Advanced Metallic Interconnect Development

Z. Gary Yang, Gordon Xia, Prabhakar Singh, Jeff Stevenson

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**Interconnect Development**

**Objectives:**
- Develop cost-effective, optimized materials and coatings for intermediate temperature SOFC interconnect and interconnect/electrode interface applications.
- Identify and understand degradation processes in interconnects and at their interfaces.

**Approaches:**
- Evaluation of conventional and newly developed alloys (chemical, electrical, mechanical properties, cost).
- Investigation and understanding of degradations in bulk alloy interconnects and at their interfaces under SOFC operating conditions.
- Materials development
  - Surface modification
  - Bulk modification or alloy development
  - Cathode/interconnect interfaces
Focus Areas & Progress

- Study of Ni-based alloys.
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions.
- Development of cathode-side functional interfaces.
Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces
Ferritic Stainless Steels: Status and Issues

Crofer22 APU

In-situ X-Ray Diffraction Analysis

- M: Fe-Cr substrate
- C: Cr₂O₃
- S: (Mn,Cr)₃O₄ spinel

Scale volatility;
- Long term oxidation resistance under SOFC operating conditions;
- Life time scale electrical properties;
- Mechanical/thermomechanical stability.

Battelle
Study and Evaluation of Ni-Based Alloys

Why Ni-based Alloys?

- Excellent oxidation resistance, super high temperature strength, and good manufacturability.
- Formation of NiO top scale as potential Cr stopping layer.
- CTE can be modified through alloying.
- Scale can be potentially engineered for improved electrical conductivity.

Questions

- Can the required combination of properties be found in a single alloy composition?
- Cost?

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### Nominal composition, wt%

<table>
<thead>
<tr>
<th>Alloys*</th>
<th>Ni</th>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Cb</th>
<th>Ti</th>
<th>Al</th>
<th>B</th>
<th>V</th>
<th>Others</th>
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<tbody>
<tr>
<td>Haynes242</td>
<td>Bal</td>
<td>8.0</td>
<td>2.0b</td>
<td>2.5b</td>
<td>0.03b</td>
<td>0.8b</td>
<td>0.8b</td>
<td>25.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.5b</td>
<td>0.006b</td>
<td>--</td>
<td>0.5b Cu</td>
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<tr>
<td>LTES700</td>
<td>Bal</td>
<td>12.0</td>
<td>18.0</td>
<td>1.1</td>
<td>0.9</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
<td></td>
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<td></td>
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<tr>
<td>Hastelloy C-4</td>
<td>Bal</td>
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<td>3.0b</td>
<td>2.0b</td>
<td>0.01b</td>
<td>1.0b</td>
<td>0.08b</td>
<td>16.0</td>
<td>--</td>
<td>--</td>
<td>0.70</td>
<td>--</td>
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<tr>
<td>Hastelloy S</td>
<td>Bal</td>
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<td>3.0b</td>
<td>2.0b</td>
<td>0.02b</td>
<td>0.5</td>
<td>0.4</td>
<td>15.0</td>
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<td>--</td>
<td>0.25</td>
<td>0.015b</td>
<td>--</td>
<td>0.02La</td>
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<tr>
<td>Haynes230</td>
<td>Bal</td>
<td>22.0</td>
<td>3.0b</td>
<td>5.0b</td>
<td>0.10</td>
<td>0.5</td>
<td>0.4</td>
<td>2.0</td>
<td>14.0</td>
<td>--</td>
<td>--</td>
<td>0.3</td>
<td>0.015</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Haynes242, C, S, and 230 were developed by Haynes International; LTES700 by Mitsubishi Heavy Industries.
Low CTE Ni-Based Alloys

- Traditional Ni-based alloys have a CTE of 15.0~19.0 µm/m.K⁻¹ (RT~800°C). A relatively low CTE of 13.0~14.5 µm/m.K⁻¹ (RT~800°C) can be achieved via alloying.
- Mo, W, Ti and Al reduce CTE of Ni-based alloys; while Cr, Ta+Nb and Co increase it;
- Cr concentration has to be relatively low in these alloys.

\[ \alpha = 13.87 + 7.28 \times 10^{-2} Cr + 3.75 \times 10^{-2} (Ta + 1.95 Nb) + 1.98 \times 10^{-2} Co - 1.84 \times 10^{-2} Al - 7.95 \times 10^{-2} W - 8.24 \times 10^{-2} Mo - 1.63 \times 10^{-1} Ti \]

Yamamoto, et al.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>TECx10⁻⁶ K⁻¹ (from manufacturers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer22 APU</td>
<td>12.2 RT-760°C</td>
</tr>
<tr>
<td>Haynes242</td>
<td>12.2-13.9 20-540-760°C</td>
</tr>
<tr>
<td>LTES700</td>
<td>13.6 RT-760°C</td>
</tr>
<tr>
<td>Hastelloy C-4</td>
<td>13.3-14.4 20-540-760°C</td>
</tr>
<tr>
<td>Hastelloy S</td>
<td>13.3-14.4 20-540-760°C</td>
</tr>
<tr>
<td>Haynes 230</td>
<td>15.2 25-800°C</td>
</tr>
</tbody>
</table>

From in-house measurement
After oxidation at 800°C for 300 hours in moist AIR.

