MINIMIZING CR-EVAPORATION FROM BALANCE OF PLANT COMPONENTS BY UTILIZING COST-EFFECTIVE ALUMINA-FORMING AUSTENITIC STEELS

Xingbo Liu
West Virginia University

Mike Brady
Oak Ridge National Laboratories

June 15, 2018
Background - SOFC Cathode Degradation

- Microstructural changes (loss effective TPB area)
  - Grain growth
  - Coarsening of the particles
  - Surface re-construction
- Strontium segregation related issues
  \[ 2Sr_{La}^i + V_{O,LSCF}^{**} + 2O_{O}^{x} \leftrightarrow 2SrO(s) \]
- Chemical reaction with YSZ electrolyte.
  \[ La_2O_3(s) + 2ZrO_2(s) \rightarrow La_2Zr_7O_3(s) \quad SrO(s) + ZrO_2(s) \rightarrow SrZrO_3(s) \]
- Poisoning of the cathode (e.g. by CO_2, chromium species etc.)
  \[ SrO(s) + H_2O(g) \rightarrow Sr(OH)_2(s) \quad SrO(s) + CO_2(g) \rightarrow SrCO_3(s) \]
  \[ 2Cr_2O_3(s) + 3O_2(g) + 4H_2O(g) \rightarrow 4CrO_2(OH)_2(g) \]
Cr$_2$O$_3$ Related Degradations

- Cr poisoning of SOFC Cathode

\[
\begin{align*}
\text{Cr}_2\text{O}_3(s) + 1.5\text{O}_2(g) &= 2\text{CrO}_3(g) \\
\text{Cr}_2\text{O}_3(s) + 1.5\text{O}_2(g) + 2\text{H}_2\text{O}(g) &= 2\text{CrO}_2(\text{OH})_2(g)
\end{align*}
\]

- Reactions with other components

\[
\begin{align*}
2\text{Cr}_2\text{O}_3(s) + 4\text{BaO}(s) + 3\text{O}_2(g) &= 4\text{BaCrO}_4(s) \\
\text{CrO}_2(\text{OH})_2(g) + \text{BaO}(s) &= \text{BaCrO}_4(s) + \text{H}_2\text{O}(g)
\end{align*}
\]

J. Power Sources 152 (2005) 156–167

- Cr Sources: Interconnect and BOP

J. Power Sources 162 (2006) 1043–1052
SOFC Interconnect Coatings

- Various Spinel Coatings (Mn-Co, Mn-Cu, etc.)
- PVD, CVD, Spray, Electroplating, EPD

Electroplating Mn-Co


EPD Mn-Co spinel

Hui Zhang, Zhaolin Zhan, Xingbo Liu, JPS 196 (2011) 8041-8047

Coating impedes degradation of SOFCs

Research at West Virginia University is conducted in collaboration with scientists from the Department of Energy’s National Energy Technology Laboratory. The results of this collaboration have led to the development of a novel microstructure control process to improve SOFC performance.

The new process uses an electroplating technique that significantly improves key performance attributes, including higher electric conductivity, improved mechanical properties, and lower material costs. The researchers are now investigating how best to use these materials in practical applications.

Further improvements are anticipated as new materials are developed. These advancements are expected to significantly enhance SOFC performance and reduce costs.
Project Technical Approaches

Developing Cost-Effective Alumina Forming Austenitic Stainless Steels (AFA), to replace Austenitic Stainless Steel 316L and Ni-base Superalloy Inconel 625, for Key Balance of Plant (BOP) components, to minimize Cr-Poisoning of SOFC Cathode.
AFA Form Transient Al-Rich Oxide Overlying Inner, Columnar α-Al₂O₃

TEM of HTUPS 4 After 1000 h at 800°C in Air + 10% Water Vapor

- α-Al₂O₃ the source of the excellent oxidation resistance
- Occasional transient nodules 0.5-5 μm thick, some Nb-oxide also detected
Project Objectives – Phase I

- Develop and utilize cost-effective alumina forming austenitic steels (AFAs) for balance of plant (BOP) components and pipes in solid oxide fuel cell (SOFC) systems to minimize the Cr-poisoning and improve system stability;

- Systematically investigate the influence of the operation condition, i.e., temperature and moisture, on the oxidation and Cr-release from the AFA steels, and their effects on the degradation of SOFC performance

- Prepare for Phase II of the project, in which we will manufacture and test the related BOP components in industrial SOFC systems
Multiple AFA Grades Under Study for Balance of Cost, Processability, Cr-Evaporation, and Oxidation

