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

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• Subcontract: James Knapp (Praxair Surface Technologies)
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• Yang Ren (Argonne National Laboratory)
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Outline

• I. Introduction
  • $\text{La}_2\text{Zr}_2\text{O}_7$ vs. YSZ
  • Multilayer TBC structure

• II. Experiments
  • High density $\text{La}_2\text{Zr}_2\text{O}_7$
  • Low density $\text{La}_2\text{Zr}_2\text{O}_7$

• III. Theoretical study of properties of $\text{La}_2\text{Zr}_2\text{O}_7$

• IV. Summary
Limitation of yttria stabilized zirconia

• Zirconia partially stabilized with 7 wt% yttria (7YSZ) is the current state-of-the-art thermal barrier coating material.

• However, at temperatures higher than 1200 °C, YSZ layers are prone to **sintering**, which increases thermal conductivity and makes them less effective.

• The sintered and densified coatings can also **reduce thermal stress and strain tolerance**, which can reduce the coating’s durability significantly.
Motivation and objective

- To further increase the operating temperature of turbine engines, alternate TBC materials with lower thermal conductivity, higher operating temperatures and better sintering resistance are required.
- The **objective** of the project is to develop a novel lanthanum zirconate based multi-layer thermal barrier coating system.
- The ultimate goal is to develop a manufacturing process to produce pyrochlore oxide based coating with improved high-temperature properties.
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 $\text{La}_2\text{Zr}_2\text{O}_7$?

Compared with YSZ, $\text{La}_2\text{Zr}_2\text{O}_7$ 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 ($^\circ$C)</td>
<td>2680</td>
<td>2300</td>
</tr>
<tr>
<td>Maximum Operating Temperature ($^\circ$C)</td>
<td>1200</td>
<td>&gt;1300</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m-K) (@ 800$^\circ$C)</td>
<td>2.12</td>
<td>1.6</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion ($\times 10^{-6}$/K) (@1000 $^\circ$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 $^\circ$C)</td>
<td>0.64</td>
<td>0.54</td>
</tr>
</tbody>
</table>
Layered coating architecture

• The coefficient of thermal expansion of La$_2$Zr$_2$O$_7$ (10x$10^{-6}$/K) is lower than those of both substrate and bondcoat (about 15x$10^{-6}$/C @ 1000 °C). As a result, the thermal cycling properties may be a concern

• The layered topcoat architecture is believed to be a feasible solution to improve thermal strain tolerance

• In this work, we develop a multi-layer, functionally graded, pyrochlore oxide based TBC system
La$_2$Zr$_2$O$_7$ powder morphology

Powder surface morphology
- Spherical shape with rough surface
- Good flowability and high density
- Particle size between 30 ~ 100 µm

Powder cross-section
- Porous interior

+ 125 µm

- 125 µm
Microtrac standard range particle analyzer’s percent passing data show that the average powder size, $D_{50}$, is $\sim 65 \mu m$.
### Chemical composition - ICP-MS

All elements measured in weight percent unless otherwise specified. Sampling Method per ASTM B215.

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Test Method</th>
<th>Test Lab</th>
<th>Min</th>
<th>Max</th>
<th>Result</th>
<th>OK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Oxide</td>
<td>ICP</td>
<td>NSL Analytical Services</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Ferric Oxide</td>
<td>ICP-MS</td>
<td>NSL Analytical Services</td>
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<td>0.1</td>
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<td></td>
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<tr>
<td>Hafnium Oxide</td>
<td>ICP</td>
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<td>0.8</td>
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<tr>
<td>Lanthanum Oxide</td>
<td>By Difference</td>
<td>NSL Analytical Services</td>
<td>57</td>
<td></td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Other Oxides Total</td>
<td>ICP-MS</td>
<td>NSL Analytical Services</td>
<td>1.5</td>
<td>0.4</td>
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<td></td>
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<tr>
<td>Silicon Dioxide</td>
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<tr>
<td>Titanium Dioxide</td>
<td>ICP-MS</td>
<td>NSL Analytical Services</td>
<td>0.5</td>
<td>0.0</td>
<td>Yes</td>
<td></td>
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<tr>
<td>Uranium + Thorium</td>
<td>ICP-MS</td>
<td>NSL Analytical Services</td>
<td>0.05</td>
<td>0.02</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>Zirconium Oxide</td>
<td>ICP</td>
<td>NSL Analytical Services</td>
<td>41</td>
<td></td>
<td>Yes</td>
<td></td>
</tr>
</tbody>
</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
Element analysis of cross-section

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>28.51</td>
<td>74.28</td>
</tr>
<tr>
<td>Zr L</td>
<td>27.21</td>
<td>12.43</td>
</tr>
<tr>
<td>La L</td>
<td>44.28</td>
<td>13.29</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight%</th>
<th>Atomic%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O K</td>
<td>17.42</td>
<td>60.37</td>
</tr>
<tr>
<td>Zr L</td>
<td>31.92</td>
<td>19.40</td>
</tr>
<tr>
<td>La L</td>
<td>50.67</td>
<td>20.23</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Higher La, and lower Zr and O contents are inside of powder than on surface.
La$_2$Zr$_2$O$_7$ powder XRD analysis

