Advanced Thermal Barrier Coatings for Next Generation Gas-Turbine Engines Fueled by Coal-Derived Syngas

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Ms. Amanda Krause

Collaborators
Prof. Sanjay Sampath (Stony Brook Univ.)
Dr. Ramesh Subramanian (Siemens Energy; Cost Share)

Support
DoE NETL University Coal Research Program

DoE Project Officer
Dr. Jason Hissam

Grant No.
DE-FE0008933
Gas-Turbine Engines: $55B by 2015

Aero (65%)  Power (35%)

Siemens SG5-8000H
340 MW
Natural Gas

P&W
GP7000

GE90
128K lbs Thrust

~20% Electricity Worldwide

Langston, 2011
Motivation

* Need for Higher Power and Efficiency
  - Aircraft Propulsion
  - Electricity Generation

* Need for Higher Hot-Section Temps.

* Materials “Bottleneck”:
  - Improved Structural Alloys
  - Ceramic Matrix Composites
  - Ceramic Thermal Barrier Coatings (TBCs)

Perepezko, 2009
Ceramic Thermal Barrier Coatings (TBCs)

- **Engines**
  - Aero
  - Power

- **Blades/Vanes, Combustors, Shrouds**

- **Strain-Tolerant, Low Th. Cond.**

- **Up to 300 °C Temp. Reduction**

- **Improved**
  - Performance
  - Efficiency
  - Durability

* Science, 2002; MRS Bull., 2012
Ceramic TBCs

Electron-Beam Physical Vapor Deposition

Air Plasma Spraying (APS)

* Low Thermal Conductivity (ZrO$_2$ + 7 wt% Y$_2$O$_3$ Solid Soln.: 7YSZ)
* High Porosity (15 - 20%); Thickness 100 to 500 $\mu$m
* “Strain Tolerant” to Accommodate Th. Exp. Mismatch with Metal
Thermal Barrier Coatings (TBCs)

After Evans, 2009

Push for Higher Temperatures => New Materials Issues
Sources of Silicate Deposits in Aero Engines

Calcium-Magnesium-Alumino-Silicate (CMAS) Sand

* Sandstorms: ~0.1 mg/m³
  (Ansmann, et al. 2003)
* Ambient: ~0.01 mg/m³
* Runways: >1.0 mg/m³ (?)
* Sand Ingested by Engines: 1 to 100 g/h
  (Depends on Engine, Bypass Ratio...)

Damage to TBCs and Engines
Sources of Silicate Deposits in Aero Engines

Volcanic Ash CMAS

* Eyjafjallajökull Eruption in Iceland in 2010

* Shut Down of Vast European Air Space for Several Days

* Economic Loss Approaching $2B

* Conc.: No-Fly Zone: >4.0 mg/m$^3$
  Limited-Fly: 2.0-4.0 mg/m$^3$
  Unrestricted: <2.0 mg/m$^3$
  (Sultana, 2010)

Damage to TBCS and Engines

Photo: P. Greenfield
Sources of Silicate Deposits in Power Engines

* USA Electricity Generation by Source in 2012

* USA Total ~4,000 Billion KWh
  (World ~20,000 Billion KWh)

Need for Environmentally Responsible, Efficient Way of Using Available Coal

http://www.eia.doe.gov/fuelelectric.html
Sources of Silicate Deposits in Power Engines

Fly Ash CMAS
- Syngas Produced from Abundant Coal + H₂O
- CO₂ Capture/Sequester
- IGCC Plants Highly Efficient (~55%)
- H₂-Rich Syngas-Fired: Higher Temps., Water
  - F-Class: 1370 °C
  - H-Class: 1430 °C
  - J-Class: 1480 °C
  - X-Class: 1700 °C
- Syngas has Fly Ash (0.4 mg/m³) (R. Wenglarz)
- Amb. Dust (0.01-0.1 mg/m³)
- Kgs/day

Damage to TBCs and Engines

Integrated Gasification Combined Cycle (IGCC)

