed/Targeted)</td>
<td></td>
</tr>
<tr>
<td>Measured by ICP-OES</td>
<td></td>
</tr>
<tr>
<td>Measured by EDS</td>
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<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>MgO</th>
<th>Al(_2)O(_3)</th>
<th>SiO(_2)</th>
<th>Fe(_2)O(_3)</th>
<th>NiO</th>
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</thead>
<tbody>
<tr>
<td>(Design/Targeted)</td>
<td>33.8</td>
<td>9.0</td>
<td>6.7</td>
<td>46.0</td>
<td>3.0</td>
<td>1.5</td>
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<tr>
<td>Measured by ICP-OES</td>
<td>38 ± 2</td>
<td>9.0 ± 0.5</td>
<td>6.9 ± 0.3</td>
<td>41 ± 2</td>
<td>3.8 ± 0.2</td>
<td>1.37 ± 0.07</td>
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<tr>
<td>Measured by EDS</td>
<td>36 ± 1</td>
<td>8.4 ± 0.3</td>
<td>7.5 ± 0.2</td>
<td>43 ± 1</td>
<td>3.9 ± 0.1</td>
<td>1.5 ± 0.1</td>
</tr>
</tbody>
</table>

DSC traces of CMAS during heating and cooling up to 1500 °C at 5 °C/min.

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![DSC traces of CMAS during heating and cooling up to 1500 °C at 5 °C/min.](image-url)
CMAS Related Degradations in EBCs

- **CMAS effects**
  - Significantly reduce melting points of the EBCs and bond coats
  - More detrimental effects with thin airfoil EBCs
  - CMAS weakens the coating systems, reducing strength and toughness
  - MAS increase EBC diffusivities and permeability, thus less protective as an environmental barrier
  - CMAS interactions with heat flux, thermal cycling, erosion and thermomechanical fatigue
    - Reaction layer spallations
    - Accelerated CMC failure when CMAS intact with CMCs

CMAS induced melting and failure
CMAS Related Degradations in EBCs - Continued

- CMAS effects on EBC temperature capability
  - Silicate reactions with NaO$_2$ and Al$_2$O$_3$ silicate

Phase diagrams showing yttrium di-silicate reactions with SiO$_2$, NaO and Al$_2$O$_3$
CMAS Related Degradations in EBCs - Continued

- CMAS effects on EBC temperature capability
  - Rare earths generally have limited temperature capability below 1500°C in the RE$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ based systems,
  - Smaller ionic size REs have higher melting points

Solidus temperature in Ln$_2$Si$_2$O$_7$-Al$_6$Si$_2$O$_{13}$-SiO$_2$ system as function of ionic radius

Rare Earth Dissolutions in CMAS Melts

- Large ionic size rare earths showed higher concentration dissolutions in the CMAS melt for ZrO$_2$-RE$_2$O$_3$ oxide systems.

Gustavo and Zhu, International Conference on Advanced Ceramics and Composites, 2016
CMAS Related Degradations in EBC coated CMCs – Laboratory Heat Flux Tests

- CMAS effects on EBC-CMC temperature capability tested in laser high heat flux creep-rupture rig
  - Accelerated failure of CMC in loading high heat flux conditions

Front heated CMAS side | Back cooled side

EBC coated CVI-MI CMC with NdYb silicate RESi bond coat, tested Tsurface 2600°F; Tback 2450°F

![Images of EBC coated CMC with CMAS effects](example_images)

![Graph showing creep strain vs. time](example_graph)

Creep strain, %
Time, h
Selected EBC systems

- HfO$_2$-RE-Si, along with co-doped rare earth silicates and rare earth alumino-silicates, for optimized strength, stability and temperature capability
- CMAS infiltrations can reduce the strength
EBC CMAS Surface Initial Nucleation, Dissolution Reactions

- Ytterbium- and yttrium-silicate silicates reactions and dissolutions in CAMS
- More sluggish dissolution of ytterbium as compared to yttrium

Ytterbium di-silicate surface CMAS melts: 50 h 1300°C

Ytterbium di-silicate surface CMAS melts: 5 h 1500°C

Yttrium mono-silicate surface CMAS melts: 50 h 1300°C

Yttrium silicate surface CMAS melts: 5 h 1500°C

Rare Earth Apatite Grain Growth

Grain growth of apatite phase at 1500°C at various times

Ytterbium silicate system

50 hr
150 hr
200 hr

Yttrium silicate system

50 hr
150 hr
200 hr
Rare Earth Dissolution in CMAS Melts

- Non stoichiometric characteristics of the CMAS – rare earth silicate reacted apatite phases – up to 200 h testing
- Difference in partitioning of ytterbium vs. yttrium in apatite
  - Average $\text{AEO/RE}_2\text{O}_3$ ratio $\sim 0.68$ for ytterbium silicate – CMAS system
  - Average $\text{AEO/RE}_2\text{O}_3$ ratio $\sim 0.22$ for yttrium silicate – CMAS system

