Thermochemistry of Protective Coatings and Molten Silicate Debris

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Outline of Presentation

• Ceramic Coating Materials

• Experimental Thermodynamics
  - Integral thermodynamic quantities: High Temperature Reaction Calorimetry

• Rare earth Silicates and Zirconia based Coatings Exposed to Mineral Dust Particles (CMAS) and High Temperature Calorimetry

• Enthalpies of Formation of Calcium Rare-earth Silicate Oxyapatites and High Temperature Drop Solution Calorimetry (AlexSys)
Ceramic Coating Materials

- Thermal Barrier Coatings (TBCs): Reduce heat flux towards the underlining material
  7YSZ, 31YSZ, 16RESZ (RE = Y, Gd and Yb), Gd$_2$Zr$_2$O$_7$

- Environmental Barrier Coatings (EBCs): Barrier to chemically corrosive agents
  Y$_2$Si$_2$O$_7$ and Yb$_2$Si$_2$O$_7$
Experimental Thermodynamics: High Temperature Calorimetry

1. Coating Materials - Mineral Dust Particles

HT Drop Solution Calorimetry @ 1500 °C
-coating materials dropped into the calorimeter containing molten silicate debris solvent (CaO-MgO-Al₂O₃-SiO₂ or CMAS)

\[ \Delta H_{ds} = \Delta H_{TTD} + \Delta H_s \]
\[ \Delta H_s = \Delta H_{mix} + \Delta H_{fusion} \]
\[ \Delta H_{reaction} = n\Delta H_s, \text{coating} - n\Delta H_s, \text{reaction products} \]

- Process is favored: more exo (negative) or less endo (positive)
- Coating selection

2 – Calcium Rare-earth Silicate Oxyapatites

HT Drop Solution Calorimetry @ 805 °C
-Calium rare-earth silicate oxyapatites dropped into the calorimeter containing lead borate solvent

\[ \Delta H_f \text{ for } Ca_2RE_8Si_6O_{26} (Y, \text{Nd, Sm, Gd, Dy, Er, Er, and Yb}); \text{ main corrosion product between CMAS and coating materials} \]

- Stability increases: more exo (negative)
- Input into thermodynamic codes
Rare earth Silicates and Zirconia based Coating Materials Exposed to Mineral Dust Particles (CMAS) and High Temperature Calorimetry

Rare earth Silicates and Zirconia based Coatings Exposed to Mineral Dust Particles (CMAS) and High Temperature Calorimetry

- Collaboration between NASA GRC and University of California, Davis (Prof. Alexandra Navrotsky)
- Combination of three calorimetric techniques and High Temperature X-ray diffraction
  1. High Temperature Solution Calorimetry – uses molten CMAS as a solvent
  2. Drop-and-catch (DnC) calorimetry
  3. Differential thermal analysis (DTA)
- Coating Materials
  - TBCs – 7YSZ, 31YSZ, 16RESZ (RE = Y, Gd and Yb), Gd$_2$Zr$_2$O$_7$
  - EBCs – Y$_2$Si$_2$O$_7$ and Yb$_2$Si$_2$O$_7$
- Reaction Products
  - Apatites - CaY$_4$Si$_3$O$_{13}$ and CaYb$_4$Si$_3$O$_{13}$
- CMAS with varying Ca/Si (0.27, 0.48 and 0.71)

High Temperature Solution Calorimetry

Setaram MHTC-96 – UC Davis

\[ \Delta H_{ds} = \Delta H_{TTD} + \Delta H_s \]

\[ \Delta H_{reaction} \] assuming apatite formation

\[ \Delta H_{mix} \] knowing \[ \Delta H_{fusion} \]

Drop-and-Catch (DnC) Calorimetry

Designed and built at UC Davis

$\Delta H_{\text{mix}} = \Delta H_s - \Delta H_{\text{fusion}}$

High Temperature Solution Calorimeter

DnC on 7YSZ sample

Differential Thermal Analysis (DTA)

Setaram Setsys Evolution – UC Davis

\[ \Delta H_{\text{mix}} = \Delta H_s - \Delta H_{\text{fusion}} \]

High Temperature Solution Calorimeter

DTA on Yb$_2$Si$_2$O$_7$ and CaYb$_4$Si$_3$O$_{13}$

Calorimetric Results

Enthalpies of solution of the coating materials and apatites measured by high temperature calorimetry in molten CMAS at 1723 K.