• Two temperature regimes of interest: 700-800°C and 900-950°C
  - temperature targets vary with component and SOFC manufacturer

• Upper-temperature oxidation limit for AFA composition dependent
  - ≤ 850°C: Fe-25Ni-14Cr-(3-3.5)Al-(1-2.5)Nb-(0.1-0.2C) *base
  - 900-1000°C: Fe-(25-35)Ni-(15-18)Cr-4Al-(1-2.5)Nb-(0.1-0.2C) *base ± Hf, Y, Zr

• Cost and ease of processing varies with alloy content
  - higher Ni, Nb, and Hf, Y, Zr increases cost
  - Zr lower cost than Hf, easier processing

*Minor additions of Mn, Si, Mo, W, B, etc. also used in some AFA compositions
**Material Compositions**

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>Al</th>
<th>Nb</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>C</th>
<th>B</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AFA for ≤ 800°C use</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MOD 2 OCD</td>
<td>51</td>
<td>25</td>
<td>14</td>
<td>4</td>
<td>1</td>
<td>2</td>
<td>0.15</td>
<td>2</td>
<td>0</td>
<td>0.15</td>
<td>0.01</td>
<td>0.5Cu</td>
</tr>
<tr>
<td>OC5</td>
<td>51</td>
<td>25</td>
<td>14</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>0.15</td>
<td>2</td>
<td>1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.5Cu</td>
</tr>
<tr>
<td>OC4</td>
<td>49</td>
<td>25</td>
<td>14</td>
<td>3.5</td>
<td>2.5</td>
<td>2</td>
<td>0.15</td>
<td>2</td>
<td>1</td>
<td>0.1</td>
<td>0.01</td>
<td>0.5Cu</td>
</tr>
<tr>
<td><strong>AFA for ≥ 850°C use</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCF</td>
<td>49</td>
<td>25</td>
<td>14</td>
<td>4</td>
<td>2.5</td>
<td>2</td>
<td>0.15</td>
<td>2</td>
<td>1</td>
<td>0.2</td>
<td>0.01</td>
<td>0.5Cu</td>
</tr>
<tr>
<td>OC11</td>
<td>49</td>
<td>25</td>
<td>15</td>
<td>4</td>
<td>2.5</td>
<td>2</td>
<td>0.15</td>
<td>2</td>
<td>0</td>
<td>0.1</td>
<td>0.01</td>
<td>0.5Cu Hf, Y</td>
</tr>
<tr>
<td>35Ni</td>
<td>39</td>
<td>35</td>
<td>18</td>
<td>3.5</td>
<td>1</td>
<td>2</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
<td>0.15</td>
<td>0.01</td>
<td>0.5Cu Hf, Y</td>
</tr>
<tr>
<td><strong>Benchmark commercial Cr₂O₃-forming alloys</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>310S</td>
<td>53</td>
<td>20</td>
<td>25</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0.75</td>
<td>0.75</td>
<td>0</td>
<td>0.08</td>
<td>0</td>
<td>0.5Cu</td>
</tr>
<tr>
<td>625</td>
<td>5</td>
<td>61</td>
<td>22</td>
<td>0.2</td>
<td>3</td>
<td>0.4</td>
<td>0.25</td>
<td>8</td>
<td>0</td>
<td>0.04</td>
<td>0</td>
<td>0.2Ti</td>
</tr>
</tbody>
</table>

- Rare element additive;
- Benchmark samples;

- *Alloy compositions confirmed by bulk chemical analysis.*
Experimental set up and Test Matrix

Fresh sample test: 10% H₂O, 500 hours

<table>
<thead>
<tr>
<th>Sample</th>
<th>OC4</th>
<th>OC5</th>
<th>OCF</th>
<th>310S</th>
<th>New 35 Ni</th>
<th>OC-11</th>
<th>MOD 2 OC-D</th>
<th>Alloy 625</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C*</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>—</td>
<td>—</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>850 °C</td>
<td>✓</td>
<td>in process</td>
<td>in process</td>
<td>✓</td>
<td></td>
<td>—</td>
<td></td>
<td>in process</td>
</tr>
<tr>
<td>900 °C</td>
<td>✓</td>
<td>—</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>—</td>
<td>✓</td>
</tr>
</tbody>
</table>

*Note: at 700°C, the Cr release was below the detection limit for the AFA alloys and Ni-base alloy 625 control.

