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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NASA Environmental Barrier Coatings (EBCs) and Ceramic Matrix Composite (CMC) System Development

- **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)

**Temperature Capability**

- **2800°F combustor TBC**
- **2500°F Turbine TBC**

**Increase in \( \Delta T \) across T/EBC**

- **3000°F+ (1650°C+)**
- **2700°F (1482°C)**
  - 2700°F SiC/SiC CMC airfoil and combustor technologies
  - 2700°F SiC/SiC thin turbine EBC systems for CMC airfoils
  - **2700°F (1482°C) Gen III SiC/SiC CMCs**

**Ceramic Matrix Composite**

- **Gen II – Current commercial**
- **Gen III**
- **Gen. IV**

**Single Crystal Superalloy**

- **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 SiO$_2$ content typically ranging from 43-49 mole%; such as NASA’s CMAS (with NiO and FeO)
Calcium Magnesium Alumino-Silicate (CMAS) Systems Used in Laboratory Tests - Continued

- NASA modified version (NASA CMAS)
- CMAS SiO\textsubscript{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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<tbody>
<tr>
<td>(Designed/Targeted)</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>33.8</td>
</tr>
<tr>
<td>MgO</td>
<td>9.0</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>6.7</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>46.0</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>3.0</td>
</tr>
<tr>
<td>NiO</td>
<td>1.5</td>
</tr>
</tbody>
</table>

| Measured by ICP-OES           |                 |
| CaO                           | 38 ± 2          |
| MgO                           | 9.0 ± 0.5       |
| Al\textsubscript{2}O\textsubscript{3} | 6.9 ± 0.3   |
| SiO\textsubscript{2}          | 41 ± 2          |
| Fe\textsubscript{2}O\textsubscript{3} | 3.8 ± 0.2 |
| NiO                           | 1.37 ± 0.07     |

| Measured by EDS               |                 |
| CaO                           | 36 ± 1          |
| MgO                           | 8.4 ± 0.3       |
| Al\textsubscript{2}O\textsubscript{3} | 7.5 ± 0.2  |
| SiO\textsubscript{2}          | 43 ± 1          |
| Fe\textsubscript{2}O\textsubscript{3} | 3.9 ± 0.1 |
| NiO                           | 1.5 ± 0.1       |

DSC traces of CMAS during heating and cooling up to 1500 °C at 5 °C/min.
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 $\text{RE}_2\text{O}_3$-$\text{Al}_2\text{O}_3$-$\text{SiO}_2$ based systems,
  - Smaller ionic size REs have higher melting points

Solidus temperature in $\text{Ln}_2\text{Si}_2\text{O}_7$-$\text{Al}_6\text{Si}_2\text{O}_{13}$-$\text{SiO}_2$ 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

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

![Graph showing strength vs. temperature for different EBC systems]
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

Yttrium silicate system
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 AEO/RE$_2$O$_3$ ratio ~ 0.68 for ytterbium silicate – CMAS system
  - Average AEO/RE$_2$O$_3$ ratio ~ 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.

(Yb,Gd,Y)$_2$Si$_{2-x}$O$_{7-2x}$ in CMAS, 1300°C
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 ~9mol%)
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

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

- SiO₂ 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

CMAS Partitioning on RE-Si bond coat, 1500°C, 100hr
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\textsubscript{2}O\textsubscript{3} content (17-22 mole%)
  - Eutectic region with high Al\textsubscript{2}O\textsubscript{3} content ~1200°C melting
  - Loss of SiO\textsubscript{2} due to volatility

Grain boundary final phase – low SiO\textsubscript{2} and high Alumina

Fig. 4. The 10% MgO plane of the system CaO-MgO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} showing the isotherms and fields of primary crystallization. A.T. Prince, J. Amer. Ceram. Soc., 37(9)1954 p402-408