- M: alloy substrate
- G-γ’ precipitates
- S: M₃O₄ (spinel)
- C: Cr₂O₃
- N: NiO

Intensity (a.u.)

Scale Structure and Composition

Haynes242
Crack

Hastelloy S

Haynes230
Scale Structure and Composition

After oxidation at 800°C for 300 hours in moist HYDROGEN.

M: alloy substrate
G-γ’ precipitates
S: M₃O₄ (spinel)
C: Cr₂O₃

Haynes230
Hastelloy S
Haynes240
The measurement was carried out at 800°C in moist air.
Summary

**Ferritic Stainless Steels**
- The newly developed FSS demonstrates reduced scale volatility, good CTE matching, reduced scaled resistance, and improved surface compatibility with sealing glasses.
- There is however a need for further improvement in long term scale chemical, electrical, and mechanical stability (for temperatures >700°C).

**Ni-Based Alloys**
- CTE of Ni-based alloys can be adjusted to a relatively low value via lowering Cr% and adding metal elements such as W, Mo, etc.
- The decreased Cr% may however raises concerns over the oxidation resistance of an alloy in cathode environment; The heavy alloying also creates nonlinearity in the CTE curve.
- A scale with a NiO outer-layer can be formed on low Cr% Ni-alloys in cathode-side environment, but its suitability as an electrically conductive protective layer is questionable.
Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces
Oxidation Behavior of Alloys under Interconnect Dual Exposures

Motivation:
- Oxidation study has been a common area of interest, but typically under single atmosphere exposure.
- Dual exposures are commonly found in SOFC stacks and BOP, as well as other systems.
- Understanding helps develop robust materials.

Materials studied:

- NiBS
  - Haynes 230-22%Cr
  - Hastelloy S-17%Cr FeSS
  - Haynes 242-8%Cr
  - E-brite-27%Cr
  - Crofer22-22%Cr
  - AISI430-17%Cr

Variables:
- Alloy composition
- Isothermal vs. cycling
- Moisture
The DUAL exposures lead to an anomalous oxidation behavior of ferritic stainless steels under the SOFC interconnect dual exposure conditions; The anomalous oxidation behavior appears to be caused by hydrogen diffusion from the fuel side to the airside of alloy interconnects.

For 430 with 17% Cr, dual exposures enhanced the iron transport in the scale on the airside, leading to hematite formation and localized attack;

For Crofer22 (22% Cr), Fe enrichment was found in the spinel layer after isothermal oxidation; thermal cycling resulted in the hematite nodule formation and localized attack;

For ferritic stainless steels with enough chromium, e.g. E-brite (27% Cr), the accelerated iron transport and iron oxide formation are inhibited, though differences in scale microstructure and morphology are observed.
Crofer22 APU: Effects of Moisture

Grown on the coupon in moist (3%H₂O) air only and on the airside of the coupon that was **ISOTHERMALLY** heat-treated at 800°C, 300 hours.

Presence of moisture accelerated the anomalous oxidation.
Haynes 230: Oxidation Behavior

Grown on the coupon in **air only** (ambient air) and on the **airside** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.

<table>
<thead>
<tr>
<th>2θ</th>
<th>Intensity (counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>S</td>
</tr>
<tr>
<td>35</td>
<td>C</td>
</tr>
<tr>
<td>40</td>
<td>G</td>
</tr>
<tr>
<td>45</td>
<td>S</td>
</tr>
<tr>
<td>50</td>
<td>N</td>
</tr>
<tr>
<td>55</td>
<td>G</td>
</tr>
<tr>
<td>60</td>
<td>S</td>
</tr>
</tbody>
</table>

- **M**: alloy substrate
- **G**: γ’ precipitates
- **S**: M₃O₄ (spinel)
- **C**: Cr₂O₃
- **N**: NiO

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Air exposure at both sides

Airside of dual exposures
Hastelloy S: Oxidation Behavior

Grown on the coupon in **air only** and on the **airside** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.