C + 2H₂O → CO₂ + 2H₂

Coal, Biomass, Tar

Raw Syngas

Flue Gases

Heat Recovery Steam Generator

Steam Turbine

Generator

Electricity

Gas Turbine

DoE FutureGen

Sequester or Use CO₂

Mercury Sulfur

Oxygen

Purified Syngas

Removal

CO₂

OxygenGas

OxygenElectricity

OxygenHot Exhaust Gases

OxygenHeat Recovery Steam Generator

OxygenFlue Gases
IGCC Power Plants

Tampa Electric, FL, USA

Wabash River, IN, USA

Kemper, MS, USA

Boundary Dam, Canada

DoE
Sources of Silicate Deposits in Power Engines

Fly Ash (Lignite) Injection Tests on Hot Vanes (without TBC)

1010 °C
1 h Fly Ash Injection

1066 °C
0.5 h Fly Ash Injection

J. Bons
Thermo-Chemo-Mechanical Damage of TBCs

Accumulation → Melting → Penetration, Exfoliation → Loss of Strain Tolerance

GE (R. Darolia)  DoD (R. Kowalik)  Krämer et al., 2008  DoE (R. Wenglarz)
Molten Silicates Damage to APS 7YSZ TBCs

Air Plasma Spray (APS)
7 wt% $Y_2O_3$ Stabilized ZrO$_2$ (7YSZ) TBC

Substrate 30 µm

Plasma Jet (10,000 K, 130 m.s$^{-1}$)

Powder Injection

1” Diam.

7YSZ $t'$ phase has high toughness due to reversible ferroelastic toughening.

S. Sampath

Chevalier et al. 2009
Major CMAS Compositions

Composition (mol% Cation Basis)

Average Earth's Crust
Saudi Sand
Airport Runway Sand
Mt. St. Helen's Volcanic Ash
Eyjafjallajökull Volcanic Ash
Subbituminous Fly Ash
Bituminous Fly Ash
Lignite Fly Ash
Simulated CMAS Sand

After Levi et al., 2012
Remelted Lignite Fly Ash (CMAS)

* Remelted (1500 °C) Lignite Fly Ash (Ball-Milled): Glass Powder
* Glass Transition -> Surface Crystallization -> Crystallization -> Melting
* Fully Molten at 1350 °C; Refreezes as Bulk Glass
* TBC/CMAS Experiments at ~1350 °C to Ensure Molten Glassy CMAS
APS 7YSZ TBCs Interactions with Fly Ash CMAS

CMAS Fly Ash (30 mg.cm⁻²)

APS 7YSZ Free-Standing TBC

Heat-Treatment 1340 °C, 24 h

TBC Fully Penetrated
### APS 7YSZ TBCs Interactions with Fly Ash CMAS

**Near Top**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom %</th>
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<td>Na</td>
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<td>Fe</td>
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<td>Y</td>
<td>3</td>
</tr>
<tr>
<td>Zr</td>
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</tr>
</tbody>
</table>

**EDS Composition Atom % Cation Basis**

- Y: 9, Zr: 91
- Si: 2, Ca: 3, Fe: 1, Zr: 84

**Near Bottom**

<table>
<thead>
<tr>
<th>Element</th>
<th>Atom %</th>
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<tbody>
<tr>
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<td>Y</td>
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<tr>
<td>Zr</td>
<td>49</td>
</tr>
</tbody>
</table>

- Na: 2, Mg: 4, Al: 14, Si: 29, Ca: 18, Fe: 2, Y: 4, Zr: 27

**t-ZrO₂**

**m-ZrO₂**
CMAS Damage Mechanisms in 7YSZ

* CMAS Melts into a Glass
* Infiltrates Pores/Cracks
* Penetrates 7YSZ Grain Boundaries
* Dilatation and Exfoliation
* Reaction Between CMAS and 7YSZ: Dissolution of Some $t'$-7YSZ, Reprecipitation as Y-Depleted $m$-ZrO$_2$ and $t$-ZrO$_2$, Glass Y-Enriched
* Little Effect on Glass Composition with Small Amount of Solute (Y$_2$O$_3$) in TBC: Y:Zr :: 0.083:1

Optimized 7YSZ TBCs
Not Suitable for Repelling CMAS Attack
CMAS Damage Mitigation Approach

