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

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Outline

• Introduction
• Coating fabrications
• Single ceramic layer (SCL) architecture
• Double ceramic layer (DCL) architecture
• Characterization of physical and mechanical properties
  • Microstructure and composition
  • Porosity and hardness
  • Bond strength test
  • Erosion test
• Characterization of thermal properties
  • Thermal conductivity and specific heat measurements
  • Jet engine thermal shock tests
  • Thermal gradient mechanical fatigue tests
• Summary and future work
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, alternative 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: $A_2B_2O_7$. 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

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

<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 (x10^-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$_7$ (10x10$^{-6}$/°C) is lower than those of both substrate and bondcoat (about 15x10$^{-6}$/°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$_7$ spray powder morphology

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

Powder cross-section
- Porous interior

+ 125 µm

- 125 µm
TEM image of La$_2$Zr$_2$O$_7$
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.

Wavelength 0.108 Å

credit: Yang Ren @ ANL
Coating fabrication using APS

- $\text{La}_2\text{Zr}_2\text{O}_7$ coatings were deposited using air plasma spray (APS) technique by a Praxair patented plasma spray torch.
- Haynes 188 superalloy was used as the substrate.

<table>
<thead>
<tr>
<th>Haynes 188</th>
<th>Co</th>
<th>Ni</th>
<th>Cr</th>
<th>W</th>
<th>Si</th>
<th>C</th>
<th>La</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>(w%)</td>
<td>39</td>
<td>22</td>
<td>22</td>
<td>14</td>
<td>0.35</td>
<td>0.10</td>
<td>0.03</td>
<td>3</td>
<td>1.25</td>
</tr>
</tbody>
</table>

- The bond coat is Ni-based intermetallic LN-65 using APS, with a thickness of 228 $\mu$m

<table>
<thead>
<tr>
<th>LN-65</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Y</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(w%)</td>
<td>67.3</td>
<td>21.12</td>
<td>9.94</td>
<td>1.02</td>
<td>0.19</td>
</tr>
</tbody>
</table>

- Controlled spray parameters:
- Powder feed ratio
- Torch current
- Torch gas (Argon), Carrier gas (Argon), Shield gas (Argon), Secondary gas (Hydrogen)
- Standoff distance
- Sample rig surface rotation speed (RPM and surface speed)
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• Introduction
• Coating fabrications
  • Single ceramic layer (SCL) architecture – dense coating
  • Double ceramic layer (DCL) architecture
• Characterization of physical and mechanical properties
  • Microstructure
  • Hardness and Young’s modulus
  • Bond strength test
  • Erosion test
• Characterization of thermal properties
  • Thermal properties
  • Jet engine thermal shock tests
  • Thermal gradient mechanical fatigue tests
• Summary and future work
Cross sectional view of dense coating

Processing parameters (powder feed rate, surface speed, current, stand off) were varied to control the porosity.
Nanoindentation Young’s modulus vs. displacement

![Graph showing the relationship between Young’s modulus (GPa) and displacement (nm).]
Nanoindentation Young’s modulus

Specimen species

- 5279-13 line #1: 159.50 ± 5.73
- 5279-14 line #2: 156.00 ± 10.03
- 5279-15 line #3: 133.02 ± 9.52
- 5279-17 line #5: 121.76 ± 6.81
- 5279-18 line #6: 116.26 ± 5.85
Nanoindentation hardness

![Graph showing hardness values](image)

**Hardness (GPa)**

- 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: $7.0 \pm 0.6$

**Specimen species**

- 5279-15 line #3
Vicker’s indentation hardness

Hardness (GPa)

5.41 ± 0.33  5.51 ± 0.25  5.32 ± 0.28  4.85 ± 0.29  4.82 ± 0.24

Specimen species

10 μm
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↓

[Hardness = 1.99 × (100-porosity) -100]
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Cross sections of SCL La$_2$Zr$_2$O$_7$ coatings
Vickers hardness indentation
Nanoindentation

#3

#4

#5
Vickers indentation hardness

![Bar chart showing Vickers indentation hardness for five samples. The hardness values are: #1: 4.22 ± 0.14 GPa, #2: 4.22 ± 0.20 GPa, #3: 3.97 ± 0.44 GPa, #4: 4.09 ± 0.30 GPa, #5: 3.90 ± 0.45 GPa.](image)
Nano indentation Young’s modulus vs. displacement
Nanoindentation Young’s modulus

