Development of SOFC Interconnects and Coatings

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Presentation Outline

► Objectives
► Background
  ■ AISI 441
  ■ Spinel coatings for steel interconnects
► Results:
  ■ Performance of Ce-modified MnCo spinel-coated AISI 441
  ■ Effect of alloy surface treatments
  ■ Optimization of Ce-modified MnCo spinel coatings
  ■ Alternative coating compositions
► Conclusions
► Future Work
► Acknowledgements
Objectives

Global Objectives
- Develop cost-effective, optimized materials and fabrication approaches for intermediate temperature alloy-based SOFC interconnects
- Identify, understand, and mitigate degradation processes in alloy-based interconnects

Specific Objectives
- Improved understanding of performance of Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) spinel coatings on AISI 441 steel
  - ASR, oxidation behavior, scale adhesion at 800 and 850ºC
- Evaluation of alloy surface treatments
  - Collaborations with Allegheny Ludlum and NETL-Albany
- Optimization of Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) spinel coatings
  - Ultrasonic spray process; effect of coating thickness
- Evaluation of cost reduction approaches
  - Reduced Co content to lower coating cost
  - Metallic precursors
Candidate Interconnect Alloy: AISI 441

- Ferritic stainless steel: Good CTE match to other components; Electrically conductive Cr-based oxide scale
- Inexpensive - Manufactured via conventional melt metallurgy
  - No vacuum processing required
- Similar to AISI 430, but additions of Nb and Ti improve high temperature strength and prevent formation of insulating SiO₂ layer at alloy/scale interface
- Similar to all other FSS, relatively high oxidation rate at SOFC operating temperatures (and volatility of Cr) indicates need for protective coating
- Also, relatively weak scale adherence (no RE in alloy)

Typical Analysis:

<table>
<thead>
<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>La</th>
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</thead>
<tbody>
<tr>
<td>AISI 441</td>
<td>18</td>
<td>0.35</td>
<td>0.30</td>
<td>0.01</td>
<td>0.05</td>
<td>0.34</td>
<td>0.023</td>
<td>0.002</td>
<td>0.22</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>AISI 430</td>
<td>16-18</td>
<td>≤1.0</td>
<td>≤0.12</td>
<td>≤1.0</td>
<td>≤0.04</td>
<td>≤0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crofer 22 APU</td>
<td>23.0</td>
<td>0.4-0.8</td>
<td>0.030</td>
<td>≤0.02</td>
<td>≤0.02</td>
<td>0.02</td>
<td>0.050</td>
<td>≤0.2</td>
<td>0.04-0.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Allegheny Technologies, Inc.; Thyssen Krupp
Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) Spinel Coatings

- High electrical conductivity
  
  \[ \sigma_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} = 10^{3\sim4} \sigma_{\text{Cr}_2\text{O}_3} \]

- Good CTE match to FSS and anode-supported cells

\[ \text{CTE}_{\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4} \approx 11 \times 10^{-6} \text{K}^{-1}, 20 \text{ – } 800 \text{°C} \]

- Chemically compatible with contact pastes, cathodes

- Cr-free composition

- CeO\(_2\) inclusions improve scale adhesion of alloy substrate (rare earth effect)

Coating Provides:

- Reduced Cr volatility from steel
- Improved scale adhesion
- Reduced oxidation rate of alloy:

<table>
<thead>
<tr>
<th>(k_p) ((\text{g}^2/\text{cm}^4\text{-s}))</th>
<th>800\°C</th>
<th>850\°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce-MC coated 441</td>
<td>2 \times 10^{-14}</td>
<td>1 \times 10^{-13}</td>
</tr>
<tr>
<td>Bare 441</td>
<td>5 \times 10^{-14}</td>
<td>3 \times 10^{-13}</td>
</tr>
</tbody>
</table>
Performance of Ce-modified $(\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4$ spinel coatings on AISI 441 steel
Area Specific Resistance (ASR) Measurements

\[ \text{ASR}_{\text{cathode-interconnect}} = \Phi(\text{scale}, \text{contactmaterial}, \text{coatings}) \]