* Vigorous Reaction Between TBC and CMAS

* Large Amount of Solute in ZrO$_2$-Based TBC: Solute:Zr :: 1:1 (cf. Y:Zr :: 0.083:1 in 7YSZ)

* Rapid Accumulation of Solute in CMAS Glass Over Short Penetration Depth

* Crystallization of Modified CMAS

* Refractory Crystallized Phases Seal TBC

* Arrest of CMAS Front
TBC/CMAS Reactivity: Optical Basicity (Λ) Concept

* Used in Glass Science to Determine Chemical Reactivity (Duffy et al.)
* Based on Lewis Acid-Base Theory
* Ability of O^{2-} to Donate Electrons
* Depends on the Polarizability of the Cation(s)
* Measured Using UV-Spectroscopy, XPS, Refractivity, Electronegativity
* Λ = X_A × Λ_A + X_B × Λ_B + X_C × Λ_C + ...

* Reactivity Between Oxides Proportional to ΔΛ: Large ΔΛ TBC/CMAS

Duffy; Dimitrov and Sakka
Major CMAS Compositions: Optical Basicities

After Levi et al., 2012
CMAS Damage Mitigation Approach: Optical Basicity and “Model” Study

* Effects of “Solute” Type and Concentration in TBC Ceramics
  - Ionic Radii: $\text{Gd}^{3+} > \text{Y}^{3+} > \text{Yb}^{3+}$
  - Concentration: Low and High

<table>
<thead>
<tr>
<th>TBC Compositions</th>
<th>Solute:Zr Ratio</th>
<th>$\Lambda$</th>
<th>$\Delta\Lambda$ (Fly Ash $\Lambda$ 0.63)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7YSZ</td>
<td>0.083:1</td>
<td>0.87</td>
<td>0.24</td>
</tr>
<tr>
<td>6.8GdSZ</td>
<td>0.083:1</td>
<td>0.88</td>
<td>0.25</td>
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<tr>
<td>$\text{Y}_2\text{O}_3.2\text{ZrO}_2$</td>
<td>1:1</td>
<td>0.92</td>
<td>0.29</td>
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<tr>
<td>$\text{Gd}_2\text{Zr}_2\text{O}_7$</td>
<td>1:1</td>
<td>1.00</td>
<td>0.37</td>
</tr>
<tr>
<td>$\text{Yb}_2\text{Zr}_2\text{O}_7$</td>
<td>1:1</td>
<td>0.89</td>
<td>0.26</td>
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High Reactivity Between TBCs and Fly Ash CMAS Expected
TBC Ceramics/CMAS Interactions: “Model” Study

* Effects of “Solute” Type and Concentration in TBC Ceramics

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<td>6.8GdSZ</td>
<td>0.083:1</td>
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<tr>
<td>$\text{Y}_2\text{O}_3\cdot2\text{ZrO}_2$</td>
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</tr>
<tr>
<td>$\text{Gd}_2\text{Zr}_2\text{O}_7$</td>
<td>1:1</td>
</tr>
<tr>
<td>$\text{Yb}_2\text{Zr}_2\text{O}_7$</td>
<td>1:1</td>
</tr>
</tbody>
</table>

* Partially Sintered Ceramic Pellets (~15% Porosity)

* Sand CMAS Glass: $\Lambda = 0.63$

Acta Mat. 2012
TBC Ceramics/CMAS Glass Interactions

7YSZ
3.9 m% Y2O3
Y:Zr::0.08:1

Y2O3·2ZrO2
33.3 m% Y2O3
Y:Zr::1:1

6.8GdSZ
3.9 m% Gd2O3
Gd:Zr::0.08:1

Gd2Zr2O7
33.3 m% Gd2O3
Gd:Zr::1:1

Yb2Zr2O7
33.3 m% Yb2O3
Yb:Zr::1:1
TBC Ceramics/CMAS Interactions

1200 °C; 24 h

Measured Cation(s):Zr Atomic Ratio in Pellet

* Solute Concentration Most Effective
* At High Conc.: Gd < Yb < Y in Effectiveness
* Almost Complete Suppression in $Y_2O_3\cdot2ZrO_2$

