Degradation of TBC Systems in Environments Relevant to Advanced Gas Turbines for IGCC Systems

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DOE PROGRAM: DE-FOA-0000459

Seth Lawson, Program Manager, DOE/NETL

Project Awarded 10/01/2011 (36 months duration)
Integrated Gasification Combined Cycle

IGCC Process

Sources of Deposits:
- Ambient air passing through turbine
- Upstream components
- Fuel source (coal)

Thermal Barrier Coatings used in **hottest sections** of turbines

TBCs subjected to **deposits** and multi-oxidant **gas environments**

$$O_2 + CO_2 + H_2O + SO_2 \ldots$$

Comparison of Typical Deposits

- Engine deposits in combustion turbines contain oxides similar to CMAS
- Variability due to location and fuel source (coal, syngas, ng)
- Coal and IGCC ash also contain sulfates that will be liquid

Typical IGCC Fly-Ash

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>56</td>
<td>19</td>
<td>3.2</td>
<td>5</td>
<td>0.7</td>
<td>0.04</td>
<td>0.7</td>
<td>0.6</td>
<td>4.1</td>
<td>0.6</td>
<td>3.3</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Example of Commercial Fly Ash

Class C Fly ash

Composition (wt. %)

As reported:

<table>
<thead>
<tr>
<th>Element</th>
<th>wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>26.4</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.1</td>
</tr>
<tr>
<td>CaO</td>
<td>33.4</td>
</tr>
<tr>
<td>MgO</td>
<td>8.0</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.4</td>
</tr>
</tbody>
</table>

From Boral Material Technologies
Source: Plant Scherer, GA (pulverized coal)
Reactions of Fly Ash with YSZ

YSZ isothermal exposure to “class C” ash in dry air.

Melted ash has severely degraded the YSZ

Composition (wt. %)

- SiO$_2$: 26%
- Al$_2$O$_3$: 20%
- Fe$_2$O$_3$: 6%
- CaO: 33%
- MgO: 8%
- Na$_2$SO$_4$: 5%
- K$_2$SO$_4$: 1%

Some infiltration of ash constituents, partial melting

1300 °C, 100h

1200 °C, 24h

1100 °C, 100h

“$T_m$”
Main Aims of Present Study

• Determine the effects of fly-ash deposits at temperatures below ash liquidus.

• Systematically assess the interplay between prototypical deposit chemistries (i.e., ash oxide and sulfate constituents) and environmental oxidants (i.e., $O_2$, $H_2O$ and $CO_2$) on the high-temperature degradation behavior of advanced TBC systems.

• Determine the combined effects of deposit-induced attack at relatively low temperatures on TBC performance.

• Establish reliable test procedures for assessing deposit-induced degradation of TBCs in different gas atmospheres.
Two TBC Systems Studied

Provided by Praxair Surface Technologies, a collaborator on this project

- **Low Density (HP-LD)**
  - Substrate: 2nd generation Ni-base single crystal superalloy (René N5 or PWA 1484)
  - Bond Coat: NiCoCrAlY (Ni-22Co-16Cr-13Al-0.5Y wt.%) applied by Ar-shrouded plasma spraying at PST
  - TBC: Standard YSZ composition – 7wt.%Y₂O₃ – deposited by APS at thickness of ~380 µm

- **Dense Vertically Cracked (DVC)**
  - Vertical Cracks

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Substrate: 2nd generation Ni-base single crystal superalloy (René N5 or PWA 1484)

Bond Coat: NiCoCrAlY (Ni-22Co-16Cr-13Al-0.5Y wt.%) applied by Ar-shrouded plasma spraying at PST

TBC: Standard YSZ composition – 7wt.%Y₂O₃ – deposited by APS at thickness of ~380 µm
Experimental Setup

**Thermal Cycling Experimental Setup**

**Isothermal Testing at 1100°C:** *Free-standing YSZ*
- Reactions between YSZ/deposit
- Phase transformation in YSZ

**Cyclic Testing between 1100°C/160°C:** *DVF and HPLD TBCs*
- Early failure from fly-ash
- Atmospheric Effects

**Gas Atmospheres:**
- Dry Air
- Air+steam
Testing of 7YSZ top coat

High-CaO Ash
• Reaction with YSZ
• Additions of sulfate
• Cyclic failure of TBCs

High SiO₂-Ash
YSZ Reaction with Synthetic Ash

Dry Air exposures at 1100°C, 72h

Increasing CaO

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Wt%</th>
<th>Oxide</th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50</td>
<td>SiO₂</td>
<td>10</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>25</td>
<td>Al₂O₃</td>
<td>5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10</td>
<td>Fe₂O₃</td>
<td>2</td>
</tr>
<tr>
<td>MgO</td>
<td>5</td>
<td>MgO</td>
<td>1</td>
</tr>
<tr>
<td>CaO</td>
<td>10</td>
<td>CaO</td>
<td>82</td>
</tr>
</tbody>
</table>

Reaction product predominantly **CaZrO₃**

Same reaction with pure CaO and high-CaO ash
Consequences of CaZrO$_3$

Thermal Cycling in lab air with CaZrO$_3$ layer

200 Cycles: 45min hold at 1100°C, 10min cool to 45°C

- TBC reacted with CaO isothermally for 72h, then tested in cyclic furnace
- Very little spallation of CaZrO$_3$ layer at YSZ surface
- No significant overall affect on TBC performance
Testing of 7YSZ top coat

