Reduced Cost Bond Layers for Multi-Layer Thermal/Environmental Barrier Coatings

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Participants

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  - Visiting scholars
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- **Plasma Processes LLC**
  - Kyle Murphree
  - Tim McKechnie
Introduction

- Thermal barrier coatings (TBCs) to increase operating temperature of gas turbine engines
- Ca-Mg-Al-Si oxides (CMAS) injected into engine degrade TBCs
- Pyrochlore oxides offer potential for improved resistance to CMAS corrosion and reduced thermal conductivity
Outline

- Thermal conductivity
- Cubic fluorite vs. pyrochlore
- CMAS composition
Experimental

- Synthesis of pyrochlore
  - Co-precipitation
- CMAS exposure
  - Melt / solidify Ca-Mg-Al-Si oxide mixtures
  - Crush glass, apply to pyrochlore pellet
  - Expose to 1200-1300°C
- Characterization
  - XRD, SEM / EDS
- Thermal Conductivity
Crystal Structure

Cubic Fluorite

Pyrochlore

Ordering of Ln / Zr

A.R. Cleave (2006)

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Plasma Sprayed Gd$_2$Zr$_2$O$_7$

Plasma-sprayed Gd$_2$Zr$_2$O$_7$ not pyrochlore
Plasma Sprayed YSZ / Gd$_2$Zr$_2$O$_7$
**Gd₂Zr₂O₇: Cubic Fluorite and Pyrochlore**

Gd₂Zr₂O₇

- Cubic fluorite (Sintered at 1575°C)
- Pyrochlore (Sintered at 1500°C)

**Synthesize cubic fluorite Gd₂Zr₂O₇ with higher sintering temperature**
Sintered $\text{Gd}_2\text{Zr}_2\text{O}_7$

- Pyrochlore
- Cubic Fluorite
Thermal Conductivity Measurement

Constant heat flux through known / unknown samples
Measure temperature gradients
Thermal Conductivity Measurement

Steel heat source / sink
Thermal Conductivity of Gd$_2$Zr$_2$O$_7$

Average $\kappa$ at 300°C
Pyrochlore (blue open): 0.51 Wm$^{-1}$K$^{-1}$
Cubic Fluorite (red filled): 0.67 Wm$^{-1}$K$^{-1}$
(Student t test $P = 0.008$)
Thermal Conductivity of Gd$_2$Zr$_2$O$_7$ after CMAS Exposure at 1300°C

**Pyrochlore**
- Blue: No CMAS exposure
- Green: 10 hours at 1300°C
- Green: 20 hours at 1300°C

**Cubic Fluorite**
- Blue: No CMAS exposure
- Green: 10 hours at 1300°C
- Green: 20 hours at 1300°C
Thermal Conductivity of $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS Exposure at 1300°C

\[ \kappa \text{ at 300°C} \]

- **Cubic Fluorite**
  - 0 hours vs. 20 hours
  - $P = 0.03$

- **Pyrochlore**
  - 10 hours vs. 20 hours
  - $P = 0.70$

- **Pyrochlore**
  - 0 hours vs. 10 hours
  - $P = 0.06$

- **Pyrochlore**
  - 0 hours vs. 20 hours
  - $P = 0.001$

- **Cubic Fluorite**
  - 20 hours
  - $P = 0.51$

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Cubic Fluorite $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS at $1300^\circ\text{C}$ for 10 hours
Cubic Fluorite $Gd_2Zr_2O_7$ after CMAS at $1300^\circ C$

Mostly CMAS +Mg / ↓ Gd

$Al-Si-Ca-Gd-Zr-O$

↑Al

10 hours

20 hours
Pyrochlore Gd$_2$Zr$_2$O$_7$ after CMAS at 1300°C

Increased variation in penetration depth after 20 hours
Pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS at 1200°C for 20 hours

Dense layer forms after reaction with CMAS
Pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS at 1200°C for 40 hours

Gd-containing silicate
Zr-rich cubic fluorite

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Cubic Fluorite $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS at 1200°C for 5 hours

Zr-rich cubic containing fluorite silicate

Spectrum

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Pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS at 1300°C for 20 hours

Cubic fluorite structure after reaction

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Pyrochlore Gd$_2$Zr$_2$O$_7$ after CMAS at 1300°C for 20 hours

Proportion of cubic fluorite higher near surface
Pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS for 20 hours

Peak position of cubic fluorite (i.e. composition) function of temperature.
Cubic Fluorite $\text{Gd}_2\text{Zr}_2\text{O}_7$ after CMAS at 1200°C

Cubic fluorite peak shifts for cubic fluorite $\text{Gd}_2\text{Zr}_2\text{O}_7$
Gd$_2$Zr$_2$O$_7$ Lattice Parameter Correction

Note: Lattice parameters for cubic fluorite are for 8 unit cells (i.e. 2$a$) to facilitate comparison with the pyrochlore structure.
Gd₂Zr₂O₇ Lattice Parameter