<table>
<thead>
<tr>
<th>Material in CMAS (0.71 Ca/Si)</th>
<th>Avg. Avg. reaction time (min)</th>
<th>ΔH_s (kJ/g-atom)</th>
<th>ΔH_{mix} (kJ/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7YSZ</td>
<td>7</td>
<td>-4.78 ± 1.14</td>
<td></td>
</tr>
<tr>
<td>16RESZ</td>
<td>15</td>
<td>12.71 ± 1.41</td>
<td></td>
</tr>
<tr>
<td>31YSZ</td>
<td>20</td>
<td>17.86 ± 1.51</td>
<td></td>
</tr>
<tr>
<td>Gd_2Zr_2O_7</td>
<td>10</td>
<td>-7.59 ± 0.65</td>
<td></td>
</tr>
<tr>
<td>Y_2Si_2O_7</td>
<td>9</td>
<td>19.46 ± 2.88</td>
<td></td>
</tr>
<tr>
<td>Yb_2Si_2O_7</td>
<td>11</td>
<td>12.38 ± 0.65</td>
<td></td>
</tr>
<tr>
<td>CaY_4Si_3O_13</td>
<td>8</td>
<td>4.78 ± 1.00</td>
<td></td>
</tr>
<tr>
<td>CaYb_4Si_3O_13</td>
<td>7</td>
<td>11.57 ± 0.72</td>
<td></td>
</tr>
</tbody>
</table>

Enthalpies and entropies of fusion of the coating materials, and enthalpies of mixing between molten CMAS and the coating materials at 1723 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>ΔH_{fusion}^* (kJ/g-atom)</th>
<th>ΔH_{mix} (kJ/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7YSZ</td>
<td>19.73 ± 3.06</td>
<td>-24.51 ± 3.27</td>
</tr>
<tr>
<td>Yb_2Si_2O_7</td>
<td>13.73 ± 0.73</td>
<td>-1.35 ± 0.98</td>
</tr>
<tr>
<td>CaYb_4Si_3O_13</td>
<td>11.43 ± 0.52</td>
<td>0.14 ± 0.89</td>
</tr>
</tbody>
</table>

Process is more favored: more exo (negative) or less endo (positive).

Calorimetric Results

\[ \Delta H_{\text{reaction}} \rightarrow \text{Process is favored: more exo (negative) or less endo (positive)} \]

Enthalpies of reaction between the coatings and CMAS melt assuming apatite formation at 1723 K

1 - \( \text{Zr}_{0.88} \text{Y}_{0.12} \text{O}_{1.94(\text{xl})} + 0.09\text{SiO}_2(\text{CMAS}) + 0.03\text{CaO}_{(\text{CMAS})} = 0.03\text{CaY}_4\text{Si}_3\text{O}_{13(\text{xl})} + 0.88\text{ZrO}_2(\text{CMAS}) \)

2 - \( \text{Zr}_{0.53} \text{Y}_{0.47} \text{O}_{1.77(\text{xl})} + 0.35\text{SiO}_2(\text{CMAS}) + 0.03\text{CaO}_{(\text{CMAS})} = 0.12\text{CaY}_4\text{Si}_3\text{O}_{13(\text{xl})} + 0.53\text{ZrO}_2(\text{CMAS}) \)

3 - \( \text{Y}_2\text{Si}_2\text{O}_7(\text{xl}) + 0.5\text{CaO}_{(\text{CMAS})} = 0.5\text{CaY}_4\text{Si}_3\text{O}_{13(\text{xl})} + 0.5\text{SiO}_2(\text{CMAS}) \)