**High-CaO Ash**
- Reaction with YSZ
- Additions of sulfate
- Cyclic failure of TBCs

High SiO$_2$-Ash
Synthetic Ash with/without Addition

- Found that it is mainly CaO from fly-ash that reacts directly with YSZ
- Fly ash typically contains sulfates

Reactions in dry air at 1100°C, 72h

Addition of $K_2SO_4$ to synthetic ash causes infiltration of Ca into YSZ
Synthetic Ash + $K_2SO_4$ Addition

Free-standing DVC YSZ, reacted for 72h, 1100°C in dry air

**Ash Composition**

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>K$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>63</td>
<td>16.2</td>
<td>8.1</td>
<td>1.8</td>
<td>0.9</td>
<td>10</td>
</tr>
</tbody>
</table>
Consequence of Infiltration

Thermal Cycling in Lab Air
140 Cycles: 45min hold at 1100°C, 10min cool to 45°C

High-CaO Deposit without K₂SO₄

High-CaO Deposit with K₂SO₄

Early failure of DVC TBC caused by infiltration of top coat
Reaction with CaO+K$_2$SO$_4$

Free-standing DVC YSZ reacted with CaO+50wt%K$_2$SO$_4$, 1100°C, in dry air

- Short times: CaO and K$_2$SO$_4$ both infiltrate
- Longer times: Loss of K$_2$SO$_4$, CaO reacts with YSZ
Reaction with CaO+K\textsubscript{2}SO\textsubscript{4} 

70h Dry Air Exposures at 1100°C 

0.1\text{CaO}-0.90\text{K}_2\text{SO}_4 

0.5\text{CaO}-0.5\text{K}_2\text{SO}_4 

- Very low solubility of CaO in liquid K\textsubscript{2}SO\textsubscript{4} 
- Increased CaO in deposit correlates with increased CaZrO\textsubscript{3} penetration 
- Suggests CaO carried in suspension with liquid K\textsubscript{2}SO\textsubscript{4}
Testing of 7YSZ top coat

**High-CaO Ash**
- Reaction with YSZ
- Additions of sulfate
- **Cyclic failure of TBCs**

**High SiO₂-Ash**
TBC Failure after Cyclic Exposure

How does infiltration of CaZrO$_3$ affect **TBC performance**?

Thermal Cycling in dry air: 45min at 1100°C/15min at 160°C

<table>
<thead>
<tr>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>K$_2$SO$_4$</td>
</tr>
<tr>
<td>FeS</td>
</tr>
</tbody>
</table>

“High-CaO”
Ash+$0.05$K$_2$SO$_4$+$0.05$FeS

**DVC TBC Failure with deposit**

**DVC TBC Failure without deposit**
TBC Failure after Cyclic Exposure

Stress in TBC from CTE mismatch

\[ \sigma_o = E_{tbc} \frac{\Delta\alpha \Delta T}{1 - \nu} \]

Key parameters affecting stress in top coat: E, \( \alpha \), \( \Delta T \)

Typical Values

<table>
<thead>
<tr>
<th>Material</th>
<th>E (Gpa)</th>
<th>( \alpha ) (x10^{-6} C^{-1}ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>30-50</td>
<td>11-13</td>
</tr>
<tr>
<td>Metal</td>
<td>200</td>
<td>17.1</td>
</tr>
</tbody>
</table>

Free-standing YSZ heat treated 72h: 3-Pt Bend Test

No Deposit

E = 30 \pm 3 GPa

With Deposit

E = 132 \pm 19 GPa

Significant increase in elastic modulus
Contributes to overall increased stress

TBC Failure after Cyclic Exposure

TBC Degradation in HPLD Top Coat
Thermal Cycling in dry air: 45min at 1100°C/15min at 160°C

Failure Without Deposit

Failure With Deposit

CaZrO₃ Infiltration
Very Little CaZrO₃

Early Failure of TBCs from High-CaO Ash Deposit

<table>
<thead>
<tr>
<th></th>
<th>Cycles to Failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Deposit</td>
<td>1200</td>
</tr>
<tr>
<td>Deposit</td>
<td>1000</td>
</tr>
<tr>
<td>No Deposit</td>
<td>800</td>
</tr>
<tr>
<td>Deposit</td>
<td>500</td>
</tr>
</tbody>
</table>

DVC
HPLD
Testing of 7YSZ top coat

High-CaO Ash
- Reaction with YSZ
- Additions of sulfate
- Cyclic failure of TBCs

High SiO$_2$-Ash
High-SiO₂ Ash Exposed to YSZ

- Effects of lower-CaO ash that should **not** form CaZrO₃?
- Infiltrated cracks at YSZ surface contain ash constituents
- Some liquid infiltration likely

**72h Exposure in Dry Air, 1100°C**

<table>
<thead>
<tr>
<th></th>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>22.5</td>
</tr>
<tr>
<td>CaO</td>
<td>9</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9</td>
</tr>
<tr>
<td>MgO</td>
<td>4.5</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>10</td>
</tr>
</tbody>
</table>
Cyclic TBC Exposure to High-SiO\textsubscript{2} Ash

Early Failure of HPLD TBCs with “high-SiO\textsubscript{2}” ash with K\textsubscript{2}SO\textsubscript{4}.

Thermal Cycling in dry air: 45min at 1100°C/15min at 160°C.