Acta Mat. 2012
Gd$_2$Zr$_2$O$_7$

Primary Crystallized Phase in Arrest Region:
Ca$_2$Gd$_8$(SiO$_4$)$_6$O$_2$

Acta Mat. 2012
$\text{Y}_2\text{O}_3.2\text{ZrO}_2(\text{ss})$

Primary Crystallized Phase in Arrest Region: $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{O}$

$\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{O}$

$c\text{-ZrO}_2(\text{ss})$

$\text{Y}_2\text{O}_3.2\text{ZrO}_2(\text{ss})$

Acta Mat. 2012
Yb$_2$Zr$_2$O$_7$

Primary Crystallized Phase in Arrest Region:
\[ \text{Ca}_4\text{Yb}_6(\text{SiO}_4)_6\text{O} \]

Yb$_2$Zr$_2$O$_7$

\[ [021] \]

\[ [103] \]

\[ 40 \mu m \]

Acta Mat. 2012
TBC Ceramics/CMAS Interactions

XRD of Powder Mixtures (50:50) Heat-Treated at 1200 °C, 24 h

Acta Mat. 2012
Silicate Apatites

* $\text{Gd}_2\text{Zr}_2\text{O}_7$
  - Forms $\text{Ca}_2\text{Gd}_8(\text{SiO}_4)_6\text{O}_2$
  - $\text{A}^\text{I}$: All (2) $\text{Ca}^{2+}$ + 2 $\text{Gd}^{3+}$
  - $\text{A}^\text{II}$: 6 $\text{Gd}^{3+}$
  - $(\text{Ca}_2\text{Gd}_2)\text{Gd}_6(\text{SiO}_4)_6\text{O}_2$
  - Need 8 Gd Atoms

* $\text{Y}_2\text{O}_3\cdot 2\text{ZrO}_2(\text{ss})$
  - Forms $\text{Ca}_4\text{Y}_6(\text{SiO}_4)_6\text{O}$
  - $\text{A}^\text{I}$: All (4) $\text{Ca}^{2+}$
  - $\text{A}^\text{II}$: All (6) $\text{Y}^{3+}$
  - Need 6 Y Atoms

* $\text{Yb}_2\text{Zr}_2\text{O}_7$
  - Forms $\text{Ca}_4\text{Yb}_6(\text{SiO}_4)_6\text{O}$
  - $\text{A}^\text{I}$: All (4) $\text{Ca}^{2+}$
  - $\text{A}^\text{II}$: All (6) $\text{Yb}^{3+}$
  - Need 6 Yb Atoms, But Apatite Crystallization Propensity Decreases with RE Size

(Quintas et al., 2008)

\[ \text{A}^\text{I} \quad \text{A}^\text{II} \quad 6(\text{SiO}_4)_6\text{O}_x \]

<table>
<thead>
<tr>
<th>Cation “A”</th>
<th>$\text{A}^\text{I}$ Site (pm)</th>
<th>$\text{A}^\text{II}$ Site (pm)</th>
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<tbody>
<tr>
<td>Lu$^{3+}$</td>
<td>103</td>
<td>-</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>104</td>
<td>93</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>106</td>
<td>95</td>
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<tr>
<td>Y$^{3+}$</td>
<td>108</td>
<td>96</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>111</td>
<td>100</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>113</td>
<td>102</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>116</td>
<td>-</td>
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<tr>
<td>Ca$^{2+}$</td>
<td>118</td>
<td>106</td>
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<tr>
<td>Ce$^{3+}$</td>
<td>120</td>
<td>107</td>
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<tr>
<td>La$^{3+}$</td>
<td>122</td>
<td>110</td>
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</table>

Harder to Crystallize Apatite

Need More RE$^{3+}$ to Form Apatite

Shannon, 1976

* Acta Mat. 2012
$Y_2O_3.2ZrO_2(\text{ss})$ APS TBCs

Jacobson et al., 2004
**Y_{2}O_{3}.2ZrO_{2}(ss) APS TBCs**

**Single-Phase Cubic (Fluorite)**

- Data
- Fit

\[ a = 5.2105(4) \text{ Å} \]

