Effect of Co-Doping on High Temperature Phase Stability of Plasma-Sprayed Yttria-Stabilized Zirconia

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Thermal Barrier Coatings

• Used in gas-turbine engines as a protective layer for engine structures

• A 200 µm thick ceramic topcoat can lower the surface temperature by more than 200°C → engine efficiency increases by ~ 6 – 12%²

• Typical topcoat material: zirconia-based ceramics:
  ➢ Low thermal conductivity
  ➢ Similar thermal expansion coefficient

Introduction

Plasma Spraying of Ceramic Topcoat

7.6 mol. % YO$_{1.5}$-ZrO$_2$ (7.6YSZ) powders

- Injected into the plasma

Accelerated and melted in hot plasma

- Powder velocity --- 100 to 550 m/s$^1$
- Powder temperature --- above $T_{\text{melt}}$ of YSZ (2680$^\circ$C)
- Coatings with lamellar structure
- Rapid solidification $\rightarrow$ metastable tetragonal phase

Metastable Phase in Plasma-Sprayed YSZ

- Redistribution of yttria prohibited ➔ t’-ZrO₂ with 7.6 mol% YO₁.₅, instead of equilibrium phases

- Desirable for TBCs
  - Low thermal conductivity
  - Non-transformable to monoclinic phase
Stability of t’-ZrO₂ Phase

Partitioning of t’-ZrO₂ at high service temperature

- t’-ZrO₂ (7.6 mol. % YO₁.₅)
- Partition at Elevated Temp
  - t’-ZrO₂ → c-ZrO₂ (15 mol.% YO₁.₅)
  - t’-ZrO₂ → t-ZrO₂ (4 mol.% YO₁.₅)
  - t’-ZrO₂ → m-ZrO₂

- Detrimental to cyclic life (volume change associated with t→m transformation)
- Stabilize t’-ZrO₂
  Co-doping with secondary cations
Starting Powder and Co-Dopants Studied

- Spray-dried 7.6 mol. % YO$_{1.5}$-ZrO$_2$ (7.6YSZ) powder

- Co-dopant: cations with large ionic radius (Ca$^{2+}$ and Yb$^{3+}$)

<table>
<thead>
<tr>
<th>Ion Type</th>
<th>Zr$^{4+}$</th>
<th>Yb$^{3+}$</th>
<th>Y$^{3+}$</th>
<th>Ca$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radius (nm)</td>
<td>0.084</td>
<td>0.99</td>
<td>0.102</td>
<td>0.112</td>
</tr>
</tbody>
</table>
Infiltration of Co-Dopants into Spray-Dried Powders

- Dissolve hydrous Ca(NO$_3$)$_2$ or Yb(NO$_3$)$_3$ in ethanol
- Vacuum infiltrate powders with co-dopant solution
- Dry at 110°C
- Calcine at 1100°C
- Plasma-spray to form coatings

<table>
<thead>
<tr>
<th>Powder</th>
<th>Salts</th>
<th>Dopant Conc. *</th>
<th>Designated Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6YSZ</td>
<td>Ca(NO$_3$)$_2$ • 4H$_2$O</td>
<td>2% Ca</td>
<td>2Ca/7.6YSZ</td>
</tr>
<tr>
<td>7.6YSZ</td>
<td>Ca(NO$_3$)$_2$ • 4H$_2$O</td>
<td>5% Ca</td>
<td>5Ca/7.6YSZ</td>
</tr>
<tr>
<td>7.6YSZ</td>
<td>Yb(NO$_3$)$_3$ • 5H$_2$O</td>
<td>2% Yb</td>
<td>2Yb/7.6YSZ</td>
</tr>
</tbody>
</table>

* Based on % substitution of total cation sites
Heat-Treatment of Coatings

- Coatings heat-treated at 1200°C for 10hrs or 100hrs
- Heating rate 10°C/min

X-Ray Diffraction Analysis

- Coatings crushed for analysis
- Cu-Kα radiation
- $2\theta = 72-76^\circ \rightarrow$ differentiate $c$-ZrO$_2$ and $t'$-ZrO$_2$
- XRD data were deconvoluted using TOPAS

Chemical Analysis of Plasma-Sprayed Coatings

• Co-dopants were successfully incorporated into coatings

<table>
<thead>
<tr>
<th>Coating</th>
<th>Element Tested</th>
<th>Expected Secondary Dopant Conc. (mol%)</th>
<th>Tested Secondary Dopant Conc. (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6YSZ</td>
<td>Ca</td>
<td>&lt;0.44</td>
<td>0.24</td>
</tr>
<tr>
<td>2Ca/7.6YSZ</td>
<td>Ca</td>
<td>2</td>
<td>1.75</td>
</tr>
<tr>
<td>5Ca/7.6YSZ</td>
<td>Ca</td>
<td>5</td>
<td>4.1</td>
</tr>
<tr>
<td>2Yb/7.6YSZ</td>
<td>Yb</td>
<td>2</td>
<td>2.69</td>
</tr>
</tbody>
</table>

• Tested by NSL using mass spectroscopy
• Based on % substitution of total cation sites
Phase Evolution of 7.6YSZ Baseline

- As-sprayed coating exhibits a single t’-ZrO$_2$ phase
- Shift of (004)t’ peak after 10 hrs at 1200°C (indicating increase in lattice parameter c in tetragonal structure)
- Limited partitioning observed after 100 hrs at 1200°C
Phase Evolution of 2Ca/7.6YSZ