XRD data show that the powder composition is La$_2$Zr$_2$O$_7$
In situ Synchrotron XRD shows no compositional change at high temperatures.
Design of Layered TBCs

1. Low density layer, 7YSZ
   Bond coat
   Ni based superalloy substrate
   (1)

2. High density vertically cracked layer, 7YSZ
   Bond coat
   Ni based superalloy substrate
   (2)

3. Bond coat
   Ni based superalloy substrate
   (3)
I. Introduction
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III. Theoretical study of properties of La$_2$Zr$_2$O$_7$

IV. Summary
Dense coating

TBC

Substrate (HS188)
XRD analysis of coating and powder

XRD shows that coating compositions are same as those of the powder
Cross section view of dense coating

Processing parameters (powder feed rate, surface speed, current, stand off) were varied to control the porosity.
Surface microstructures
Backscattered SEM images

5279-14 line #2

Dense vertical crack (DVC)
Backscattered SEM images (cont’d)

5279-14 line #2

Dense vertical crack (DVC)
Backscattered SEM images (cont’d)

5279-14 line #2

Top

Middle

Bottom

Top

Middle

Bottom
Nano-indentation

Stress (mN)

Strain (nm)

5279-15 line #3
Summary of elastic moduli (from Nanoindentation)

Young's modulus (GPa) vs. Displacement (nm) graph showing different markers for different lines.
Summary of elastic modulus (from Nanoindentation)

Specimen species

Young’s modulus (GPa)

<table>
<thead>
<tr>
<th>Specimen species</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5279-13 line #1</td>
<td>159.50 ± 5.73</td>
</tr>
<tr>
<td>5279-14 line #2</td>
<td>156.00 ± 10.03</td>
</tr>
<tr>
<td>5279-15 line #3</td>
<td>133.02 ± 9.52</td>
</tr>
<tr>
<td>5279-17 line #5</td>
<td>121.76 ± 6.81</td>
</tr>
<tr>
<td>5279-18 line #6</td>
<td>116.26 ± 5.85</td>
</tr>
</tbody>
</table>
Summary of hardness (from Nanoindentation)

- 5279-13 line #1: $10.2 \pm 0.5$
- 5279-14 line #2: $8.8 \pm 2.1$
- 5279-15 line #3: $7.87 \pm 0.7$
- 5279-17 line #5: $7.3 \pm 0.6$
- 5279-18 line #6: $7.0 \pm 0.6$
Summary of hardness (from Vicker’s Indentation)

<table>
<thead>
<tr>
<th>Specimen species</th>
<th>Hardness (GPa) ± Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>5279-13 line #1</td>
<td>5.41 ± 0.33</td>
</tr>
<tr>
<td>5279-14 line #2</td>
<td>5.51 ± 0.25</td>
</tr>
<tr>
<td>5279-15 line #3</td>
<td>5.32 ± 0.28</td>
</tr>
<tr>
<td>5279-17 line #5</td>
<td>4.85 ± 0.29</td>
</tr>
<tr>
<td>5279-18 line #6</td>
<td>4.82 ± 0.24</td>
</tr>
</tbody>
</table>
Summary of hardness (from Rockwell’s Indentation)

- Low density coatings with porosity between 7~10 % were achieved.
- Porosity and hardness can be tuned via changing processing conditions.
- Powder feed rate↑ or current↓ → porosity↑ → hardness↓
  
  \[ \text{Hardness} = 1.99 \times (100 - \text{porosity}) - 100 \]
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• IV. Summary
Low density coating

Position A

Position B

Position C

Line 12
Low density coating (high mag.)

Position A

Position B

Position C
Low density coating (high mag.)

Position A

Position B

Position C
Summary of hardness (from Vickers indentation)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#8</td>
<td>4.22 ± 0.14</td>
</tr>
<tr>
<td>#9</td>
<td>4.22 ± 0.20</td>
</tr>
<tr>
<td>#10</td>
<td>3.97 ± 0.44</td>
</tr>
<tr>
<td>#11</td>
<td>4.09 ± 0.30</td>
</tr>
<tr>
<td>#12</td>
<td>3.90 ± 0.45</td>
</tr>
</tbody>
</table>

Hardness (GPa)
Summary of hardness (from nanoindentation)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#8</td>
<td>5.24 ± 1.14</td>
</tr>
<tr>
<td>#9</td>
<td>6.09 ± 1.06</td>
</tr>
<tr>
<td>#10</td>
<td>5.41 ± 0.13</td>
</tr>
<tr>
<td>#11</td>
<td>5.41 ± 0.82</td>
</tr>
<tr>
<td>#12</td>
<td>4.88 ± 1.44</td>
</tr>
</tbody>
</table>
Summary of Young’s modulus (from nanoindentation)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young’s modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#8</td>
<td>89.04 ± 8.83</td>
</tr>
<tr>
<td>#9</td>
<td>104.28 ± 9.45</td>
</tr>
<tr>
<td>#10</td>
<td>100.83 ± 4.08</td>
</tr>
<tr>
<td>#11</td>
<td>101.11 ± 10.72</td>
</tr>
<tr>
<td>#12</td>
<td>91.77 ± 14.55</td>
</tr>
</tbody>
</table>
Porosity of low density coating