<table>
<thead>
<tr>
<th>Wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>CaO</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
</tr>
<tr>
<td>MgO</td>
</tr>
<tr>
<td>K\textsubscript{2}SO\textsubscript{4}</td>
</tr>
</tbody>
</table>

“High-SiO\textsubscript{2}” Ash+.1K\textsubscript{2}SO\textsubscript{4}

Failure Without Deposit

With Deposit

Infiltration

No Infiltration
Summary of Top Coat Results

- Infiltration into YSZ when $K_2SO_4$ is present
- TBC degradation at temperatures below overall ash melting temperature
- Different modes of failure for DVC and HPLD top coats

![Diagram showing the relationship between YSZ substrate, deposit, CaZrO$_3$, and infiltration with different conditions of CaO and SiO$_2$.]

- High CaO Formation leads to No K$_2$SO$_4$, No Infiltration.
- High SiO$_2$ No reaction with YSZ leads to No K$_2$SO$_4$, No Reaction.
- CaZrO$_3$ Formation with K$_2$SO$_4$ leads to Infiltration.
- Similar overall effect on TBC lifetime.
- Different mechanism of infiltration.
- Early Failure
Bondcoats: corrosion-resistant metallic coatings

Overlay: MCrAlY (M=Ni,Co)
- Two-phase $\beta$-$\gamma$ structure
- Commonly used in land-based turbines for power generation


Al-rich $\beta$-phase, source of Al to form $\text{Al}_2\text{O}_3$ TGO

NiCrAl, at. %
$T = 1100 \, ^\circ\text{C}$

$\beta$-NiAl
$\gamma'$-Ni$_3$Al
$\gamma$-Ni
$\alpha$-Cr

after N. Dupin et al, Calphad 25 (2001)
MCrAlY Bondcoats – Background

Bondcoats: corrosion resistant metal coatings

Identified modes of degradation:
- air oxidation; thermal cycling
- sulfate-induced accelerated attack: type I and type II hot corrosion
- fly ash-induced corrosion

Fly ash oxide-sulfate mixtures found to cause degradation of NiCoCrAlY alloys at intermediate temperatures (900-1100 °C)

Ni-30Co-30Cr-12Al-0.1Y, 50 h at 1100 °C
CO₂-20H₂O

Class C ash (wt. %)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>26</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20</td>
</tr>
<tr>
<td>CaO</td>
<td>33</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6</td>
</tr>
<tr>
<td>MgO</td>
<td>8</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>5</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>1</td>
</tr>
</tbody>
</table>

Fly Ash Corrosion
Factors Considered in the “Bondcoat” Study

1. Experimental protocol
2. Reactivity of class C ash, effect of alloy composition
3. Reactivity of individual oxides: \textit{CaO in this presentation}
4. Interactions between oxide and sulfate constituents, and gas \( p_{SO_3} \) and temperature

Factors affecting fly-ash corrosion

Alloy
- phase compositions
- \( \gamma-\beta \) fractions
- Y content

Deposit
- sulfates
- oxides

Environment
- temperature
- gas (air vs \( CO_2-H_2O \))
- \( p_{O_2}, p_{SO_3} \)
Experimental conditions:

- Cast NiCoCrAlY alloys used in place of thermally sprayed coatings
- 50 h exposures at 900 °C and 1100 °C

Deposits:
- Class C fly ash
- Individual oxides, sulfates
- Synthetic mixtures:

<table>
<thead>
<tr>
<th>Acidic oxide</th>
<th>Basic oxide</th>
<th>Sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>CaO</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>SiO₂</td>
<td>MgO</td>
<td></td>
</tr>
</tbody>
</table>
**Mode of Reaction with Class C Ash**

1100 °C
Ni-30Co-27Cr-12Al-0.1Y

Class C ash
CO$_2$-20%H$_2$O

With no deposit, all alloys studied formed external Al$_2$O$_3$ scales in all atmospheres

CO$_2$-20%H$_2$O, no deposit, 50 h

1 h

50 h
Effect of Alloy Composition

1100 °C, 50 h
CO₂-20%H₂O

NiCoCrAl
Pseudo-ternary diagram
\( x_{\text{Co}} = 0.3 \)
\( T = 1100 \, ^{\circ}\text{C} \)

Ni-30Co-30Cr-12Al-0.1Y
\((\gamma-16\beta)\)

Ni-30Co-27Cr-16Al-0.1Y
\((\gamma-34\beta)\)

Ni-19Co-15Cr-24Al-0.1Y
\((\gamma-65\beta)\)

Extent of degradation decreases with increasing \( \beta \) fraction.
Effect of Y Content

1100 °C, 50 h
Ni-19Co-15Cr-24Al

Dry air,
No deposit

CO₂-20%H₂O,
class C ash

Number and size of Y-Al oxide pegs very sensitive to Y content.
Significant degradation of “overdoped” alloy in the presence of ash deposit.
Factors Considered in the Study

1. Experimental protocol
2. Reactivity of class C ash, effect of alloy composition
3. **Reactivity of individual oxides**: CaO
4. Interactions between oxide and sulfate constituents, and gas $p_{SO_3}$ and temperature

Factors affecting fly-ash corrosion

**Alloy**
- phase compositions
- $\gamma$-$\beta$ fractions
- Y content

**Deposit**
- sulfates
- oxides

**Environment**
- temperature
- gas (air vs $CO_2-H_2O$)
- $p_{O_2}$, $p_{SO_3}$
Exposure to Individual Oxides

Ni-19Co-16Cr-23Al-0.1Y (γ-65β)
1100 °C, 50 h
dry air

Thermally grown Al₂O₃ reacts at a significant rate with CaO and MgO
Exposure to CaO in Dry Air

Reaction with CaO: two distinct processes

Transient stage: reaction rate much higher for low $\beta$ fraction.