4 - \( \text{Yb}_2\text{Si}_2\text{O}_7(\text{xl}) + 0.5\text{CaO}_{(\text{CMAS})} = 0.5\text{CaYb}_4\text{Si}_3\text{O}_{13(\text{xl})} + 0.5\text{SiO}_2(\text{CMAS}) \)

<table>
<thead>
<tr>
<th>Enthalpy change</th>
<th>( \Delta H_{\text{reaction}} ) (kJ/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_1 = \Delta H_{\text{sol}}(\text{Zr}<em>{0.88} \text{Y}</em>{0.12} \text{O}<em>{1.94(\text{xl}, 1450^\circ\text{C})}) - 0.03 \Delta H</em>{\text{sol}}(\text{CaY}_4\text{Si}<em>3\text{O}</em>{13(\text{xl}, 1723 \text{K})}) )</td>
<td>-4.92 ± 1.14</td>
</tr>
<tr>
<td>( \Delta H_2 = \Delta H_{\text{sol}}(\text{Zr}<em>{0.53} \text{Y}</em>{0.47} \text{O}<em>{1.77(\text{xl}, 1450 ^\circ\text{C})}) - 0.1175 \Delta H</em>{\text{sol}}(\text{CaY}_4\text{Si}<em>3\text{O}</em>{13(\text{xl}, 1723 \text{K})}) )</td>
<td>17.30 ± 1.51</td>
</tr>
<tr>
<td>( \Delta H_3 = \Delta H_{\text{sol}}(\text{Y}_2\text{Si}_2\text{O}<em>7(\text{xl}, 1450 ^\circ\text{C})) - 0.5 \Delta H</em>{\text{sol}}(\text{CaY}_4\text{Si}<em>3\text{O}</em>{13(\text{xl}, 1723 \text{K})}) )</td>
<td>17.07 ± 2.92</td>
</tr>
<tr>
<td>( \Delta H_4 = \Delta H_{\text{sol}}(\text{Yb}_2\text{Si}_2\text{O}<em>7(\text{xl}, 1450 ^\circ\text{C})) - 0.5 \Delta H</em>{\text{sol}}(\text{CaYb}_4\text{Si}<em>3\text{O}</em>{13(\text{xl}, 1723 \text{K})}) )</td>
<td>6.60 ± 0.74</td>
</tr>
</tbody>
</table>

**High temperature X-ray diffraction**

Crystalline phases detected during heating of ceramic material coatings and NASA CMAS powder mixture up to 1666 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1465 – 1666</td>
<td>$\text{Ca}_4\text{Y}_6\text{O(SiO}_4\text{)}_6$ apatite</td>
</tr>
<tr>
<td></td>
<td>$\text{Al(Al}<em>{1.27}\text{Si}</em>{0.728}\text{O}_{4.864})$, mullite</td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}<em>2\text{Mg}</em>{0.75}\text{Al}<em>{0.5}\text{Si}</em>{1.75}\text{O}_7$, akermanite</td>
</tr>
<tr>
<td></td>
<td>$\text{MgSiO}_3$, clinoenstatite</td>
</tr>
<tr>
<td>1161 – 1465</td>
<td>$\text{Ca}<em>2\text{Mg}</em>{0.46}\text{Al}<em>{1.99}\text{Si}</em>{1.52}\text{O}_7$, akermanite</td>
</tr>
<tr>
<td></td>
<td>$\text{MgSiO}_3$, enstatite</td>
</tr>
<tr>
<td></td>
<td>$(\text{Ca}<em>{12}\text{Al}</em>{14}\text{O}<em>{32})\text{O}</em>{1.32}$, mayenite</td>
</tr>
<tr>
<td>1566 – 1666</td>
<td>$\text{Ca}_4\text{Yb}_6\text{O(SiO}_4\text{)}_6$ apatite</td>
</tr>
<tr>
<td>298 – 1666</td>
<td>$\text{Zr(SiO}_4\text{)}$, zircon</td>
</tr>
<tr>
<td></td>
<td>m, t and c YSZ</td>
</tr>
<tr>
<td></td>
<td>$\text{SiO}_2$, quartz</td>
</tr>
<tr>
<td></td>
<td>$\text{CaSiO}_3$, wollastonite</td>
</tr>
</tbody>
</table>