- Porosity: 11.4%
- Thickness: \( \approx 300 \text{ μm} \)

**Thermal Conductivity (W/m·K)**

\[ \text{Temperature (°C)} \]

- 7YSZ (Wang et al. 2010)

In Collaboration with Prof. S. Sampath
$Y_2O_3\cdot 2ZrO_2(ss)$ APS TBCs: Fly Ash CMAS

CMAS Fly Ash (30 mg.cm$^{-2}$)

1340 °C, 24 h

Fly Ash CMAS Penetration ~17%
Y$_2$O$_3$.2ZrO$_2$(ss) APS TBCs: Fly Ash CMAS

EDS Composition
Atom % Cation Basis

<table>
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<th>Element</th>
<th>Atom %</th>
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<tr>
<td>Y</td>
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<tr>
<td>Zr</td>
<td>42</td>
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$Y_2O_3.2ZrO_2$ (ss) APS TBCs: Fly Ash CMAS

c-ZrO$_2$(ss) Apatite
Y$_2$O$_3$.2ZrO$_2$(ss) APS TBCs: Fly Ash CMAS

Primary Phases in Arrest Region:
Apatite + c-ZrO$_2$(ss)

<table>
<thead>
<tr>
<th>At.% ($\Lambda$)</th>
<th>Ca</th>
<th>Si</th>
<th>Y</th>
<th>Zr</th>
<th>Al</th>
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<td>50</td>
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<td>Apatite (0.72)</td>
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<td>25</td>
<td>37.5</td>
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<td>Z-1 (0.90)</td>
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Y$_2$O$_3$.2ZrO$_2$(ss): Fly Ash CMAS

XRD of Powder Mixture (50:50)  
Heat-Treated at 1340 °C, 24 h

\[
\begin{align*}
\text{Intens. (arb. units)} \\
\text{2θ (deg.)}
\end{align*}
\]

- c-ZrO$_2$(ss) (Fluorite)
- Ca$_4$Y$_6$(SiO$_4$)$_6$O (Apatite)
- Y$_2$Al$_5$O$_{12}$ (Garnet)
Fly Ash CMAS Damage Mitigation Approach

* Vigorous Reaction Between TBC and Fly Ash CMAS
* Large Amount of Solute in \( \text{Y}_2\text{O}_3\cdot 2\text{ZrO}_2 \) (ss): \( \text{Y} : \text{Zr} :: 1:1 \) (cf. \( \text{Y} : \text{Zr} :: 0.083:1 \) in 7YSZ)
* Rapid Accumulation of Solute in CMAS Glass Over Short Penetration Depth
* Crystallization of Modified CMAS
* Refractory Crystallized Phases (e.g. Apatite) Seal TBC
* Arrest of CMAS Front
Thermo-Chemo-Mechanical Testing

* Arrest of Penetrating Front
* Still ~17% TBC Thickness Penetrated: Stiffer Glaze
* Partial Loss of Strain Tolerance: TBC Spallation
* Conventional Furnace Cyclic Testing
Conventional Furnace Cyclic Testing

* Maximum Temperature Limited by Substrate

\[ \Delta T_{\text{sur}} - \Delta T_{\text{sub}} = 0 \]
Thermal-Gradient Cyclic Testing

* Substrate at Lower Temperature

Δₜₜₚ > 0

Temperature

Δₜₜₚ Δₜₖₜ

Tₘₜₚ Tₖₜ

Tₜₚ Tₖₜ

Δₜₜₚ Tₜₖₜ Δₜₖₜ

Time

Δₜₜₚ - Δₜₖₜ > 0
Mechanics & Testing of Deposits-Penetrated TBCs

\[ G_{IC} = 30 \text{ J/m}^2; \ \lambda = 0.25; \text{ Deep Delamination} \]

\[ \Delta T_{sur} - \Delta T_{sub} \ (\degree C) \]

\[ \Delta T_{sub} \ (\degree C) \]

\[ h/H = 0.5, 0.3, 0.2 \]

