Novel Functional Graded Thermal Barrier Coatings in Coal-fired Power Plant Turbines

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Acknowledgement

• **Subcontractor** (Praxair Surface Technologies): James Knapp

• **Industrial collaborators** (Praxair Surface Technologies): John K. Anderson, Vlad Belov, Don Lemen, Li Li

• **Graduate students** (IUPUI): Xingye Guo, Yi Zhang
Outline of Talk

• I. Introduction
  i. Pyrochlore oxide
  ii. Double-layer thermal barrier coating

• II. Results (September 1, 2012- June 1, 2013)
  i. Powder fabrication and characterizations
  ii. Design of double-layer structure

• III. Summary / Future work
Goals

• The objective of the project is to investigate a novel double-layer functional graded coating material, pyrochlore oxide, for thermal barrier coating (TBC) applications.
• The ultimate goal is to develop a manufacturing process to produce the pyrochlore oxide based coating with improved high-temperature corrosion resistance.
Pyrochlore-type rare earth zirconium oxides (Re$_2$Zr$_2$O$_7$, Re = rare earth) are promising candidates for thermal barrier coatings, high-permittivity dielectrics, potential solid electrolytes in high-temperature fuel cells, and immobilization hosts of actinides in nuclear waste.

Pyrochlore crystal structure: A$_2$B$_2$O$_7$. A and B are metals incorporated into the structure in various combinations. (credit: NETL)
Why La$_2$Zr$_2$O$_7$?

Compared with YSZ, La$_2$Zr$_2$O$_7$ has

- Higher temperature phase stability. No phase transformation
- Lower sintering rate at elevated temperature
- Lower thermal conductivity
- Lower CTE (can be enhanced by CeO$_2$ doping)

Phase diagram of La$_2$O$_3$–ZrO$_2$
## YSZ vs. La$_2$Zr$_2$O$_7$

<table>
<thead>
<tr>
<th>Materials property</th>
<th>8YSZ</th>
<th>La$_2$Zr$_2$O$_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Point (°C)</td>
<td>2680</td>
<td>2300</td>
</tr>
<tr>
<td>Maximum Operating Temperature (°C)</td>
<td>1200</td>
<td>&gt;1300</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m-K) (@800°C)</td>
<td>2.12</td>
<td>1.6</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (x10^-6/K) (@1000 °C)</td>
<td>11.0</td>
<td>8.9-9.1</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>6.07</td>
<td>6.00</td>
</tr>
<tr>
<td>Specific heat (J/g-K) (@1000 °C)</td>
<td>0.64</td>
<td>0.54</td>
</tr>
</tbody>
</table>
La$_2$Zr$_2$O$_7$ Fabrication Methods

- Solid-state reaction

- Coprecipitation–calcination method

- Sol-gel method

However, currently only small quantity powders were made at lab scale. There is an urgent need to develop a scalable method to produce large quantity of La$_2$Zr$_2$O$_7$

Layered Coating System

- The coefficient of thermal expansion of La$_2$Zr$_2$O$_7$ ($10 \times 10^{-6}$/K) is lower than those of both substrate and bondcoat (about $15 \times 10^{-6}$/K). As a result, the thermal cycling properties may be a concern.
- The layered topcoat is believed to be a feasible solution.
- In this work, we develop a double-layer, functionally graded, pyrochlore oxide based TBC system.
Scalable Thermal Spray Powder Production

- The powders are produced using a reengineered spray drying and sintering technique at Praxair Surface Technologies.
- La$_2$O$_3$ and ZrO$_2$ particles are mixed into a water based slurry, and then spray dried or atomized into a powder form, using a rotary wheel style spray drier to convert the liquid slurry into dry particles of an agglomerated La$_2$O$_3$/ZrO$_2$ powder.
- These spray dried particles are sintered in a gas fired kiln to achieve powder particles of an appropriate particle structure.
- The sintered cake is de-agglomerated to break down the cake, and screened to a particle size distribution suitable for spray.
- The resulting powder is then blended in a "V" blender to make a homogenous mixture of the variety of particle sizes.
- Approximately 150 lb of La$_2$Zr$_2$O$_7$ powders are produced in a single batch.
La$_2$Zr$_2$O$_7$ Powder Morphology

- Spherical shape with porous surface
- Good flowability and high density
- Particle size between 30 – 100 µm
Microtrac standard range particle analyzer’s percent passing data show that the average powder size, $D_{50}$, is $\sim 65 \, \mu m$.
X-ray Diffraction (XRD) Analysis