Summary

Rare-Earth Silicates and Zirconia based coatings

- Enthalpies of solution for YDS, YbDS, Y and Yb – apatites, 16RESZ and 31YSZ are moderately positive except for 7YSZ and Gd$_2$Zr$_2$O$_7$
- Enthalpies of solution of YDS and YbDS becomes less endothermic with decreasing Ca/Si while an opposite trend is observed for Gd$_2$Zr$_2$O$_7$
- Apatite formation is only favorable over coating dissolution in terms of enthalpy for 7YSZ
- Mixing Enthalpies of YbDS and Yb apatite are less exothermic than 7YSZ
- The energetics for apatite formation in the case of silicates is favorable when other intermediate phases are present
  - Y$_2$Si$_2$O$_7$ - CMAS reaction, akermanite, mullite and clinoenstatite were detected between 1161 and 1465 K
  - Yb$_2$Si$_2$O$_7$ - CMAS reaction, akermanite, enstatite and mayenite were detected between 1161 and 1465 K prior to the detection of apatite at 1566 K.

Energetics of Calcium Rare-earth Silicate Oxyapatites

Corrosion product of Ceramic Coatings
Ca$_2$RE$_8$Si$_6$O$_{26}$ (Y, Nd, Sm, Gd, Dy, Er, and Yb)
Rare – earth silicates (EBCs) + silicate debris (CMAS) = Rare-earth silicate oxyapatites

$^{IX}M(1)_{4}^{VII}M(2)_6^{(IV)TO_4}_6X_2$ – generic formula
M – Rare-earth or alkaline earth
X – mono or divalent anions
T – p - block element
Superscript – coordination number

RE$_{10}$Si$_6$O$_{27}$ – interstitial oxygen
RE$_{9.33}$Si$_6$O$_{26}^{0.67}$ – cation vacancies
RE$_8$AE$_2$Si$_6$O$_{26}$ – stoichiometric
AE – alkaline earth

High Temperature Solution Calorimetry

Setaram “AlexSys”
NASA GRC

\[ \Delta H_{ds} = \Delta H_{TTD} + \Delta H_s \]

\[ \text{Calcium RE oxyapatites} \]

\[ \text{RE oxides} \]

\[ \text{Quartz} \]

\[ \text{Lime} \]

\[ \text{Calcium RE oxyapatites} \]

\[ \Delta H_1 = - \Delta H_{ds} \]

\[ \Delta H_2 = 4\Delta H_{ds} \]

\[ \Delta H_3 = 6\Delta H_{ds} \]

\[ \Delta H_4 = 2\Delta H_{ds} \]

\[ \Delta H_5 = \Delta H_{f, ox} \]

\[ \text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}(\text{xl, 25 °C}) = \text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}(\text{sol, 800 °C}) \]

\[ 4\text{RE}_2\text{O}_3(\text{xl, 25 °C}) = 4\text{RE}_2\text{O}_3(\text{sol, 800 °C}) \]

\[ 6\text{SiO}_2(\text{xl, 25 °C}) = 6\text{SiO}_2(\text{sol, 800 °C}) \]

\[ 2\text{CaO}(\text{xl, 25 °C}) = 2 \text{CaO}(\text{sol, 800 °C}) \]

\[ 2\text{CaO}(\text{xl, 25 °C}) + 6\text{SiO}_2(\text{xl, 25 °C}) + 4\text{RE}_2\text{O}_3(\text{xl, 25 °C}) = \text{Ca}_2\text{RE}_8\text{Si}_6\text{O}_{26}(\text{xl, 25 °C}) \]
Calorimetric Results

Enthalpy of formation of the Rare – earth silicate oxyapatites Versus their ionic potential (Z/r)


Summary

Calcium Rare-earth Apatites

• Apatites are significantly more stable relative to their binary oxides
• Calcium RE silicate oxyapatites are more stable than the RE oxyapatites with cation vacancies
• Apatite phases become more stable as the ionic potential decreases or the ionic radius become larger