- Contact Layers
- ~12psi
- Interconnect (coated)
- Simulated cathode with dense body and porous surface layers
- Current Density: 0.5A.cm\(^{-2}\)

ASR Stack (3 sets)
Long-Term ASR measurements: 800 and 850°C

800°C except where noted.
ASR Testing including Thermal Cycling

![Graph showing ASR testing results for different materials. The x-axis represents time in hours, ranging from 0 to 4000, and the y-axis represents ASR (mOhm-cm²), ranging from 0 to 50. The legend indicates three materials: Ce02MC LSM 800C, Ce05MC LSM 800C, and Ce05MC LSCF 800C. The graph shows the ASR values for each material over time.]
SEM/EDS/EBSD Analysis

- Ti-doped Chromia
- Hexagonal Corundum structure
- Cr-Mn spinel Cubic

Cr (red) - Mn (green) - Co (blue)
Effects of Temperature on Scale Growth and Adhesion

Spallation observed (scale/alloy interface) after 1670 hours at 850°C
No evidence of spallation in long term ASR test (no thermal cycling)
Effect of Surface-Treatment on Oxidation Behavior of Spinel-coated 441

**800°C**

- **Allegheny Ludlum**: Mill Reference, De-siliconized, Surface blasted, Surface ground, Temper rolled
- **NETL Albany**: Ce surface treatment
- All coated with Ce-MnCo spinel, heat-treated in air at 800°C for up to 10,000 hours
  - As expected, no spallation after 2000 hours

<table>
<thead>
<tr>
<th>Surface Treatment</th>
<th>Ave. Scale Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mill Reference (1200 grit)</td>
<td>2.23 ± 0.17</td>
</tr>
<tr>
<td>De-siliconized</td>
<td>1.71 ± 0.14</td>
</tr>
<tr>
<td>Surface ground</td>
<td>3.83 ± 0.97</td>
</tr>
<tr>
<td>Surface blasted</td>
<td>3.27 ± 0.40</td>
</tr>
<tr>
<td>Temper rolled</td>
<td>1.55 ± 0.18</td>
</tr>
<tr>
<td>Ce Treatment</td>
<td>3.27 ± 0.68</td>
</tr>
</tbody>
</table>
Effect of Surface-Treatment on Oxidation Behavior of Spinel-coated 441 (continued)

- **850°C**
  - As-received 441 w/ Ce-MC spinel coating
    - Typically observe spallation at scale/alloy interface after 1000 - 1500 hours
  - NETL-Albany Ce surface treatment
    - No spallation observed on uncoated, surface treated coupons after 5100 hours, possibly due to enhanced RE effect from higher Ce level at surface
    - Testing of spinel-coated coupons in progress
  - Shot-peened 441 (Metal Improvement Co.)
    - No spallation observed on uncoated coupons after 2500 hours or on coated coupons after 2000 hours
    - Testing of spinel-coated coupons in progress
  - Allegheny Ludlum surface treatments w/ spinel coating
    - To be initiated in near future

- **Post-test analysis:**
  - Evaluate scale adhesion
    - Visual inspection for spallation
    - Indentation for quantification of interfacial strength to allow for prediction of interconnect lifetime
Optimization of Ce-modified \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\) spinel coatings
Ultrasonic spray coating: Optimization of Spray Parameters

Design Of Experiment Optimization (DOE Optimization) With Taguchi, Grey-Taguchi method and ANOVA (Analysis of Variance)

Wide Mode
- Viscosity: 5cp
- Coating speed: 100mm/sec
- Head height: 35mm
- Ink feeding rate: 1ml/sec
- Air flow rate: 30ml/sec