Calculated
0 Gd - Cation CN VIII: r_{Zr^{4+}} = 0.84 Å, r_{Gd^{3+}} = 1.053 Å
0.5 Gd - Cation CN VII: r_{Zr^{4+}} = 0.78 Å, r_{Gd^{3+}} = 1.0 Å

After CMAS at 1300°C
Cubic fluorite peak position not affected by original crystal structure

After CMAS at 1200°C
ZrO$_2$-Gd$_2$O$_3$ Phase Diagram

Gd / Zr in cubic fluorite increases with increasing temperature

T = tetragonal
F = cubic fluorite
M = monoclinic
P = pyrochlore
C, B, H = Gd$_2$O$_3$ phases
YSZ / $\text{Gd}_2\text{Zr}_2\text{O}_7$ coating exposure at 1200°C for 20 hours

CMAS

Air
YSZ / Gd$_2$Zr$_2$O$_7$ coating CMAS at 1200°C for 20 hours

EDS analysis (atomic%)

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YSZ / Gd$_2$Zr$_2$O$_7$ coating x-ray diffraction

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25 35 45 55 65 75 85

GZO coating - CMAS for 20 hrs at 1200°C (#13 - ground powder)
GZO coating - CMAS for 20 hrs at 1200°C (#13 - powder)
GZO coating - CMAS for 20 hrs at 1200°C (#13)
GZO coating - CMAS for 20 hrs at 1200°C (#14)
GZO coating - CMAS for 20 hrs at 1200°C (#15)
GZO Coating (#12)
## CMAS Compositions

<table>
<thead>
<tr>
<th>Source</th>
<th>Oxide</th>
<th>CMAS</th>
<th>CaO-lean CMAS</th>
<th>CMAS / CaCO₃</th>
<th>CMAS / CaSO₄</th>
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<td>CaO</td>
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Surface after CMAS Exposure at 1300°C for 20 hours

Surface morphologies similar – larger crystals on sample with CaCO$_3$. 

CMAS

CMAS / CaCO$_3$

CMAS / CaSO$_4$

CaO-lean CMAS
Cross-Section after CMAS Exposure at 1300°C for 20 hours

Dense reaction layer – thickest for CaO-deficient composition
Gd$_2$Zr$_2$O$_7$ after CMAS at 1300°C for 20 hours – SEM / EDS

Elemental Distribution (mol%)
Gd$_2$Zr$_2$O$_7$ after CMAS at 1300°C for 20 hours – XRD

Gd$_2$Zr$_2$O$_7$ + CMAS at 1300°C for 20 hours

- As-corroded
- Top 20 µm removed
- Top 40 µm removed
- Before corrosion

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Gd$_2$Zr$_2$O$_7$ after CaO-lean CMAS at 1300°C for 20 hours – SEM / EDS
Gd$_2$Zr$_2$O$_7$ after CaO-lean CMAS at 1300°C for 20 hours – XRD

Gd$_2$Zr$_2$O$_7$ + CaO-lean CMAS at 1300°C for 20 hours

As-corroded
Top 20 µm removed
Top 40 µm removed
Before corrosion

Intensity

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Gd$_2$Zr$_2$O$_7$ after CMAS / CaCO$_3$ at 1300°C for 20 hours – SEM / EDS

Elemental Distribution (mol%)
Gd$_2$Zr$_2$O$_7$ after CMAS / CaCO$_3$ at 1300°C for 20 hours – XRD

Gd$_2$Zr$_2$O$_7$ + CaO-lean CMAS + CaCO$_3$ at 1300°C for 20 hours

- As-corroded
- Top 20 µm removed
- Top 40 µm removed
- Top 60 µm removed
- Before corrosion

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Gd$_2$Zr$_2$O$_7$ after CMAS / CaSO$_4$ at 1300°C for 20 hours – SEM / EDS

Elemental Distribution (mol%)
Gd$_2$Zr$_2$O$_7$ after CMAS / CaSO$_4$ at 1300°C for 20 hours – XRD

Gd$_2$Zr$_2$O$_7$ + CaO-lean CMAS + CaSO$_4$ at 1300°C for 20 hours

As-corroded
Top 20 µm removed
Top 40 µm removed
Before corrosion
Effect of CMAS composition

CaO-lean reaction product
- Thickest reaction layer \((311)_{\text{CF}} / (622)_{\text{Pyr}}\)
- Lowest Gd – largest \((311)_{\text{CF}}\)

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Uneven CMAS loading can lead to different reaction geometries.
Stress and Temperature Distributions

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Stress Concentration

Highest stress at CMAS / reaction layer interface

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Conclusions

- Reaction product has higher thermal conductivity than lanthanide zirconate – higher conductivity material fills the pores
- Cubic fluorite and pyrochlore $\text{Gd}_2\text{Zr}_2\text{O}_7$ react similarly with CMAS
- More reaction with CaO-deficient CMAS