Advanced Alloy
Interconnect Development

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Presented at the SECA CTP Review Meeting
Albany, NY
September 30, 2003
**Interconnect Development**

**Objectives:**
- Develop cost-effective, optimized materials for intermediate temperature interconnect and its interface applications.
- Identify and understand degradation processes in candidate alloys.

**Approach:**
- Screen testing of conventional and newly developed alloys (chemical, electrical, mechanical properties, cost).
- Investigation of oxidation/corrosion behavior of alloys and scale stability under SOFC operating conditions.
- Materials development.
  - Surface modification (surface doping, overlay coatings, cladding).
  - Bulk modification or alloy development.
  - Cathode/interconnect interfaces.
**Highlights of Achievements**

- Developed standardized testing capability for evaluation of SOFC interconnect alloys
- Identified and evaluated suitable candidate alloys using systematic screening techniques.
- Developed conductive oxide coated alloy interconnects for improved stability.
- Evaluated newly developed alloys, including Crofer22 APU and ZMG232.
- Examined oxidation/corrosion behavior of steels and superalloys.
# Evaluation of Newly Developed Alloys

<table>
<thead>
<tr>
<th>FSS</th>
<th>Fe</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ti</th>
<th>Al</th>
<th>P</th>
<th>S</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer22 APU</td>
<td>Bal.</td>
<td>22.0</td>
<td>0.005</td>
<td>0.5</td>
<td>--</td>
<td>0.08</td>
<td>--</td>
<td>0.016</td>
<td>0.002</td>
<td>0.06La</td>
</tr>
<tr>
<td>ZMG232</td>
<td>Bal.</td>
<td>22.0</td>
<td>0.02</td>
<td>0.5</td>
<td>0.40</td>
<td>--</td>
<td>0.21</td>
<td></td>
<td></td>
<td>0.04La 0.02Zr</td>
</tr>
</tbody>
</table>

Crofer is a trade mark of ThyssenKrupp; ZMG is a trade mark of Hitachi Metals, Ltd.

**Properties relevant to SOFC applications:**

- Thermal expansion;
- Scale growth and oxidation resistance;
- Scale electrical conductivity;
- Scale evaporation;
- Compatibility with seals;
- Scale adherence and seal bonding strengths.
Some Fe-Cr ferritic compositions (including Crofer22 APU) demonstrate good CTE matching to the Ni/YSZ anode.
Oxidation Resistance

\[ \xi^2 = k_p t = \frac{K}{(\chi \rho)^2} \]

Chromia former

Alumina former

Parabolic rate constants (x10^{-14} g^2 cm^{-4} s^{-1})

<table>
<thead>
<tr>
<th>Material</th>
<th>800°C</th>
<th>700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer22 APU</td>
<td>35</td>
<td>7</td>
</tr>
<tr>
<td>AL 453</td>
<td>19.84</td>
<td>0.88</td>
</tr>
<tr>
<td>446</td>
<td>13.32</td>
<td>0.61</td>
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<tr>
<td>E-brite</td>
<td>3.53</td>
<td>0.04</td>
</tr>
<tr>
<td>Fecralloy</td>
<td>0.35</td>
<td>0.15</td>
</tr>
<tr>
<td>Alpha-4</td>
<td>0.88</td>
<td></td>
</tr>
</tbody>
</table>
Formation of (Mn, Cr) Spinel Top Layer

Crofer22 APU was heat treated at 800°C for 1,200 hours in air.
Scale Electrical Conductivity

Extrapolation of the 2,000 h test gives an ASR of about 200 mΩ.cm² after 40,000 h.
Chromia Scale Evaporation

The chromia evaporation rate is relatively low, compared with other alloys.

Is this low enough?

Chromium Release Rate at 850°C*
*After Hilpert, et al.

Chromia evaporation rate is relatively low, compared with other alloys.

Is this low enough?

Plansee Ducralloy

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### Evaluation of ZMG232

<table>
<thead>
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<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>RE</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZMG232</td>
<td>Bal.</td>
<td>22</td>
<td>.5</td>
<td>0.40</td>
<td>.21</td>
<td>0.04La, 0.22Zr</td>
</tr>
<tr>
<td>Crofer22 APU</td>
<td>Bal.</td>
<td>22</td>
<td>.5</td>
<td>--</td>
<td>--</td>
<td>0.06La</td>
</tr>
</tbody>
</table>

The Si level in ZMG232 is enough to form a silica layer that leads to an increased electrical resistance.
**Summary**

**Newly developed ferritic stainless steels demonstrate:**
- Good CTE matching;
- Reduced scale electrical resistance;
- Increased scale adherence;
- Decreased chromia evaporation.

**There is HOWEVER, a need for further improvement in:**
- Scale electrical conductivity in the long term;
- Scale evaporation;
- Scale adherence and sealing effectiveness;
- Corrosion resistance under dual environments.
# Dual Atmosphere Study

<table>
<thead>
<tr>
<th>FSS</th>
<th>Fe</th>
<th>Ni</th>
<th>Cr</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Mo</th>
<th>W</th>
<th>Ti</th>
<th>Al</th>
<th>RE</th>
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<tbody>
<tr>
<td>AISI430</td>
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<td>16.0</td>
<td>0.1</td>
<td>1.0</td>
<td>1.0</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Crofer22 APU</td>
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<td>0.005</td>
<td>0.5</td>
<td>--</td>
<td>--</td>
<td>0.08</td>
<td>--</td>
<td>0.06La</td>
<td></td>
</tr>
<tr>
<td>E-brite</td>
<td>Bal.</td>
<td>--</td>
<td>26.0</td>
<td>0.001</td>
<td>0.01</td>
<td>0.025</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Haynes 230</td>
<td>1.5</td>
<td>Bal.</td>
<td>22.0</td>
<td>0.10</td>
<td>0.5</td>
<td>0.4</td>
<td>1.4</td>
<td>14</td>
<td>--</td>
<td>0.3</td>
<td>0.02La .005B</td>
</tr>
</tbody>
</table>

**FeSS** {FeSS}

**NiBS** {NiBS}

Variables:
- Temperature, 700~800°C
- Time, 300 hours
- Fuel, H₂+3% H₂O
- Heating, isothermal and cycling.
Crofer22 APU: Structure of Scales

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

Air exposure on both sides of the tested coupon.