Narrow Mode
- Viscosity: 5cp
- Coating speed: 100mm/sec
- Head height: 15mm
- Ink feeding rate: 0.5ml/sec
- Air flow rate: 40ml/sec
Ultrasonic spray process currently used for aluminization and spinel coating of interconnects/frames for PNNL's single/multiple stack fixture testing
Optimization of Ce-MC Spinel Coatings

▶ Adaptation of ultrasonic spray process to Ce-modified spinel powder
  - Extension of previous optimization of fabrication process for unmodified spinel

▶ Effect of coating thickness on oxidation resistance of AISI 441
  - Two studies in progress: Sprayed coatings, Screen-printed coatings
    - ~5, 10, 20 microns thick
    - Oxidation for 2000 hours
Alternative Interconnect Coating Compositions

- Reduce Co content to reduce coating cost
  - Mn oxide (Cobalt-free)
  - Mn-Co oxide coatings: Reduced Co content relative to $(Mn_{0.5}Co_{0.5})_3O_4$
Initial Study: ASR of Mn oxide coated 441 at 800°C

ASR of Mn coating on 441

Slope = $4.15 \times 10^{-3}$ mΩ·cm²/h
Oxide scale thickness as $f(\text{time})$

Rapid scale growth under Mn oxide coating: Intrinsic or bad microstructure?
Optimization of Mn oxide Protective Coatings on AISI 441

- Densification study of Mn oxide coatings prepared from Mn powder
  - Effect of particle size distribution
  - Effect of binder system and binder/solids ratio
- Optimization via SEM analysis
- Evaluation via electrical resistance testing (ASR)
Effect of particle size
SEM of Mn oxide coating on AISI 441

As received powder, <10um  milled powder, <5um  milled powder, <3um

The coatings prepared using Mn powder with smaller particle size showed more uniform surface.
ASR Evaluation of Mn Coated 441 Samples

ASR increased linearly with time on oxidation even though the improved Mn oxide coatings appeared to be gas tight.
Cross-section SEM Images of Mn Coated 441 after ASR Measurement

Composition from SEM

Mixed Mn powder (30% <3µm+70%10µm)
Alternative Mn-Co oxide coatings:

Reduced Co content relative to \((\text{Mn}_{0.5}\text{Co}_{0.5})_3\text{O}_4\)
SEM Images of Mn-Co Oxide Coated 441
(after ASR measurements at 800°C for ~500hrs)

Mn20Co1 (33μm)  Mn10Co1 (41μm)  Mn6Co1 (18μm)

Prepared from metal precursors according to listed molar ratios
ASR of Reduced Cobalt Coatings

ASR Measurement Data / 800°C

- Mn-only
- Mn20Co1
- Mn10Co1
- Mn6Co1

Specific Resistance (mOhms·cm²) vs. Time (hours)
Effect of Co Content on Rate of ASR Increase
Summary

- MnCo spinel coatings on AISI 441 exhibit excellent long-term performance at 800ºC
- At 850ºC, MnCo spinel coatings exhibit low, stable ASR obtained after 4,000 hours
  - Scale adhesion issues observed at 850ºC
  - Additional studies/approaches, including alloy surface treatments, are in progress
- Ultrasonic spray process for application of MnCo spinel coatings has been optimized
- MnCo oxide coatings with substantially reduced Co content appear to be promising approach for reducing coating cost
  - Mn oxide coatings did not provide low, stable ASR
Future Work

- Continue to evaluate long-term stability and electrical performance of Ce-MC spinel-coated 441 steel
  - Evaluate at 800 and 850°C
  - Long-term evaluation in stack test fixture
- Evaluate effect of alloy surface treatments on oxidation and spallation resistance of Ce-MC coated 441
- Optimize thickness, and automated ultrasonic spray process, for Ce-modified spinel coatings
- Reduce cost of protective coatings through elimination of reducing heat treatment and/or minimization or elimination of Co content
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