Steady-state: reaction rate similar for both alloys, higher than in the absence of CaO deposit.
Exposure to CaO in dry air

Reaction with CaO: two distinct processes

1100 °C, 50 h

**Low β alloys**

Ni-30Co-33Cr-12Al-0.1Y (γ-18β)

Reaction rate decreases when alloy passivates.

**High β alloys**

Ni-19Co-16Cr-23Al-0.1Y (γ-65β)

Steady-state reaction of CaO with TGO to form xCaO-yAl₂O₃ layers; minimal alloy consumption.
Exposure to CaO in Dry Air

Ni-30Co-33Cr-12Al-0.1Y (γ-18β) 1100 °C

CaO-Cr₂O₃ phase diagram

eutectic at 1061 °C

γ composition (at. %):

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>23</td>
<td>32</td>
<td>37</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Reaction CaO-Cr₂O₃ to form a liquid


Ni-30Co-33Cr-12Al-0.1Y (γ-18β)

γ composition (at. %):

<table>
<thead>
<tr>
<th></th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td>32</td>
<td>37</td>
<td>8.2</td>
</tr>
</tbody>
</table>

→ as γ is consumed, Al is rejected until Al₂O₃ can form
Exposure to CaO in dry air

Susceptibility to transient attack determined by distribution of Cr-rich $\gamma$ phase in alloy

- **low $\beta$ alloy**
  - transient $\text{Cr}_2\text{O}_3$
  - $\gamma$ connected
  - highly susceptible to transient attack

- **high $\beta$ alloy**
  - transient $\text{Cr}_2\text{O}_3$
  - $\gamma$ isolated
  - non-susceptible to transient attack

Transient attack extremely severe for 100% $\gamma$ alloy

Ni-33Co-35Cr-7Al-0.1Y, 50 h at 1100 °C

$> 150 \mu m$

no passivation

50 μm

In service conditions (thermal cycles), reaction product spallation will cause transient stage to be repeated.
Exposure to CaO in Dry Air

Ni-19Co-16Cr-23Al-0.1Y
(γ-65β)

50 h, 1100 °C

How does Al₂O₃ reaction to form xCaO-yAl₂O₃ affect Al consumption?
Kinetics of $\text{Al}_2\text{O}_3$ formation-destruction

$\text{Al}_2\text{O}_3$ growth rate equation:

$$\frac{dX}{dt} = \frac{p}{2X} - \alpha \frac{q}{2\sqrt{qt}}$$

Analytical solution:

$$X^2 = kt$$
$$k = \frac{1}{2} \left[ 2p + \alpha^2 q - \alpha \sqrt{4p + \alpha^2 q} \right]$$

CaO deposit: enhanced Al consumption → decreased lifetime

Example:
190 µm bondcoat
Time for $\beta$ depletion through half-thickness
No deposit: 31,000 h
CaO: 16,000 h
i.e., 48 % reduction
Factors Considered in the Study

1. Experimental protocol
2. Reactivity of class C ash, effect of alloy composition
3. Reactivity of individual oxides: CaO
4. Interactions between oxide and sulfate constituents, and gas $p_{SO_3}$ and temperature

Factors affecting fly-ash corrosion
Role of Ash Oxide and Sulfate Contents

1100 °C

Synthetic C-ash

C-ash with no sulfates

Sulfates only (Na$_2$SO$_4$)

<table>
<thead>
<tr>
<th>Class C ash (wt. %)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>Na$_2$SO$_4$</th>
<th>K$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>26</td>
<td>20</td>
<td>33</td>
<td>6</td>
<td>8</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

Ni-30Co-30Cr-12Al-0.1Y CO$_2$-20%H$_2$O

Ni-30Co-30Cr-12Al-0.1Y dry air

Ni-30Co-27Cr-12Al-0.1Y dry air

Combination of sulfates and oxides is needed to cause alloy degradation.
Deposit reactivity at 1100 °C

1100 °C
CO$_2$-20H$_2$O-1.6O$_2$
Ni-30Co-27Cr-12Al-0.1Y

Al$_2$O$_3$-30%CaO

Formation of xCaO-yAl$_2$O$_3$ layers

Al$_2$O$_3$-30%CaO-10%SiO$_2$-10%Na$_2$SO$_4$

Breakaway and repassivation; similar to class C ash reaction

Acidification of Na$_2$SO$_4$ melt by SiO$_2$ probable cause of Al$_2$O$_3$ failure
**Effect of $p_{SO_3}$ at 1100 °C**

1100 °C
Al$_2$O$_3$-CaO

CO$_2$-H$_2$O-O$_2$ $\rightarrow$ O$_2$-0.1SO$_2$

Consumption of Al$_2$O$_3$:

$$x\text{Al}_2\text{O}_3 + y\text{CaO} = C_xA_y$$

CaSO$_4$ = CaO + SO$_3$

$\rightarrow$ CaO is not stable in O$_2$-0.1SO$_2$
Effect of $p_{SO_3}$ at 1100 °C