Sample size: 25 mm × 20 mm × 1 mm, polished up to 800 grit before use.
Effect of Temperature on the Cr-Evaporation

- Cr evaporation rate increased with the increase of temperature.
- The Cr release rate keeps relatively stable after 850 °C;
Effect of Temperature on the Cr-Evaporation

Microstructure vs. Temperature for 310S
Effect of Temperature on the Cr-Evaporation

Microstructure vs. Temperature for OC4
Effect of Alloy Composition on the Cr-Evaporation

XRD of the corrosion films.

310s vs. OC4, at 850 °C, 10% H₂O 500 h.
SEM and EDS Analysis for the Surface of 310S

Different area SEM images for 310S after 850 °C for 500 hours in air with 10% water vapor and EDS spectrums.

Si disappear
Cross section of 310S: STEM-EDX mapping and XPS depth profiling by ORNL

XPS depth profiling might be corresponding to the area A, while the STEM element mapping corresponding to the area B. This indicates the corrosion film is not uniformly covered on the surface. Some areas are not covered with Cr-rich oxide.
Notes: before crystal Cr$_2$O$_3$ layer forming on the top of the corrosion scale, the surface is rich of Si-containing composition.
SEM and EDS Analysis for the surface of OC4

SEM images for OC4 after 850 °C for 500 hours in air with 10% water vapor and EDS spectrums.
OC4 Cross Section: Analyzed by FuelCell Energy
OC4 Cross Section: line scan by *FuelCell Energy*
Cross Section of OC4: STEM-EDX Mapping and XPS Depth Profiling by ORNL

- Continuous inner \( \text{Al}_2\text{O}_3 \)
- Duplex transient scale of middle \( \text{Cr}_2\text{O}_3 \) rich + outer Mn-Cr-Al oxide
- Cr release rate decrease with time after transient cut off by \( \text{Al}_2\text{O}_3 \)?

Multi-Layer scale formed on AFA OC-4 after 500 h at ~850°C in Air + 10% \( \text{H}_2\text{O} \).

- Continuous inner \( \text{Al}_2\text{O}_3 \)
- Duplex transient scale of middle \( \text{Cr}_2\text{O}_3 \) rich + outer Mn-Cr-Al oxide
- Cr release rate decrease with time after transient cut off by \( \text{Al}_2\text{O}_3 \)?
AFAs vs. Chromia-forming 310S and Ni-base Alloy 625 at 900 °C, 10% H₂O 500 h.

- Little difference among AFA alloys at 900 °C (all “good”, especially for OC11).
- AFA significantly lower oxidation than Cr₂O₃ forming 310S.
AFAs vs. Chromia-forming 310S and Ni-base Alloy 625 at 900 °C, 10% H₂O 500 h.

Fe-(25-35)Ni-(15-18)Cr-4Al-(1-2.5)Nb-(0.1-0.2C) base + rare element (Hf and Y) show highest resistance for Cr evaporation.
OC11 (rare elements additive) show the lowest Cr evaporation rate. Thus, was further investigated and characterized in detail.

OC11 at Higher Temperature

OC11-1: 900 °C, 1000 h 10% H₂O

OC11: 900 °C

OC11: 1000 °C

Normal scale

excessive scale

OC11: 1000 °C, 1000 h 10% H₂O
STEM and EDX mapping for OC11-1 Tested at 900 °C for 1000 h in 10% H₂O₂

• Minor Cr, Fe, Mn in transient; Nb enrich at transient/Al₂O₃
• Hf enrich at columnar Al₂O₃
STEM and EDX mapping for OC11 Tested at 1000 °C for 1000 h in 10% H₂O

Surface and cross-section of **excessive scale**.
STEM and EDX mapping for OC11 tested at 1000 °C for 1000 h in 10% H₂O

Surface and cross-section of normal scale.
XPS Shows Al-rich Oxide on OC11 25Ni + Hf, Y AFA after 1000 h in Air with 10% H₂O

- **Al₂O₃ base oxide scale with only a few % Cr at outer surface**
- **XPS averaged over 400 micron spot**
Oxidation kinetics (mass evolution)

- Low oxidation rates were exhibited by the AFA alloys at 800 °C, whereas Cr-forming 310S stainless steel exhibited higher oxidation behavior;

- At 900 °C, the OC11 and 35Ni AFA alloys exhibited significantly lower Cr evaporation rate than 310S and 625. AFA alloys OC4 and OC5 transitioned to scale spallation and mass loss.

- At 1000 °C, the 310S and 625 transitioned to scale spallation and mass loss, whereas the OC11 and 35Ni AFA alloys exhibited low rates of oxidation consistent with protective alumina scale formation.