<table>
<thead>
<tr>
<th>Samples</th>
<th>Young's modulus (Gpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>89.04 ± 8.83</td>
</tr>
<tr>
<td>#2</td>
<td>104.28 ± 9.45</td>
</tr>
<tr>
<td>#3</td>
<td>100.83 ± 4.08</td>
</tr>
<tr>
<td>#4</td>
<td>101.11 ± 10.72</td>
</tr>
<tr>
<td>#5</td>
<td>91.77 ± 14.55</td>
</tr>
</tbody>
</table>
Nanoindentation hardness

**Hardness (GPa)**

- Samples #1: 5.24 ± 1.14
- Samples #2: 6.09 ± 1.06
- Samples #3: 5.41 ± 0.13
- Samples #4: 5.41 ± 0.82
- Samples #5: 4.88 ± 1.44
Porosity of low density SCL coating

<table>
<thead>
<tr>
<th>Line #</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>5.3182</td>
<td>11.36</td>
</tr>
<tr>
<td>8</td>
<td>5.2587</td>
<td>12.36</td>
</tr>
<tr>
<td>9</td>
<td>5.2584</td>
<td>12.36</td>
</tr>
<tr>
<td>10</td>
<td>5.2917</td>
<td>11.81</td>
</tr>
<tr>
<td>11</td>
<td>5.2614</td>
<td>12.31</td>
</tr>
<tr>
<td>12</td>
<td>5.0089</td>
<td>16.52</td>
</tr>
</tbody>
</table>

Low density coatings with porosity between 11~17% were achieved.
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Double ceramic layer (DCL) architectures

**#6**
- Porous La$_2$Zr$_2$O$_7$ top coat
- Bond coat (NiCrAlY)
- Substrate (Haynes-188)
- 432 μm
- 228 μm

**#7**
- Porous 8YSZ top coat
- Bond coat (NiCrAlY)
- Substrate (Haynes-188)
- 432 μm
- 228 μm

**#8**
- Porous La$_2$Zr$_2$O$_7$ coat
- Porous 8YSZ coat
- Bond coat (NiCrAlY)
- Substrate Haynes-188
- 305 μm
- 228 μm

**#9**
- Porous La$_2$Zr$_2$O$_7$ coat
- Dense 8YSZ coat
- Bond coat (NiCrAlY)
- Substrate Haynes-188
- 305 μm
- 228 μm

Indicates variations in coatings and substrate layers for different DCL architectures.
Interfaces of DCL coatings

#6 La$_2$Zr$_2$O$_7$ and bond coat interface

#7 porous 8YSZ and bond coat interface

#8 La$_2$Zr$_2$O$_7$ and porous 8YSZ interface

#9 La$_2$Zr$_2$O$_7$ and dense 8YSZ interface
Energy-dispersive X-ray spectroscopy

Applied heat treatments on sample #8

Heat treatment
1080°C 4h
Ar atmosphere

LD La₂Zr₂O₇, 12 mils

LD 8YSZ, 5 mils
Vickers hardness of DCL

Hardness (GPa)

Sample 6  |  Sample 7  |  Sample 8  |  Sample 9
--- | --- | --- | ---
3.96±0.6  |  3.58±1.01  |  3.21±0.77  |  4.32±0.6
4.86±1.66  |  7.05±1.01  |

Layers:
- Porous 8YSZ layer
- Dense 8YSZ layer
- La$_2$Zr$_2$O$_7$ layer
Bond strength test

Epoxy (FM 1000 adhesive film) to glue coating buttons to a mating cap. Tensile test according to ASTM-C-633.