$1100 \, ^{\circ}C$

$Al_2O_3-CaO$

$CO_2-H_2O-O_2 \rightarrow O_2-0.1SO_2$

- $CaSO_4 \rightarrow Al_2O_3$
- ash + Cr, Co oxide

Effect of $p_{SO_3}$ at 1100 °C

$CaSO_4 + 6Al_2O_3 = CA_6 + SO_3$

$3CaSO_4 + Al_2O_3 = C_3A + 3SO_3$

$CaSO_4 + Al_2O_3 = CA + SO_3$

$\rightarrow CaSO_4$ is more stable than the aluminates (i.e., CaO is neutralized)
Effect of Temperature on CaO Reactivity

CO$_2$-20H$_2$O-1.6O$_2$
Al$_2$O$_3$-CaO
Ni-30Co-27Cr-12Al-0.1Y

1100 °C

$\text{C}_x\text{A}_y$ layers + continuous Al$_2$O$_3$ → alloy passivated

Mixed oxides + Al$_2$O$_3$ protrusions → no passivation

900 °C
Kinetics of $\text{Al}_2\text{O}_3$–CaO Reaction

Net growth rate of $\text{Al}_2\text{O}_3$

$$\frac{dX}{dt} = \frac{p}{2X} - \alpha \frac{q}{2\sqrt{qt}} \quad \rightarrow \quad \begin{cases} X^2 = kt \\ k = \frac{1}{2} [2p + \alpha^2 q - \alpha \sqrt{q(4p + \alpha^2 q)}] \end{cases}$$

$p$: parabolic constant for pure oxidation, from TGA with no deposit
$q$: parabolic growth rate of $C_xA_y$, from thickness measurements

Minimum Al concentration to sustain $\text{Al}_2\text{O}_3$ growth (Wagner’s analysis)

$$j_{\text{alloy}} = \frac{N_{\text{Al}}^0 - N_{\text{Al}}^i}{V_{\text{alloy}}} \sqrt{\frac{D_{\text{Ni}}}{\pi t}} \\ j_{\text{oxide}} = \frac{1}{V_{\text{oxide}}} \sqrt{\frac{k}{2t}}$$

$$j_{\text{Al}}^{\text{alloy}} = j_{\text{Al}}^{\text{oxide}}$$

$$N_{\text{Al}}^0 = \frac{2V_{\text{alloy}}}{V_{\text{oxide}}} \sqrt{\frac{\pi k}{2D_{\text{Ni}}}}$$

limiting case $N_{\text{Al}}^i = 0$
Kinetics of $\text{Al}_2\text{O}_3$–$\text{CaO}$ Reaction

$\text{CO}_2$-$\text{H}_2\text{O}$-$\text{O}_2$

$\text{Al}_2\text{O}_3$-$30\%$CaO

1100 °C $\rightarrow$ 900 °C

Alloy composition: Ni-30Co-27Cr-12Al-0.1Y

<table>
<thead>
<tr>
<th>(at. %)</th>
<th>1100 °C $\alpha$-$\text{Al}_2\text{O}_3$</th>
<th>900 °C (extrapolated) $\alpha$-$\text{Al}_2\text{O}_3$</th>
<th>$\theta$-$\text{Al}_2\text{O}_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_{\text{Al}}^0$ min</td>
<td>1.4</td>
<td>0.3</td>
<td>11.1</td>
</tr>
<tr>
<td>$N_{\text{Al}}^0$ in $\gamma$</td>
<td>9.9</td>
<td>6.3</td>
<td></td>
</tr>
</tbody>
</table>

graph adapted from H.J. Grabke, Intermetallics 7 (1999)
Deposit Reactivity at 900 °C

900 °C
O_2-0.1SO_2
Ni-30Co-27Cr-12Al-0.1Y

Al_2O_3-30%CaO

CaSO_4 is more stable than all aluminates → Al_2O_3 consumed via different reaction path (sulfate-induced but solid-state) Calcium sulfo-aluminate involved?

Mixed oxide + Ca, S
Summary and Conclusions

• Reaction with CaO at 1100 °C
  - transient stage: formation of liquid Ca-Cr-O causes significant alloy degradation; extent of attack reduced with increasing $\beta$ fraction;
  - steady-state: consumption of $\text{Al}_2\text{O}_3$ sustains high Al depletion rate.

• Reaction with oxide-sulfate mixtures at 1100 °C
  - presence of $\text{SiO}_2$ or $\text{SO}_3$ (g) favor formation of very stable $\text{CaSiO}_3$ or $\text{CaSO}_4$, which effectively neutralizes CaO;
  - mixtures associating $\text{Na}_2\text{SO}_4$ with high levels of $\text{SiO}_2$ and CaO (like class C fly ash) cause breakaway oxidation; extent of attack reduced with increasing $\beta$ fraction.

• Reaction with oxide-sulfate mixtures at 900 °C
  - Both CaO (S-free gas) and CaSO$_4$ (S-containing gas) cause significant alloy degradation, although via different routes;
  - CaSO$_4$-induced attack resembles Na$_2$SO$_4$-induced attack (hot corrosion).
Summary and conclusions

- Different modes of degradation may involve conflicting alloy requirements; compromise is needed depending on application of interest;
- It is critical to fine tune the amount of reactive elements like Y.
Thank you for your attention
Additional slides (bondcoat work)
Yttrium-rich pegs are involved in severe alloy attack.

Situation similar to type II hot corrosion*.

