Interconnect-Coating Interactions: Transition Metal Spinel Oxides

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• Researchers
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Reducing Cr Poisoning in SOFCs

• Chromium poisoning
  – Oxidation of $\text{Cr}_2\text{O}_3$ to $\text{Cr}^{6+}$ species
    ($\text{CrO}_2(\text{OH})_2$ or $\text{CrO}_3$)
  – Deposition of $\text{Cr}_2\text{O}_3$ on cathode
  – Occurs even at IT-SOFC temperatures

• Cr-poisoning reduced with coating

• Alloy-coating interaction
  – Forms modified scale
  – $(\text{Mn,Co})_3\text{O}_4$: Transition from chromia to spinel

• Can lower chromium contents be used in coated alloys?
Mn-Co-Cr-O System

(Mn,Co)\(_3\)O\(_4\)-Cr\(_2\)O\(_3\) reaction

Mn\(_2\)O\(_3\) \quad Mn\(_3\)O\(_4\) \quad Co\(_2\)O\(_3\) \quad Co\(_3\)O\(_4\)

0.57 O \quad 0.60 O \quad 0.50 O

M\(_{2+}\)/M\(_{3+}\)
**Interconnect Alloy-Coating Interaction**

- Coating: \((\text{Mn,Co})_3\text{O}_4\)
- Reaction Layer: \((\text{Mn,Co,Co})_3\text{O}_4\) and \((\text{Mn,Co})\text{Cr}_2\text{O}_4\)
- Oxide scale: \(\text{Cr}_2\text{O}_3\)

**Spinel**

- Fe/Ti/Y dopants affect transport in \((\text{Mn,Co,Cr})_3\text{O}_4\) or at interface – i.e. they are not present in \((\text{Mn,Co})\text{Cr}_2\text{O}_4\)

- Reaction:
  - \(\text{Cr}^{3+}\) grows \((\text{Mn,Co})\text{Cr}_2\text{O}_4\)
  - \(\text{Mn}^{2+}\) and \(\text{Co}^{2+}\) at high \(\text{Cr}_2\text{O}_3\) activity

**Original interface**

**Low Mn solubility**

**Highly faceted morphology**
Doped \((\text{Mn,Co})_3\text{O}_4\) – 1000°C / 72 hr

**Chromium**

With dopant: Steeper gradient in \((\text{Mn,Co,Cr})_3\text{O}_4\)

Distance from sample surface

- 3% Ti: \(\text{Mn}_{1.455}\text{Co}_{1.455}\text{Ti}_{0.09}\text{O}_4\)
- 11% Ti: \(\text{MnCo}_{1.66}\text{Ti}_{0.34}\text{O}_4\)

Distance from Pt marker

- 5% Fe: \(\text{Mn}_{1.425}\text{Co}_{1.425}\text{Fe}_{0.15}\text{O}_4\)
- 3% Y: \(\text{Mn}_{1.455}\text{Co}_{1.455}\text{Y}_{0.09}\text{O}_4\)

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Doped (Mn,Co)$_3$O$_4$ – 1000°C / 72 hr

Manganese

Cobalt

Mn:Co < 1

Distance from Pt marker

3% Ti: Mn$_{1.455}$Co$_{1.455}$Ti$_{0.09}$O$_4$

5% Fe: Mn$_{1.425}$Co$_{1.425}$Fe$_{0.15}$O$_4$

11% Ti: MnCo$_{1.66}$Ti$_{0.34}$O$_4$

3% Y: Mn$_{1.455}$Co$_{1.455}$Y$_{0.09}$O$_4$

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3% Ti

Dopant Location

5% Fe

Chromium

Titanium

Iron

No dopant in (Mn,Co)Cr₂O₄ layer
Reaction LayerThickness
(900°C for 144 hrs)

- Ti and Fe additions significantly decrease the thickness of the reaction layer – small increase in CTE

Mn_{1.5}Co_{1.5}O_4
CTE = 10.6 \times 10^{-6} \degree C^{-1}

MnCo_{1.66}Ti_{0.34}O_4
CTE = 11.2 \times 10^{-6} \degree C^{-1}

MnCo_{1.66}Fe_{0.34}O_4
CTE = 12 \times 10^{-6} \degree C^{-1}
Activations Energy:

• Decreases with decreasing temperature
• Similar for doped and undoped
Conductivity of Fe- and Ti-doped (Mn,Co)₃O₄

Fe-doped: Conductivity same as Mn₁.₅Co₁.₅O₄

Ti-doped: Conductivity lower than Mn₁.₅Co₁.₅O₄ but higher than MnCo₂O₄

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Conductivity of \((\text{Mn,Co,Cr})_3\text{O}_4\)