La$_2$Zr$_2$O$_7$ 8YSZ

<table>
<thead>
<tr>
<th>Strength (MPa)</th>
<th>Load (kN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.48±1.66</td>
<td>5.31±0.33</td>
</tr>
<tr>
<td>13.59±1.97</td>
<td>6.88±0.99</td>
</tr>
</tbody>
</table>

Sample 6, SCL La$_2$Zr$_2$O$_7$  Sample 7 Porous 8YSZ
Residual stress distribution in coating

\[ \sigma_s = E_s \left[ \varepsilon_s + K \left( z + \delta \right) \right] \]
\[ \sigma_i = E_i \left[ \varepsilon_i + K \left( z + \delta \right) \right] \]

where \( \varepsilon_i = \Delta \alpha \Delta T + \sum_{k=1}^{n} \frac{E_k t_k}{E_s t_s} (\alpha_k - \alpha_i) \Delta T \)
\[ \varepsilon_s = -\sum_{i=1}^{n} \frac{E_i t_i}{E_s t_s} \Delta \alpha \Delta T \]
\[ \delta = \frac{t_s}{2} - \sum_{i=1}^{n} \frac{E_i t_i}{E_s t_s} (2h_{i-1} + t_i) \]
\[ K = -\sum_{i=1}^{n} \frac{6E_i t_i \Delta \alpha \Delta T}{E_s t_s^2} \]

where \( \alpha \) is the coefficient of thermal expansion (CTE), \( k \) is the ceramic coating layers range from 1 to \( n \), \( t_i \) is the thickness of \( i^{th} \) layer.

Erosion test

- 600±0.2g alumina sands with a diameter of 50 μm
- Spray rate 6 g/s; duration 100 s; spray angle 20°
Erosion rate & critical erosion velocity

Erosion rate describes the erosion resistance of TBC sample [1]:

\[ R_{erosion} = \frac{W_{removed \, material}}{W_{impacting \, particles}} \]

Critical erosion velocity is used to express the critical condition to initiate cracks [2]:

\[ V_{crit} = 105 \frac{E^{3/4} K_{IC}^3}{H^{13/4} \rho^{1/2} R^{3/2}} \]

- E: Young’s modulus
- H: hardness
- \( K_{IC} \): fracture toughness
- \( \rho \): density of erodent particle
- \( R \): particle radius

Relationship between $V_{crit}$ and erosion rate

![Graph showing the relationship between $1/Critical\ velocity\ (s/m)$ and Erosion\ rate\ ($\mu g/g$). The graph includes data points for samples 6, 7, 8, and 9, with a trend line indicating a positive correlation.](image)
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Thermal conductivity

Thermal conductivity is determined from thermal diffusivity $D_{th}$, specific heat capacity $C_p$, and measured density $\rho$:

$$k = D_{th} \cdot C_p \cdot \rho$$

Thermal diffusivity is measured using laser flash diffusivity system (TA instrument DLF1200). Specific heat is measured by analytical method (TA instrument DLF1200).
TBC is 90.55% dense (ρ=5.478g/cc), with a nominal thickness of 600μm
Indentation marks are from previous study
**Thermal conductivity and heat capacity map**

### Sample information

**TBC:**
- Material: La$_2$Zr$_2$O$_7$
- Thickness: $\sim$600$\mu$m (this is used in calculation)
- Density: 90.55% dense, dense density=6 g/cc, so density $\rho = 5.478$ g/cc
- Specific heat: $c = 0.54$ J/g-K @1000C

Substrate (following are room temperature properties obtained from matweb):
- Material: Haynes 188
- Density: $\rho = 8.98$ g/cc
- Thermal conductivity: $k = 10.4$ W/m-K,
- Specific heat: $c = 0.403$ J/g-K, (therefore, $\rho c = 3.62$ J/cm$^3$-K)
- Thickness used in calculation: $L = 4$ mm (may have a small effect to results)

### Test condition

Flash thermal imaging test with one flash lamp
- Imaging speed: 994 Hz; imaging duration: 3 seconds
Measured TBC thermal properties

Thermal conductivity $k$ image

Heat capacity $\rho c$ image

Predicted average TBC properties (within red rectangular area):

$$k = 0.55 \text{ W/m-K}, \quad \rho c = 2.16 \text{ J/cm}^3\text{-K}$$

- These results were based on a TBC thickness of 600 $\mu$m
- TBC specific heat @RT: $c = 0.393 \text{ J/g-K}$; predicted TBC density is: $\rho = \rho c/c = 2.16/0.393 = 5.5 \text{ g/cc}$

credit: Jiangan Sun @ ANL
Coefficient of thermal expansion (CTE)

CTE is measured using a BAEHR dilatometer from 25 to 1400 °C.