Corrosion testing

CaO deposit in lab air, 50h, 1100 °C

Better resistance with
- low $x_{Cr}$
- high $f_{\beta}$
Corrosion testing

type I hot corrosion: $\text{Na}_2\text{SO}_4$, $\text{O}_2$-1000 ppm $\text{SO}_2$, 20 h 900 °C

Better resistance with
- high $x_{\text{Cr}}$
- low $f_\beta$

[Diagram showing alloy composition space with phase transitions]

Mixed oxide

Cr-rich oxide

Cr-rich sulfide

Al$_2$O$_3$

Al, Cr oxide

Al, Cr sulfide

Protrusions
Moving forward:

• Study of alloy and thermally grown Al₂O₃ reaction with sulfates; relation with type I hot corrosion.

• Use of computational thermodynamics to design alloys which allow systematic investigation of effect of phase fraction vs phase composition; application to various types of degradation. Examples included here: CaO corrosion at 1100 °C, Na₂SO₄ corrosion at 900 °C (type I hot corrosion)
Deposit Reactivity at 900 °C

900 °C
O$_2$-0.1SO$_2$
Ni-30Co-27Cr-12Al-0.1Y

$\text{Al}_2\text{O}_3$-$\text{CaO}$

$\text{Al}_2\text{O}_3$ protrusions

$\text{mixed oxide + Ca, S}$

$\text{original Al}_2\text{O}_3$

$\text{Cr}_2\text{O}_3$

Local $\text{Al}_2\text{O}_3$ failure due to reaction with CaSO$_4$ or Na$_2$SO$_4$
CMAS Failure

Common Modes of TBC Failure

Calcium Magnesium Alumino Silicate (CMAS):
- Deposits contain CaO-MgO-Al₂O₃-SiO₂
- Melting at high temperatures ≥1250°C
- Molten deposit infiltrates top coat
- Thermo-chemical interactions with YSZ
- Thermo-mechanical interactions
Thermo-Chemical Effects

Dissolution of YSZ into CMAS melt

Re-precipitation of ZrO₂ with different microstructure and composition

Thermo-Mechanical Effects

Surface above melting point of CMAS

Cooling: delamination of TBC in infiltrated regions as a result of ΔE and ΔCTE

P. Mohan, T. Patterson, B. Yao, Y. Sohn, J. Thermal Spray Tech., 19(1-2) pp. 156-167, 2010

**Kinetics of Al$_2$O$_3$ formation-destruction**

### Reaction

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Transport</th>
<th>Kinetics</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO = Ca$^{2+}$ + O$^{2-}$</td>
<td>CaO</td>
<td>C$_x$A$_y$ growth = Al$_2$O$_3$ destruction</td>
</tr>
<tr>
<td>xCa$^{2+}$ + xO$^{2-}$ + yAl$_2$O$_3$ = C$_x$A$_y$</td>
<td>C$_x$A$_y$</td>
<td>$\frac{dY}{dt} = \frac{q}{2Y}$ = $-\frac{V_{CxA}}{yV_{Al_2O3}} \frac{(dX)_d}{dt}$</td>
</tr>
<tr>
<td>2Al$^{3+}$ + 3O$^{2-}$ = Al$_2$O$_3$</td>
<td>Al$_2$O$_3$</td>
<td>Al$_2$O$_3$ formation</td>
</tr>
<tr>
<td>NiCoCrAlY</td>
<td>Al</td>
<td>$\frac{(dX)_f}{dt} = \frac{p}{2X}$</td>
</tr>
</tbody>
</table>

→ Al$_2$O$_3$ net growth:

\[
\begin{array}{c}
\frac{dX}{dt} = \frac{(dX)_f}{dt} + \frac{(dX)_d}{dt} = \frac{p}{2X} - \alpha \frac{q}{2Y}
\end{array}
\]

\[
\begin{align*}
dY &= \frac{q}{2Y} \quad Y^2 = qt \\
Y(0) &\text{ neglected}
\end{align*}
\]

\[
\begin{align*}
dX &= \frac{p}{2X} - \alpha \frac{q}{2\sqrt{qt}} \\
\alpha &= \frac{yV_{Al_2O3}}{V_{CxA}}
\end{align*}
\]
Alloy compositions

NiCoCrAl system, at. %

\[ x_{\text{Co}} = 0.3 \]

\[ T = 1100 \, ^\circ\text{C} \]

ThermoCalc
NIST superalloy (2000) database
X. Liu, Penn State University

Samples: bulk, cast alloys

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
<th>Y</th>
<th>( f_\beta ) (%)</th>
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<tr>
<td>19 15 24 0.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>65</td>
</tr>
<tr>
<td>19 15 24 0.1</td>
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<td></td>
<td></td>
<td></td>
<td>42</td>
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<tr>
<td>30 33 16 0.1</td>
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<td>30 27 16 0.1</td>
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<td>18</td>
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<td>30 33 12 0.1</td>
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<td>16</td>
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<td>30 30 12 0.1</td>
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Testing at 1100 °C
Appendix

Low magnification micrographs

<table>
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<th>27Cr</th>
<th>30Cr</th>
<th>33Cr</th>
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<tr>
<td>12Al</td>
<td><img src="image1" alt="Micrograph" /></td>
<td><img src="image2" alt="Micrograph" /></td>
<td><img src="image3" alt="Micrograph" /></td>
</tr>
<tr>
<td>16Al</td>
<td><img src="image4" alt="Micrograph" /></td>
<td><img src="image5" alt="Micrograph" /></td>
<td><img src="image6" alt="Micrograph" /></td>
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</tbody>
</table>
## Appendix