M-metal substrate
G-γ' precipitation
C-Cr_2O_3
S-(Mn,Ni,Cr)_3O_4
N-NiO

Air exposure at both sides

Airside of dual exposures
Haynes242: Oxidation Behavior

Grown on the coupon in **air only** and on the **airside** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.

- M-metal substrate
- G-γ’ precipitation
- C-Cr₂O₃
- S-(Mn,Ni,Cr)₃O₄
- N-NiO

**Intensity (a.u.)**

**2θ**

- To air at both sides
- Air side of dual exposures

**Air exposure at both sides**

**Airside of dual exposures**
Summary

For **ferritic stainless steels** with relatively low chromium levels (22% or less), dual exposure enhances the iron transport in scale on the airside, leading to hematite formation and localized attack.

The presence of moisture enhances the anomalous oxidation, leading to localized attack.

For **Ni-based alloys**, dual atmosphere exposure tends to reduce NiO formation, and to facilitate the formation of a uniform chromia/spinel dominated scale.
Focus Areas & Progress

- Study of Ni-based alloys
- Investigation of oxidation behavior of candidate alloys under SOFC operating conditions
- Development of cathode-side functional interfaces
Cathode-Side Functional Interfaces

Before assembly

- Protection layer acts as a mass barrier to mitigate or prevent Cr migration via both gas transport and solid state reactions, as well as to decrease electrical contact resistance. The subsequently grown chromia sub-scale serves as cation and anion transport barrier, protecting the alloy interconnect.

- Contact layer promotes contact between cathodes and interconnects, and helps minimize interfacial resistance and power loss.

During operation
The provskite coatings decrease electrical resistance and mitigate or prevent Cr migration;

The growth rate of the chromia beneath the coatings and the eventual scale depends on the ionic conductivity of coatings.

Long term stability needs to be further studied.

Both bare and coated samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.
Thermal Grown Spinel Protection Layer

Concept

- Ms₃O₄ spinel
- Chromia forming alloy interconnects

During operation

- Ms₃O₄ spinel
- Cr₂O₃
- Chromia forming alloy interconnects

The protection layer is intended to be thermally grown.

Approach

- Solution coating, PVD, CVD or EC plating of spinel formation metals.
- Growth of a thin spinel layer via reactions during a heat treatment in an optimized environment.
- Formation of a spinel-chromia functional scale on interconnects during subsequent oxidation or SOFC operations.
Growth of \((\text{Mn,Co})_3\text{O}_4\) on Crofer22 APU

Current focus is on thermally grown spinels which contain no Cr and/or are more stable than \((\text{Cr,Mn})_3\text{O}_4\).

**MnCO_3+C_3O_4**
Slurry coating

Heat treating in 2.75H_2+Ar at 950ºC for 24 hours.

Oxidation in oxidizing environment

![Graph showing X-ray diffraction peaks for different compositions of Mn and Co spinels on Crofer22 APU.](image)
The (Mn,Co)$_3$O$_4$ spinel protection layer on Crofer22 APU minimizes the interfacial resistance when (La$_{0.8}$Sr$_{0.2}$)Co$_{0.5}$Mn$_{0.5}$O$_3$ used as a electrical contact.

\[ \text{ASR}_{\text{cathode/interconnect}} = \Phi(\text{scale, contacts, reactions}) \]
Summary

- Continuous, thin spinel protection layer can be thermally grown on chromia forming alloys during optimized pre-heat treating; the spinel protection layer is intended to help minimize volatilization of Cr vapor species and the interfacial electrical resistance.

- Preliminary work on Co/Mn spinel layers indicates low interfacial electrical resistance.

- Mitigation of Cr volatility to be verified experimentally.
**Future Work:**

**Study oxidation behavior under dual exposures**
- Mechanistic understanding: Interaction and transport of H/H$^+$ at the metal/oxide interface and in the oxide scale; their effects on defect structure, transport properties, scale growth.
- Study effects of dual exposure on scale electrical conductivity.
- Oxidation behavior of alloys under the reforming gas/air dual exposures.

**Investigate and develop cathode-side functional interfaces**
- Spinel protection layers: Continue to screen and search for spinels that compatible to candidate alloys and more thermochemically stable than (Mn,Cr)$_3$O$_4$; optimize processing and materials composition.
- Electrical contact layers: Continue to study the interactions between conductive oxides and candidate alloys; investigate the interfacial ASR and optimize the composition for a minimized interfacial resistance.

**Develop and investigate cladded composite-structure interconnects**
- Continue to the proof of concept investigation.
- Study interdiffusion and predict life via modeling.
- Optimize structure and compositions.
Acknowledgements

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