XRD data show that the powder composition is $\text{La}_2\text{Zr}_2\text{O}_7$

PANalytical/Philips X’pert MRD

$K_{\alpha 1}$ wavelength: 1.5405600 Å
$K_{\alpha 2}$ wavelength: 1.5443900 Å
$K_{\alpha 2} / K_{\alpha 1}$ intensity ratio: 0.5000
$K_{\alpha}$ wavelength: 1.5405600 Å
$K_{\beta}$ wavelength: 1.3922200 Å
Chemical Composition - ICP-MS

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Test Method</th>
<th>Test Lab</th>
<th>Min</th>
<th>Max</th>
<th>Result</th>
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</tr>
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<tbody>
<tr>
<td>Aluminum Oxide</td>
<td>ICP</td>
<td>NSL Analytical Services</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td></td>
<td>Yes</td>
</tr>
<tr>
<td>Ferric Oxide</td>
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<td>0.1</td>
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<td>Lanthanum Oxide</td>
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<td>Other Oxides Total</td>
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<td>1.5</td>
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<td>Titanium Dioxide</td>
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<td>Uranium + Thorium</td>
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<td>ICP</td>
<td>NSL Analytical Services</td>
<td>41</td>
<td></td>
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</table>

- Inductively coupled plasma – mass spectrometry (ICP-MS) technique was used to measure the powder compositions.
- The measurements confirms La$_2$Zr$_2$O$_7$ composition.
Vertically Cracked Intermediate Layer

- Intermediate layer (e.g., Zircoat™) between topcoat and bondcoat, characterized by the intentional vertical cracks, provides improved tolerance to the strain caused by the CTE mismatch.
- The Intermediate layer will be applied as a (1) low-density or (2) dense vertically cracked structure.

Design of Layered TBCs

1. Ni based superalloy substrate

Porous La$_2$Zr$_2$O$_7$

Low density layer, 7YSZ

Dense La$_2$Zr$_2$O$_7$

2. Ni based superalloy substrate

Porous La$_2$Zr$_2$O$_7$

High density vertically cracked layer, 7YSZ

Dense La$_2$Zr$_2$O$_7$

3. Ni based superalloy substrate

Porous La$_2$Zr$_2$O$_7$

Dense La$_2$Zr$_2$O$_7$
Air Plasma Spray (APS)

- Non-transferred electric arc excites a gas mixture generating a rapid expanding ionized stream.
- High temperature at lower velocity coating process. The most versatile process capable of spraying any material that does not sublime.
- Mostly used for spraying ceramic materials.
- ID coating capable down to approximately 3”.
- PST shrouded plasma produces metallic coatings with very low oxide.
Process Control Parameters

Typical Coating Microstructure

- Torch build
  - Powder dwell time and velocity
- Torch gas
  - Particle velocity
- Powder carrier
  - Particle melting
- Shield gas
  - Coating density and oxide
- Auxiliary carrier gas
  - Particle velocity
- Torch current
  - Particle melting
- Standoff
  - Coating density and oxide
- Powder feed rate
  - Unmelted particles
- Powder particle size distribution
  - Deposition efficiency

Typical Coatings Microstructures:

- Cr₂O₃ (LC-4)
- ZrO₂-Y₂O₃ (LZ-48)
Plasma Spray Torches

- PST 1108, 1130, 1125
- PST SG100
- TAFA PlasJet
- Metco F4
- Metco 3, 7, 9
- MetTech
- Metco Triplex
- Progressive 100HE
Furnace Cycle Oxidation Testing

- **Furnace Cycle Oxidation**
  - Isothermal test of TBC, with periodic excursions to room temperature (e.g. 1135-100°C (2075-212 °F))
  - 50 Min at Temp – Air Quench 10 min
  - CM bottom-loading furnaces

- Bottom loading furnace
- Tube furnaces

- 1 inch diameter test button with >20% spallation

- Coating spallation from component
Thermal Shock Testing

- JETS (Jet Engine Thermal Simulation)
  - Thermal gradient test of TBC
  - Ceramic layer durability assessment
  - Measured by percentage of cracking on specimen edge
Summary

• PST has successfully developed a unique manufacturing process to scale up the production of high-purity, large-quantity lanthanum zirconate powders (>150 lb) in one single batch

• The powders morphology and chemistry are characterized

• Double-layer coating systems are designed
Future Work

• Fabricate the double-layer TBC systems
• Characterize and evaluate the TBC materials and their corrosion resistances at elevated temperatures and in corrosive environments