### Phase volume fractions

*Determined by image analysis from SEM micrographs (cross-section)*

<table>
<thead>
<tr>
<th>#</th>
<th>γ (%)</th>
<th>β (%)</th>
<th>σ (%)</th>
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<tr>
<td>3</td>
<td>87</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>84</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>81</td>
<td>18</td>
<td>1.0</td>
</tr>
<tr>
<td>6</td>
<td>66</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>59</td>
<td>40</td>
<td>1.6</td>
</tr>
<tr>
<td>8</td>
<td>36</td>
<td>42</td>
<td>22</td>
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</table>

### Phase compositions

*Determined by SEM-EDS at. %, balance = Ni*

<table>
<thead>
<tr>
<th>#</th>
<th>γ (Co, Cr, Al)</th>
<th>β (Co, Cr, Al)</th>
<th>σ (Co, Cr, Al)</th>
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<td>17, 10, 33</td>
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<tr>
<td>4</td>
<td>32, 33, 8.5</td>
<td>18, 11, 32</td>
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</tr>
<tr>
<td>5</td>
<td>32, 37, 8.2</td>
<td>19, 14, 33</td>
<td>28, 58, 3.3</td>
</tr>
<tr>
<td>6</td>
<td>34, 35, 8.4</td>
<td>21, 12, 33</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>35, 37, 7.8</td>
<td>22, 14, 32</td>
<td>30, 57, 3.3</td>
</tr>
<tr>
<td>8</td>
<td>37, 37, 7.6</td>
<td>23, 14, 32</td>
<td>31, 57, 3.3</td>
</tr>
</tbody>
</table>
Oxidation (no deposit)

Weight changes

1100 °C, 50 h

All alloys form Al₂O₃ in all atmospheres

\[ \Delta m/A \ (t = 10 \text{ h}, 50 \text{ h}) \rightarrow k_p \approx 8 \times 10^{-13} \text{ g}^2\text{cm}^{-4}\text{s}^{-1} \]

typical of α-Al₂O₃ at 1100 °C
Oxidation (no deposit)

1100 °C, 50 h

**Scale thickness (µm)**

- dry air
- CO₂-20H₂O

- Thinner Al₂O₃ scales in CO₂-H₂O
- In air, less transient oxidation with higher β fraction
Oxidation (no deposit)

1100 °C, 50 h

dry air  CO₂-20H₂O

27Cr-12Al  (γ-13β)

All alloys form Al₂O₃ in all atmospheres
(high Cr and Al contents, Al₂O₃ does not form volatile compound, good barrier to carbon)

Thinner scales in CO₂-H₂O than in air.
Complex reaction morphology induced by reaction with commercial fly ash is reproduced using a synthetic mixture → ability to test various deposit compositions.
Exposure to C-ash in CO$_2$-H$_2$O

33Cr-12Al (γ-18β)

Non-uniform degradation.
Locally thick reaction product, contains large amounts of alloy constituents.

Photo-stimulated luminescence spectroscopy

Absence of θ doublet

Exposure to C-ash in CO$_2$-H$_2$O
Effect of gas composition

1100 °C
Ni-30Co-27Cr-12Al-0.1Y

Class C ash
1 h exposures

No particular effect of CO₂, H₂O or low pO₂

Nitridation due to N₂ in air

CO₂-H₂O, no deposit, 50 h

Absent a deposit, all alloys studied formed external Al₂O₃ scales in all atmospheres

CO₂-20H₂O (eq. pO₂ 40 ppm)

CO₂-20H₂O-1.6O₂

N₂-21O₂
Exposure to CaO in dry air

Ni-19Co-16Cr-23Al-0.1Y
(γ-65β)

Interaction deposited oxide-TGO with consumption of Al₂O₃, but no significant loss of alloy constituents.

from Phase diagrams for ceramists, vol. 1, Levin et al, eds (1964)
Exposure to CaO in dry air

Ni-30Co-33Cr-12Al-0.1Y
(y-18β)

1100 °C

5 h

50 h

\[ t < 5 \text{ h} \quad \text{thick top layer, } \alpha-\text{Al}_2\text{O}_3 \text{ established} \]

\[ 5 < t < 50 \text{ h} \quad \text{only } x\text{CaO-yAl}_2\text{O}_3 \text{ layers grow} \]

\[ \rightarrow \text{top layer formation is rapid, then stops (i.e., transient)} \]
Exposure to CaO in dry air

Ni-30Co-33Cr-12Al-0.1Y  (γ-18β)  1100 °C

10 h preoxidation, 40 h CaO  no preoxidation, 50 h CaO

Preoxidation prevents rapid transient attack
Large $\beta$ fraction
$\rightarrow$ same mechanism occurs to a lower extent (alloy degradation is more rapidly undercut by $Al_2O_3$).
Ash-induced degradation: reaction mechanism

Case of dry air

Evolution of the reaction morphology with reaction time

1 h  50 h  250 h

\( \gamma - \text{no AlN} \)

\( \gamma + \text{AlN} \)
Deposit reactivity at 1100 °C

1100 °C
CO₂-H₂O-O₂
Ni-30Co-27Cr-12Al-0.1Y

Al₂O₃-CaO
ash: Al₂O₃ + CₓAₜ

CₓAₜ
(= xCaO-yAl₂O₃)