Air side of dual exposures.

M = Fe-Cr Substrate
C = Cr₂O₃
S = (Mn, Cr, Fe)₃O₄

Air exposure at both sides

Fe
Cr
Mn

Air-side of dual exposures

Fe
Cr
Mn
Crofer22 APU: Structure of Scales

Grown on the coupon in fuel (H$_2$+3%H$_2$O) only and on the fuel side of the coupon that was ISOTHERMALLY heat-treated at 800°C, 300 hours.

(H$_2$+3%H$_2$O) side of the dual atmosphere exposure.

M = Fe-Cr Substrate
C = Cr$_2$O$_3$
S = Mn(Cr,Fe)$_2$O$_4$

Both sides exposed to (H$_2$+3%H$_2$O).
Crofer22 APU: Structure of Scales

Grown on the coupon in air only and on the air side of the coupon that was heat-treated at 800°C for 300 hours, with three thermal cycles.

Air-side of dual test

Cross-section: airside of dual test

Airside of the dual exposures.

2θ

M = Fe-Cr Substrate
C = Cr₂O₃
S = (Mn,Cr,Fe)₃O₄
O = Fe₂O₃

Air exposure at both sides.
AISI 430: Scale Microstructures

Air exposure at both sides

Air-side of dual exposures

Surface microstructures

Cross-sections

Fe
Cr
Mn

Fe₂O₃

Fe
Cr
Mn

20 kV ×2,000 10 μm 03s 035c

20 kV ×2,000 10 μm 03s 030b
E-brite: Scale Microstructures

Air exposure at both sides

Air side of dual exposures

(H$_2$+3%H$_2$O) at both sides

Fuel side of dual exposures

Cr$_2$O$_3$
Haynes230: Structure of Scales

Grown on the coupon in air only and on the air side of the coupon that was isothermally heat-treated at 800°C, 300 hours.
Haynes230: Cross-Sections

Grown on the coupon in **air only** and on the **air side** of the coupon that was **isothermally** heat-treated at 800°C, 300 hours.
Haynes230: Structure of Scales

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

(H₂+3%H₂O) at both sides

**Fuel side of dual atmospheres**

![Graph showing relative intensity vs. 2θ](image)

- **Cr₂O₃**
- **(Mn,Ni,Cr)₃O₄**

![Micrograph of fuel side](image)
Haynes230: Cross-Sections

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

The Dual Atmosphere exposure can lead to an anomalous oxidation/corrosion behavior of oxidation resistant alloys:

For **ferritic stainless steels** with relative low chromium level, dual exposure enhances the iron transport in scale on the airside, leading to hematite formation and a localized attack.

For **Ni-based superalloys**, e.g. Haynes230 with 22% Cr, dual exposure facilitates the formation of a uniform chromia dominated scale.
## Comparison

<table>
<thead>
<tr>
<th></th>
<th>Haynes230</th>
<th>Crofer22 APU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-base superalloy</td>
<td>Ni-22Cr-14W-2Mo-.5Mn</td>
<td>Fe-22Cr-.5Mn</td>
</tr>
<tr>
<td>Oxidation resistance</td>
<td>0.05, 700°C</td>
<td>2.0, 700°C</td>
</tr>
<tr>
<td>10⁻¹³ g² cm⁻⁴ s⁻¹</td>
<td>0.05, 700°C</td>
<td>2.0, 700°C</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>0.36, 800°C</td>
<td>7.0, 800°C</td>
</tr>
<tr>
<td>X10⁻⁶ K⁻¹</td>
<td>0.36, 800°C</td>
<td>7.0, 800°C</td>
</tr>
<tr>
<td>ASR, mΩ cm²</td>
<td>5.0, 700°C</td>
<td>4.0, 700°C</td>
</tr>
<tr>
<td>Enhanced formation of</td>
<td>10.0, 800°C</td>
<td>9.0, 800°C</td>
</tr>
<tr>
<td>uniform chromia scale</td>
<td>10.0, 800°C</td>
<td>9.0, 800°C</td>
</tr>
<tr>
<td>Dual atmosphere</td>
<td>865, RT</td>
<td>443, RT</td>
</tr>
<tr>
<td>Corrosion resistance</td>
<td>605, 760°C</td>
<td>&lt;100, 760°C</td>
</tr>
<tr>
<td>Ultimate tensile strength, σₜ (MPa)</td>
<td>605, 760°C</td>
<td>&lt;100, 760°C</td>
</tr>
<tr>
<td>Very easy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fairly easy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inexpensive</td>
<td></td>
<td></td>
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<tr>
<td>Fairly expensive</td>
<td></td>
<td></td>
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<tr>
<td>Raw materials cost</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manufacturability</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Future Work

Identifying Issues and Understanding

- Continue the systematic screening studies, with emphasis on dual atmosphere studies, including extension of dual atmosphere studies to air vs. reformate environments.
- Study scale evaporation.

Materials Development

- Modifications (bulk and/or surface) to Fe and Ni based alloys
- Cathode/interconnect interfaces.
The authors wish to thank Wayne Surdoval, Lane Wilson, and Don Collins (NETL) for their helpful discussions regarding this work. This work was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.