- AFA alloys exhibited significantly greater oxidation resistance than the Cr-forming 310 and 625 alloys in air + H₂O environments of interest for SOFC's.
Oxidation Kinetics Analysis for the Cr-Evaporation

25Ni AFA with Hf, Y, Zr Show Promising Oxidation Behavior at 1000 °C in Air + 10% H₂O

- Oxide scale spallation by Cr₂O₃ formers 625 and 310S

- AFA without Hf, Y, Zr do not form protective Al₂O₃ at 1000 °C
Oxidation Kinetics Analysis for the Cr-Evaporation

25Ni AFA with Lower Cost Zr Shows Promising Oxidation Behavior at 1000°C in Air + 10% H₂O

- Co-optimization for cost and performance in progress
  - likely can use Zr instead of Hf (Hf better but differences appear small)
  - determination if can drop Y for oxidation ≤ 950-1000°C in progress

![Graph showing specific mass change over total time (h) for different AFA material compositions.](attachment:graph.png)
Oxidation Kinetics Analysis for the Cr-Evaporation

25Ni AFA with Zr Matches Hf AFA Alloy Oxidation Behavior at 900°C in Air + 10% H₂O

- Hf, Y, Zr -free OC-E grade (higher Al, Cr) also shows promise at 900°C

- AFA significantly slower oxidation than Cr₂O₃ forming 625 and 310S
Hf, Y, Zr and Higher Nb Not Needed for 25Ni AFA at 800°C in Air + 10% H₂O

- Slow oxidation among AFA alloys at 800°C (all “good”, differences minor)
- AFA significantly slower oxidation than Cr₂O₃ forming 310H
Conclusions – Phase I

- The 6 evaluated AFA alloy variations exhibited superior oxidation resistance to benchmark chromia-forming alloys at 800-1000°C in the simulated SOFC BOP environment of air + 10% H₂O for 2000-3000 hours accumulated (testing ongoing).

- Significantly reduced Cr release rates were observed in 500 hour testing from 700-900°C; with, for example, a nearly 30x Cr release rate reduction for AFA alloy OC4 at 850°C compared to benchmark Cr₂O₃-forming 310S stainless steel.

<table>
<thead>
<tr>
<th>Sample °C</th>
<th>OC4</th>
<th>OC5</th>
<th>OCF</th>
<th>New 35 Ni</th>
<th>OC-11</th>
<th>MOD 2 OC-D</th>
<th>310S</th>
<th>Alloy 625</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C</td>
<td>&lt; 2.34 × 10⁻¹²</td>
<td>&lt; 2.14 × 10⁻¹²</td>
<td>&lt; 2.16 × 10⁻¹²</td>
<td>—</td>
<td>—</td>
<td>&lt; 2.14 × 10⁻¹²</td>
<td>2.75 × 10⁻¹²</td>
<td>&lt; 2.20 × 10⁻¹²</td>
</tr>
<tr>
<td>850 °C</td>
<td>1.09 × 10⁻¹¹</td>
<td>In progress</td>
<td>In progress</td>
<td>*</td>
<td>*</td>
<td>—</td>
<td>2.9 × 10⁻¹⁰</td>
<td>In progress</td>
</tr>
<tr>
<td>900 °C</td>
<td>4.72 × 10⁻¹¹</td>
<td>—</td>
<td>5.87 × 10⁻¹¹</td>
<td>4.62 × 10⁻¹¹</td>
<td>1.81 × 10⁻¹¹</td>
<td>—</td>
<td>3.81 × 10⁻¹⁰</td>
<td>7.36 × 10⁻¹¹</td>
</tr>
</tbody>
</table>
Future (Ongoing) Work – Phase II

- Begin optimization and down-select of 2 grades of AFA alloys for SOFC BOP testing:
  - 1 grade for $\leq 800^\circ$C operation
  - 1 more highly-alloyed grade for 850-950$^\circ$C operation.
- Long-Term Cr-release Testing to understand the kinetics
- On-cell testing to understand the degradation of cells as function of Cr
- Working with Industrial Partners (Bloom Energy & Fuel Cell Energy) on manufacturing and testing AFA components in industrial environments
Acknowledgement

- **NETL-SOFC Team**: Shailesh Vora, Heather Guedenfeld, Joel Stoffa, Jason Lewis etc.

- **Co-PIs**: Mike Brady (Oak Ridge National Lab), Hussein Ghezel-Ayagh, Ali Torabi (FCE)

- **Industrial Partner**: Samuel Kernion (Carpenter)

- **WVU**: Dr. Wenyuan Li, and Mr. Zhipeng Zeng