Al₂O₃

Al₂O₃-SiO₂-CaO

+ SiO₂

Al₂O₃

+ Na₂SO₄

Al₂O₃-SiO₂-CaO-Na₂SO₄

ash + Cr,Co,Ni oxides

new Al₂O₃

acidification of Na₂SO₄ melt by SiO₂?
Deposit reactivity at 900 °C

900 °C
O₂-SO₂
Ni-30Co-27Cr-12Al-0.1Y

Al₂O₃-CaO

ash: Al₂O₃+CaSO₄

10 µm

CaSO₄

contains Al, Cr, Ca, S

10 µm

Reaction product yet to be identified but significant amounts of Al and Cr have reacted with CaSO₄
Deposit reactivity at 900 °C

900 °C
O₂-SO₂
Ni-30Co-27Cr-12Al-0.1Y

\[
\text{Al}_2\text{O}_3 - \text{CaO} \quad \text{ash: } \text{Al}_2\text{O}_3 + \text{CaSO}_4
\]

\[
\text{SiO}_2 - \text{CaO} \quad \text{ash: } \text{SiO}_2 + \text{CaSiO}_3 + \text{CaSO}_4
\]

CaSO₄ more stable than CaSiO₃ → neutralization not effective
## TBCs Provided by PST

<table>
<thead>
<tr>
<th>dSpecimen Group #</th>
<th>Substrate Alloy</th>
<th>Bond Coat Type</th>
<th>Bond Coat Thickness (mils)</th>
<th>TBC Powder</th>
<th>TBC Density (%T.D.)</th>
<th>TBC Thickness (mils)</th>
<th>Quantity</th>
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<tbody>
<tr>
<td>1a</td>
<td>René N5</td>
<td>Dual Layer NiCoCrAlY</td>
<td>7-8</td>
<td>High Purity YSZ</td>
<td>85</td>
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<td>10</td>
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<tr>
<td>1b</td>
<td>PWA 1484</td>
<td>Dual Layer NiCoCrAlY</td>
<td>7-8</td>
<td>High Purity YSZ</td>
<td>85</td>
<td>15</td>
<td>13</td>
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<td>2a</td>
<td>René N5</td>
<td>Dual Layer NiCoCrAlY</td>
<td>7-8</td>
<td>High Purity YSZ</td>
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<td>PWA 1484</td>
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<td>High Purity YSZ</td>
<td>92</td>
<td>15</td>
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### Nominal Composition of Materials (wt\%)  

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<tr>
<th>Layer</th>
<th>Material</th>
<th>Ni</th>
<th>Co</th>
<th>Cr</th>
<th>Al</th>
<th>W</th>
<th>Mo</th>
<th>Ta</th>
<th>C</th>
<th>B</th>
<th>Re</th>
<th>Y</th>
<th>Hf</th>
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<tbody>
<tr>
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<td>René N5+</td>
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<td>6.2</td>
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<td>1.5</td>
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<td>PWA-1484</td>
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*All Other*
Thermal Barrier Coatings (TBCs)

Multi-Layered TBC System

Thermal Barrier Coatings (TBCs)

Yttria Stabilized Zirconia (YSZ) Top Coat

- ZrO₂: low thermal conductivity
- High resistance to thermal cycling
- ~7wt% Y₂O₃: t’ phase

Cyclic TBC Exposure to High-SiO$_2$ Ash

Early Failure of HPLD TBCs with “high-SiO$_2$” ash with K$_2$SO$_4$

- Failure determined by complete delamination of top coat
- Significant damage to YSZ before complete failure
### Synthetic ash mixtures

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<td>15</td>
<td>12</td>
<td>9</td>
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<tr>
<td>Fe₂O₃</td>
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<td>46</td>
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<td>70</td>
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</table>

- There is a clear boundary for the reaction to occur
- Continuous reaction layer >60% CaO in ash

**72h Exposures, Dry Air 1100°C**

- 46% CaO
- No Reaction
- 10% CaO
- No Reaction
TBC Failure After Cyclic Exposure

Comparison of failure: High-CaO Ash+5%FeS+5%K₂SO₄

HPLD Top Coat Failure

Failure in YSZ far from TGO

200 μm

DVF Top Coat Failure

Failure along TGO/BC Interface

200 μm

Location of TBC spallation is different.
TBC Failure After Cyclic Exposure

TBC Failure after 444 Cycles at 1100°C
Synthetic Ash (70%CaO) + 5%FeS + 5%K₂SO₄

TBC Failure after 1200 Cycles at 1100°C
without deposit

Similar failure, but ash causes failure to occur early.
Cyclic Exposure to High-SiO$_2$ Ash

HPLD TBC high-SiO$_2$ Ash + 0.10K$_2$SO$_4$ Dry Air
260 Cycles: Re-apply every 20 cycles

HPLD TBC high-SiO$_2$ Ash + 0.10K$_2$SO$_4$ Air+20%H$_2$O

Si, K, O
Reactions of Fly Ash with YSZ

Free-standing YSZ isothermal exposure to C-Ash in dry air 1300°C.

Destabilization of t’ phase from liquid fly-ash interaction with YSZ.

Raman spectra used to identify change from t’ phase

Different ratios of oxides can result in different melting point.

Class C Ash 1200 °C, 24h in Dry Air

Melted ash penetrated into YSZ