- As-sprayed coating exhibits a single t’-ZrO$_2$ phase
- Angular separation between (004)t’ and (400)t’ peaks increase after 10 hrs at 1200°C
- Limited partitioning observed after 100 hrs at 1200°C
Phase Evolution of 5Ca/7.6YSZ

- As-sprayed coating exhibits a single c-ZrO$_2$ phase
- Partitioning of c-ZrO$_2$ after 10 hrs at 1200°C
- Partitioning continues after 100 hrs at 1200°C
Phase Evolution of 2Yb/7.6YSZ

Results

- As-sprayed coating exhibits a single t’-ZrO₂ phase
- Angular separation between (004)t and (400)t’ peaks increases after 10 hrs at 1200°C
- Angular separation between (004)t and (400)t’ peaks continues to increase after 100 hrs at 1200°C, no c-ZrO₂ phase observed
Phase Stability of Coatings with Different Compositions

Results

- 100-hr heat-treated at 1200°C
- 2 mol. % Ca\(^{2+}\) had little effect in stabilizing t’-ZrO\(_2\) phase
- 5 mol. % Ca\(^{2+}\) destabilized 7.6YSZ
- 2 mol. % Yb\(^{3+}\) co-doping slowed down partitioning of t’-ZrO\(_2\)
Results

Tetragonality Evolution with Heat-Treatment Time

- After 10-hr heat-treatment at 1200°C
  - tetragonality of coatings increased due to the relaxation of lattice distortion
- After 100-hr heat-treatment
  - tetragonality of 2Yb/7.6YSZ continued to increase
  - tetragonality of 7.6YSZ and 2Ca/7.6YSZ close to that of as-sprayed 7.6YSZ
Equilibrium Phase Constituent of 2Yb/7.6YSZ

- 2Yb/7.6YSZ falls within t+c two phase field
- t'-ZrO₂ not thermodynamically favored over t+c

Yb₂O₃-Y₂O₃-ZrO₂ ternary phase diagram (1200°C)¹

Partitioning Kinetics

- Kinetics of the partitioning of $2\text{Yb}/7.6\text{YSZ}$ slower than $7.6\text{YSZ}$ and $2\text{Ca}/7.6\text{YSZ}$

- $r\text{Zr}^4+ < r\text{Yb}^3+ < r\text{Y}^3+ < r\text{Ca}^2+$

- $\text{Ca}^2+$ (co-dopants with larger size) increases local distortion of the anion lattice
  \- promotes the nucleation of $\text{c-ZrO}_2$ phase\textsuperscript{1,2}
  \- De-stabilizes $t'$-\text{ZrO}_2 phase
  \- Higher $\text{Ca}^2+$ concentration, less stable

- $\text{Yb}^3+$ co-doping accommodates lattice distortion
  \- Sluggish nucleation of $\text{c-ZrO}_2$ phase

\textsuperscript{1} - N. R. Rebollo, A. S. Ganhi and C. G. Levi, unpublished work
Summary

- Co-dopants were successfully incorporated to 7.6YSZ coatings via infiltration of co-dopant solutions to spray-dried powders.

- Co-doping of 5 mol% Ca$^{2+}$ destabilized 7.6YSZ. Co-doping of 2 mol% Ca$^{2+}$ did not change the stability of 7.6YSZ.

- Co-doping of 2 mol% Yb$^{3+}$ stabilized t’-ZrO$_2$ in 7.6YSZ due to the sluggish partitioning kinetics.
CaO-Y$_2$O$_3$-ZrO$_2$ ternary phase diagram (1250°C)\textsuperscript{1}
<table>
<thead>
<tr>
<th></th>
<th>7.6YSZ</th>
<th>2Ca/7.6YSZ</th>
<th>5Ca/7.6YSZ</th>
<th>2Yb/7.6YSZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-sprayed</td>
<td>t’</td>
<td>t’</td>
<td>c</td>
<td>t’</td>
</tr>
<tr>
<td>10-hr @1200°C</td>
<td>t’</td>
<td>t’</td>
<td>c+t</td>
<td>t’</td>
</tr>
<tr>
<td>100-hr @1200°C</td>
<td>t+c</td>
<td>t+c</td>
<td>c+t</td>
<td>t’</td>
</tr>
<tr>
<td>c-ZrO₂ vol.%</td>
<td>4%</td>
<td>6%</td>
<td>36%</td>
<td>0</td>
</tr>
</tbody>
</table>
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Thermal Barrier Coatings

Relative Intensity vs. 2θ for different compositions:
- 5Ca/7.6YSZ
- 2Ca/7.6YSZ
- 7.6YSZ

Peaks identified:
- (004)t
- (400)t
- (004)c
- (400)c
- (400)t'
- 2Yb/7.6YSZ
### Parameter of plasma spraying

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current (Amps)</td>
<td>900</td>
</tr>
<tr>
<td>Volts (@gun)</td>
<td>41.3</td>
</tr>
<tr>
<td>Arc gas (scfh)</td>
<td>54 (Ar)</td>
</tr>
<tr>
<td>Aux gas (scfh)</td>
<td>44 (He)</td>
</tr>
<tr>
<td>Carrier gas (scfh)</td>
<td>13 (Ar)</td>
</tr>
<tr>
<td>Powder feed rate (rpm)</td>
<td>1.5</td>
</tr>
<tr>
<td>Stand off distance (cm)</td>
<td>10.0</td>
</tr>
</tbody>
</table>

* scfh = standard cubic feet per hour