Advanced NASA EBC Developments

NASA advanced EBC systems emphasizing high stability HfO$_2$- and ZrO$_2$-RE$_2$O$_3$-SiO$_2$ EBC system, RE$_2$Si$_{2-x}$O$_{7-2x}$, such as (Yb,Gd,Y)$_2$Si$_{2-x}$O$_{7-2x}$ - Controlled dissolution and maintaining coating stability
CMAS Resistant Tests

- JETs test of more advanced coating systems at 2700F

Plasma sprayed \((\text{Gd,Y})_2\text{Si}_2\text{O}_7\), 2450 cycles

Special processed \(\text{Yb}_2\text{Si}_2\text{O}_7\), spalling at 450 Cycles

EB-PVD \((\text{Yb,Gd,Y})_2\text{Si}_2\text{O}_7\), total 4450 JETS cycles, 100h

Hybrid Hf-rare earth aluminate silicate, completed 4450 cycles, 100h

Hybrid Hybrid Zr-rare earth silicate, completed 4450 cycles, 100h
High Stability and CMAS Resistance are Ensured by Advanced High Melting Point Coating, and Multi-Component Compositions

- Generally improved CMAS resistance of NASA RESi System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration \( \sim 9\text{mol}\% \))
Advanced EBC-CMC System Demonstrated 300 hr High Cycle and Low Fatigue Durability in High Heat Flux 2700°F Test Conditions

- A turbine airfoil EBC with HfO$_2$-rare earth silicate and GdYbSi bond coat on CVI-MI CMC substrate system selected for heat flux durability testing
- Laser high heat flux rig High Cycle and Low Cycle Fatigue test performed at Stress amplitude 10 ksi, fatigue frequency 3 Hz at EBC, and 1 hr thermal gradient cycles
- Tested EBC surface temperature 1537°C (2800°F) and T bond coat temperature 1482°C (2700°F), with CMAS
- Demonstrated 300 hour durability at 2700°F+
- Determined fatigue-creep and thermal conductivity behavior of the EBC-CMC system

Specimen after 300 h testing

Test Condition Summary

- EBC/CVI-MI, Fatigue loading 10 ksi (69 MPa), R=0.05, with 1 hr Thermal LCF
- $T_{\text{EBC-surface}}$ 1537°C (2800°F)
- $T_{\text{bond coat}}$ 1482°C (2700°F)
- $T_{\text{back CMC surface}}$ 1250°C (2282°F)
Advanced EBC-CMC Fatigue Test with CMAS and in Steam Jet: Tested 300 h Durability in High Heat Flux Fatigue Test Conditions

- Advanced Hf-NdYb silicate-NdYbSi bond coat EBC coatings on 3D architecture CVI-PIP SiC-SiC CMC (EB-PVD processing)
- Further understanding water vapor - environmental interactions necessary
EBC System Designs – Effects of Composites and Clustered Compositions?

- An alternating HfO$_2$-and RE-silicate coatings (EB-PVD processing) – HfO$_2$- layer infiltration and rare earth silicate layer melting

EB-PVD Processed EBCs: alternating HfO$_2$-rich and ytterbium silicate layer systems for CMAS and impact resistance?
Summary

• CMAS degradation remains a challenge for emerging turbine engine environmental barrier coating – SiC/SiC CMC component systems
• CMAS leads to lower melting point of EBC and EBC bond coat systems, and accelerated degradations
• NASA advanced EBC compositions showed initial promise for CMAS resistance at temperatures up to 1500°C in high velocity, high heat flux and mechanical loading, from the laboratory simulated engine tests, demonstrated with various CMC substrates
• Testing helped better understanding of EBC composition designs, CMAS interactions with hafnium, zirconium and rare earth silicates, for significantly improved CMAS resistance
• We are developing better standardized CMAS testing, and working on CMAS induced life debits, helping validate life modeling; controlling the compositions for CMAS resistance while maintaining high toughness also a key emphasis
Acknowledgements

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• The authors are grateful to Dr. Michael Helminiak in the assistant of JETS tests.
CMAS Reaction Kinetics in Bond Coats

- SiO$_2$ rich phase partitioning in the CMAS melts
- Rare earth content leaching low even at 1500°C
- More advanced compositions are being implemented for improved thermomechanical – CMAS resistance
High Stability and CMAS Resistance Observed from the Rare Earth Silicon High Melting Point Coating Compositions

- Demonstrated CMAS resistance of NASA RE-Si System at 1500°C, 100 hr
- Silica-rich phase precipitation
- Rare earth element leaching into the melts (low concentration ~9 mol%)
Effect of CMAS Reactions on Grain Boundary Phases

- CMAS and grain boundary phase has higher Al$_2$O$_3$ content (17-22 mole%)
  - Eutectic region with high Al$_2$O$_3$ content ~1200°C melting
  - Loss of SiO$_2$ due to volatility

Grain boundary final phase – low SiO$_2$ and high Alumina

NASA modified CMAS

200 hr, 1500°C