<table>
<thead>
<tr>
<th>Line #</th>
<th>Batch #</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spray test</td>
<td>7</td>
<td>5279-19</td>
<td>5.3182</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>5279-20</td>
<td>5.2587</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>5279-21</td>
<td>5.2584</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>5279-22</td>
<td>5.2917</td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>5279-23</td>
<td>5.2614</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>5279-24</td>
<td>5.0089</td>
</tr>
</tbody>
</table>

Low density coatings with porosity between 11~17% were achieved.

Porosity = 1 – (Archimedes method density / fully dense density). Fully dense (theoretical) density is 6.0 g/cm³.
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• IV. Summary
Geometry optimization

La$_2$Zr$_2$O$_7$ free energy calculation

<table>
<thead>
<tr>
<th></th>
<th>Lattice parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work (VASP)</td>
<td>10.89</td>
</tr>
<tr>
<td>This work (CASTEP)</td>
<td>10.73</td>
</tr>
<tr>
<td>Liu’s work (CASTEP)</td>
<td>10.73</td>
</tr>
<tr>
<td>Tabira’s work (XRD)</td>
<td>10.802</td>
</tr>
</tbody>
</table>

La$_2$Zr$_2$O$_7$ specific heat ($C_p$) calculation

La$_2$Zr$_2$O$_7$ elastic constants calculation

- Both stress and strain have three tensile and three shear components, giving 6 components in total. The linear elastic constants form a $6 \times 6$ symmetric matrix, having 27 different components.

- For $Fm\bar{3}d$ cubic structure there are only 3 independent elastic constants $C_{11}$, $C_{12}$, $C_{44}$.

\[
\begin{bmatrix}
\varepsilon_x \\
\varepsilon_y \\
\varepsilon_z \\
\gamma_x \\
\gamma_y \\
\gamma_z \\
\end{bmatrix} =
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{21} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{31} & C_{32} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{41} & C_{42} & C_{43} & C_{44} & C_{45} & C_{46} \\
C_{51} & C_{52} & C_{53} & C_{54} & C_{55} & C_{56} \\
C_{61} & C_{62} & C_{63} & C_{64} & C_{65} & C_{66} \\
\end{bmatrix}\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z \\
\tau_x \\
\tau_y \\
\tau_z \\
\end{bmatrix}
\]

<table>
<thead>
<tr>
<th></th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
<th>Bulk modulus (GPa)</th>
<th>Shear modulus (GPa)</th>
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<tbody>
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<td>124.8</td>
<td>100.4</td>
<td>179.8</td>
<td>93.3</td>
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<tr>
<td>Liu’s work (CASTEP)</td>
<td>289</td>
<td>124</td>
<td>100</td>
<td>179</td>
<td>93</td>
</tr>
</tbody>
</table>
La$_2$Zr$_2$O$_7$ thermal conductivity calculation

Replicate 20 conventional cells along the heat flow direction to form a super cell.

Calculated temperature contour based on Fourier’s law $k = -\frac{q''}{\nabla T}$

The calculated thermal conductivity is 1.2 W/m/K at the temperature of 1000 °C, which is reasonably in agreement with the experimentally measured thermal conductivity ~1.5W/m/K [1].

Summary

• La$_2$Zr$_2$O$_7$ powder and coating’s microstructure and chemistry characterizations show that La$_2$Zr$_2$O$_7$ is stable at high temperatures, which makes it suitable for TBC applications.
• Porosity of the coating can be controlled with desirable microstructures and mechanical properties.
• First principles studies of La$_2$Zr$_2$O$_7$ were conducted to derive fundamental thermal and mechanical properties.

Future work

• Fabricate multi-layer coatings using air plasma spray
• Characterize the coating using JETS and FCT tests
• Calibrate the model with experimental data
Publications

Materials Today - Proceedings
Co-editors: Jing Zhang, Yeon-Gil Jung, The 1st International Joint Mini-Symposium on Advanced Coatings between Indiana University-Purdue University Indianapolis and Changwon National University, Indianapolis, IN, USA, March 18~20, 2014

Xingye Guo, James Knapp, Li Li, Yeon-Gil Jung, and Jing Zhang, *ab initio* calculations of structural, thermal, and mechanical properties of lanthanum zirconate, 17th U.S. National Congress on Theoretical & Applied Mechanics, East Lansing, Michigan, 2014


Xingye Guo, James Knapp, Li Li, Yeon-Gil Jung, and Jing Zhang, Novel lanthanum zirconate based thermal barrier coatings for gas turbine applications, the 5th International Congress on Ceramics, Beijing, China, 2014