Increasing Cr content in \((\text{Mn,Co})_{3-x}\text{Cr}_x\text{O}_4\)

High Cr similar to \(\text{Cr}_2\text{O}_3\)

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Conductivity of \((\text{Mn, Co, Cr})_3\text{O}_4\)

Increase in activation energy occurs for 0.5-1.0 Cr

Log Conductivity (S/cm) vs. Activation Energy (eV)

Conductivity at 800°C

Activation Energy

\(x\) in \(\text{Mn}_{1.5-0.5x}\text{Co}_{1.5-0.5x}\text{Cr}_x\text{O}_4\)

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## Experimental Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Concentration (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>H52</td>
<td>Bal.</td>
</tr>
<tr>
<td>H53</td>
<td>Bal.</td>
</tr>
<tr>
<td>H54</td>
<td>Bal.</td>
</tr>
<tr>
<td>H55</td>
<td>Bal.</td>
</tr>
<tr>
<td>AISI 441</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Alloys were supplied by Allegheny Technologies, Inc. (ATI) (Matthew Bender)

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Experimental Alloy Evaluation

- **Coatings**
  - Some samples coated with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ by Pacific Northwest National Laboratory (PNNL) (Jeffry Stevenson) using slurry coating process

- **Oxidation Exposure**
  - Cyclic oxidation at 800 C
  - Isothermal oxidation for 800 and 1600 hours at 800 C

- **Characterization**
  - Scanning electron microscopy (SEM) with energy dispersive x-ray spectroscopy (EDS)
  - X-ray diffraction (XRD)
Cyclic Oxidation at 800°C

Large initial weight gain in coated samples due to reoxidation of Co in coating.

Coated vs. Uncoated samples over time.
Parabolic Rate Constants – Cr Content

- $k_p$ of coated alloys lower than uncoated
- No strong Cr dependence
- Experimental alloys high $k_p$ than 441
Parabolic Rate Constants - Literature

Values of $k_p$ of similar to those found in the literature

Gray line/symbols for oxidation of ferritic stainless steels in air
Isothermal Oxidation at 800°C

![Graph showing weight change over time for uncoated and coated alloys in cyclic and isothermal conditions.]

- **Uncoated alloys** in **cyclic** and **isothermal** conditions show different weight gain patterns.
- **Coated alloys** in **cyclic** and **isothermal** conditions also show different weight gain patterns.

**Graph highlights:**
- Isothermal weight gains similar to cyclic.

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Cross-Sections: 13-15%Cr – 800°C/800 h

13% Cr (H52)

15% Cr (H53)

Concentration (at%) vs. Distance (μm)
Cross-Sections: 17-18%Cr – 800°C/800 h

17% Cr (H54)

18% Cr (H55)

[Graphs showing concentration profiles for Cr, Mn, Co, Fe, Ti, and Nb over distance (μm).]

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Scale Thickness – Coated Alloys after 800 hours at 800°C

- 99%+ confidence that scales for 17-18%Cr are thinner than those for 13-15%Cr
- 85%+ confidence that 13%Cr and 15%Cr are different

50 thickness measurements from SEM micrographs

Error bars represent 1 standard deviation
Reaction Layer – 800°C/800 h

Distance referenced to original interface

Cr Concentration (at%) vs. Distance (μm)

- 13/15% Cr
- 17/18% Cr
- 13% Cr
- 18% Cr

Temperature: 800°C
Time: 800 h
3-7% Mn
2-5% Co

Mn/Co Ratio – 800°C/800 h

Coating
1:1 Mn:Co

Low Mn / High Co in Cr-containing spinel

Cr³⁺ strongest preference for octahedral site

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Titanium
800°C/800 h

Ti present at alloy-scale interface
Interconnect Alloy-Coating Interaction

Oxide scale

Cr₂O₃

(Mn,Co)Cr₂O₄

(Mn,Co,Cr)₃O₄

Co²⁺

Mn²⁺

Co³⁺/Co²⁺

Mn³⁺/Mn²⁺

Cr³⁺

Growth

Reaction Layer

Coating

(Mn,Co)₃O₄

Alloy

Spinel

Original interface

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Conclusions

• Conductivity of spinel decreases with increasing Cr content
  – Decrease thickness / increase conductivity of Cr$_2$O$_3$ or Cr-rich spinel

• Low-chromium alloys with alloy additions present in 441
  – Uncoated alloys
    • Difference between Cr contents in experimental alloys less than that between experimental alloys and 441
  – Coated alloys
    • Composition gradients / phase formation similar among alloys
    • Reaction layer thicker for alloys with low Cr content
    • 17-18 %Cr better than 13-15 %Cr