No Thermal Gradient: Spontaneous Failure

Conventional Furnace Cyclic Testing Not Suitable

Model by Evans and Hutchinson, 2007
Ongoing and Future Work

* $Y_2O_3\cdot2ZrO_2$ (ss) Toughness $\sim15$ J.m$^{-2}$
* $7YSZ$ Toughness $\sim30$ J.m$^{-2}$ ($t'$-ZrO$_2$ Ferroelastic Toughening)
* Exploit High Toughness of $7YSZ$ Near Metal/Ceramic Interface
* Bi-Layer APS $Y_2O_3\cdot2ZrO_2$-$7YSZ$ TBCs
  - CMAS-Resistant Top Layer, High Toughness Bottom Layer

* Testing of Bi-Layer TBCs and $7YSZ$ TBCs
  - Gradient Rig
  - Fly Ash CMAS and Water Injection

* Characterization of Tested TBCs
  - Understanding of Damage and Mitigation Mechanisms

* Characterization of Tested TBCs
$\text{Y}_2\text{O}_3.2\text{ZrO}_2(ss)$-7YSZ Bi-Layer APS TBCs

![SEM and Y Map images with EDS Composition tables]

<table>
<thead>
<tr>
<th></th>
<th>Atom % Cation Basis</th>
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<tbody>
<tr>
<td>Y</td>
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<tr>
<td>Zr</td>
<td>47</td>
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</table>
Outlook

Need Resistance to CMAS in TBCs, EBCs

Evans, 2008
CMAS-Resistant EBCs

* Dense Coatings; Good CTE Match with CMCs; High-Temp. Stability
* Optical Basicity (OB) Concept Could be Applied to EBCs
* No Reactivity Between CMAS and EBC: Opposite of TBCs Case
* Match OBs of EBCs and Expected CMAS
* Water Vapor Causes Si-Depletion, Increases CMAS Λ: Dynamic

<table>
<thead>
<tr>
<th>EBC</th>
<th>Λ</th>
<th>ΔΛ (Fly Ash Λ 0.63)</th>
<th>Reference</th>
</tr>
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<tr>
<td>Y₄Al₂O₉</td>
<td>0.87</td>
<td>0.24</td>
<td>Fu et al., 2011</td>
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<tr>
<td>Gd₄Al₂O₉</td>
<td>0.99</td>
<td>0.36</td>
<td>Fu et al., 2011</td>
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<td>YAIO₃</td>
<td>0.80</td>
<td>0.17</td>
<td>Hazel et al., 2008</td>
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<td>GdAlO₃</td>
<td>0.89</td>
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<td>Fu et al., 2011</td>
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<td>Y₂SiO₅</td>
<td>0.79</td>
<td>0.16</td>
<td>Grant et al., 2010</td>
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<td>Yb₂SiO₅</td>
<td>0.76</td>
<td>0.13</td>
<td>Toohey et al., 2011</td>
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<td>Y₂Si₂O₇</td>
<td>0.70</td>
<td>0.07</td>
<td>Ahlborg et al., 2013</td>
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<td>Yb₂Si₂O₇</td>
<td>0.68</td>
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<td>Sc₂Si₂O₇</td>
<td>0.66</td>
<td>0.03</td>
<td>Liu et al., 2013</td>
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</table>
Summary

* Molten CMAS attack of TBCs is a growing issue with rising temperatures in both aero and power gas-turbine engines.
* 7YSZ TBCs are not well-suited to repel fly ash CMAS attack.
* The Optical Basicity concept can be used to screen CMAS-resistant TBC compositions.
* “Model” experiments indicate that high “solute” content, especially Y³⁺, in TBCs is necessary for mitigation of attack. Other TBC ceramics?
* Demonstrated processing and fly ash CMAS-resistance of Y₂O₃.2ZrO₂ APS TBCs
* Gradient testing is necessary to capture thermo-chemo-mechanical response of partially-penetrated TBCs.
* Optimization of CMAS resistance and other required properties in TBCs is necessary: bi-layer TBCs.
* The Optical Basicity concept could be applied to screening CMAS-resistant EBC compositions.
* Resistance to molten CMAS will remain a challenge as gas-turbine engine operating temperatures continue to increase.
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