Jet engine thermal shock tests (JETS)

- Jet engine thermal shock (JETS) tests are conducted to investigate the thermal cycling performance.
- TBC samples are heated to 2250 °F (1232.2 °C) at the center for 20 s, and then cooled by compressed N₂ cooling for 20 s, and then ambient cooling for 40 s.
- Temperatures are measured by thermal couple and pyrometer.
Jet engine thermal shock test (JETS) results

#6, Single layer $\text{La}_2\text{Zr}_2\text{O}_7$

#7, Porous 8YSZ

#8, Porous 8YSZ+ $\text{La}_2\text{Zr}_2\text{O}_7$

#9, Dense 8YSZ+ $\text{La}_2\text{Zr}_2\text{O}_7$
Thermal gradient mechanical fatigue (TGMF)

At 850 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCL porous 8YSZ</td>
<td>1200</td>
</tr>
<tr>
<td>DCL porous 8YSZ + La$_2$Zr$_2$O$_7$</td>
<td>220</td>
</tr>
<tr>
<td>DCL dense 8YSZ + La$_2$Zr$_2$O$_7$</td>
<td>50</td>
</tr>
</tbody>
</table>

At 1100 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCL porous 8YSZ + La$_2$Zr$_2$O$_7$</td>
<td>38</td>
</tr>
<tr>
<td>DCL dense 8YSZ + La$_2$Zr$_2$O$_7$</td>
<td>49</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

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 ~1.5 W/m/K [1].

Imaged based FEM calculation of thermal conductivity of La$_2$Zr$_2$O$_7$ TBC

\[
k = 0.538 \text{ W/m/K}
\]

\[
k = 0.550 \text{ W/m/K}
\]

\[
k = 0.723 \text{ W/m/K}
\]

Thermal conductivity of fully dense LZ $k=1.5$ W/m/K
Imaged based FEM calculation of thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$ coating

Calculated thermal conductivity $0.60 \pm 0.08 \text{ W/m-K}$, in good agreement with experimental data.
Summary

- \( \text{La}_2\text{Zr}_2\text{O}_7 \) powder, coating microstructure and chemistry characterizations show that \( \text{La}_2\text{Zr}_2\text{O}_7 \) is stable at high temperatures, which makes it suitable for TBC applications.
- Mechanical properties (hardness, bond strength) are similar to 8YSZ.
- Thermal conductivity of \( \text{La}_2\text{Zr}_2\text{O}_7 \) is lower than 8YSZ of similar porosity.
- Thermal properties using \textit{ab initio} and image-based finite element model calculations are in good agreement with experiments.

Future work

- Thermal cycling behavior of \( \text{La}_2\text{Zr}_2\text{O}_7 \) needs to be improved.
Composite coatings with buffer layers

Composite top coats: thermal conductivity + matching CTEs

Introducing buffer layer: Increasing strain compliance + Decreasing CTEs mismatch

2nd buffer layer: Further decrease CTEs mismatch
Publications and presentations

1. Jing Zhang, Yeon-Gil Jung, Li Li, co-organize “Advanced Coating Materials for Energy and Environmental Applications” symposium in Materials Science & Technology 2015 (MS&T15), October 4-8, 2015, Columbus, OH


3. Yeon-Gil Jung, Zhe Lu, Ungyu Paik, and Jing Zhang, Lifetime Performance of Thermal Barrier Coatings in Thermally Graded Mechanical Fatigue Environments, The 11th International Conference of Pacific Rim Ceramic Societies(PacRim-11), Jeju, Korea, August 30 - September 4, 2015


5. Xingye Guo, Jing Zhang, Zhe Lu, Yeon-Gil Jung, Theoretical prediction of thermal and mechanical properties of lanthanum zirconate nanocrystal, the 1st International Conference & Exhibition for Nanopia, Changwon Exhibition Convention Center, Gyeongsangnam-do Province, Miryang City, Korea, November 13-14, 2014

6. Sang-Won Myoung, Zhe Lu, Qizheng Cui, Je-Hyun Lee, Yeon-Gil Jung, Jing Zhang, Thermomechanical properties of thermal barrier coatings with microstructure design in cyclic thermal exposure, the 1st International Conference & Exhibition for Nanopia, Changwon Exhibition Convention Center, Gyeongsangnam-do Province, Miryang City, Korea, November 13-14, 2014
