SOFC Protection Based on a Cost-Effective Aluminization Process

15th Annual SECA Workshop
July 23rd 2014
1. Introduction and Motivation
2. Dual MCO/Al coated Interconnect Product Development
   - Reduction Firing Process Window
   - Single-cell Stack Testing
3. Refinement of Aluminide Coating Process
   - Microstructural Characterization
   - Compositional Modifications
5. Conclusions
Invent, Develop, Deliver

NexTech has developed a range of coatings to extend the materials lifetime of components used in SOFC systems.

SOFC Coating Development at NexTech

MCO coated IC

MCO coated current collector mesh

Catalyst coated mesh

Catalyst coated monolith

July 25, 2014
Manganese cobaltite (MCO) coating has been successfully commercialized at NexTech.

AL 441HP™ with symmetric 10 μm MCO coating
800 °C and 900 °C in humidified air with applied current density 0.5 A/cm²

Sample: stable baseline > 28,000 hours

Accelerated testing: 900 °C
Thermal Cycling
Aluminide Protection Coating

NexTech is developing an aluminide protective coating to improve high temperature oxidation/corrosion and chromium volatility resistance of metallic components used in SOFC systems.

Dual MCO/Aluminide Coated Metallic Interconnect

Coated Balance of Plant Components

- MCO active area coating
- Aluminide seal area coating
- 5 ft. long stainless steel SS316 pipes
NexTech’s coating process successfully reproduces the diffusion based surface microstructure produced by more conventional aluminization processes.

**Vapor Phase Aluminization (VPA) Coating Microstructure on SS316**

**NexTech’s Aluminide Coating Microstructure on SS316**
Utility of aluminide coating demonstrated through enhanced oxidation, chromium volatilization, and coking resistance on commercially important IC and BoP alloys.

**Preliminary Results**

**Oxidation Resistance SS304**
- Coated
- Uncoated

SS304 with and w/o aluminide coating 500 hours in humidified air at 900 °C

10X improvement oxidation resistance

**Cr Volatilization Resistance SS304**

SS304 with and w/o aluminide coating 500 hours in air at 900 °C

EDS of Cr capturing material

15X reduction chromium volatilization

**Coking Resistance SS304**
- Coated
- Uncoated

SS304 with and w/o aluminide coating 24 hours at 600 °C

18% CH₄, 45% CO, 37% CO₂

Excellent coking resistance

July 25, 2014
Demonstrated the feasibility of modified reduction co-anneal strategy to apply dual MCO/aluminide coatings.

I: Sequential MCO and Al coatings
   - MCO Coating
   - Reduction Anneal
   - Al Coating
   - Air Firing

II: Combined MCO and Al coating with co-firing
   - MCO/Al Coating
   - Modified Reduction Anneal

Aluminum Diffusion Profile
- Air Anneal
- Sequential Anneal Process
- Modified Reduction Anneal

Composition /at.% vs Depth /μm

July 25, 2014
Co-Anneal Temperature Process Window

Process window defined to achieve controlled reduction of the MCO coating to form MnO + Co cermet and required aluminum diffusion profile to form desired aluminide coating.

XRD Comparison of Reduced MCO Coatings

- Co metal
- MnO
- Substrate

pO₂/T below Mn/MnO stability line

July 25, 2014
Oxidation/Chromium Volatility Analysis

Co-anneal process does not reduce enhanced oxidation resistance and chromium volatilization resistance of coating.

AL 441HP™ with and w/o aluminide coating
1000 hours in air at 900 °C

July 25, 2014
Seal/IC Interactions

Aluminide Coating is effective at reducing detrimental glass-seal interactions.

XRD spectra of glass-seal/IC

- Coated
- Uncoated

**Chromate XRD peaks**

Ferritic SS - AL 441HP with and w/o aluminide coating
Composite glass seal (80% alumina, 20% PNNL G18 glass)
Ageing: 4 hours at 850 °C in air
Single-Cell Stack Test

Performance of dual MCO/aluminide coated interconnects evaluated in concert with all other components of an actual stack under application relevant conditions.

Dual MCO/Al coated IC: Green

Dual MCO/Al coated IC: Reduced
MCO/Al dual-coated interconnects demonstrate enhanced stack performance (improved powder density and fuel utilization) vs. no seal area coating.
Single Cell Stack Test Stand Results

Performance improvement is also demonstrated compared to existing seal area coating (CAO)

Single (28-cm² Active Area) Cell Stack

$T_{\text{AVE}} = 800^\circ\text{C}$, Diluted Hydrogen in Nitrogen

Aluminized Seal Area / Flat Manifold

CAO Coated Seal Area / Flat Manifold

July 25, 2014
Enhancement of the high temperature performance of coated 441 is based on the formation of a thin alumina surface oxide instead of a thick chromia scale.

**Uncoated**

- Thick chromia scale

**Coated (Standard Processing)**

- Alumina scale
- Depletion of aluminum diffusion layer

Ferritic stainless steel - AL 441HP with and w/o aluminide coating
1000 hours in air at 900 °C

July 25, 2014
Invent, Develop, Deliver

Post-Test Analysis: SS316

Similar long-term microstructural behavior is observed for coated SS316.

Coated SS316: As Processed

Coated SS316: $t = 500$ h

SS316 with aluminide coating
500 hours in humidified air at 900 °C

Aluminum Diffusion Profile

<table>
<thead>
<tr>
<th>Al Composition /at.%</th>
<th>Depth /µm</th>
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<tr>
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316 SS as processed
316 SS 500 h
Coating Refinement: Compositional Modifications

Process modifications A and B show promise – improved oxidation and chromium volatilization resistance compared to the standard coating process.

Oxidation and chromium volatility: 1000 hours in humidified air at 900°C
Microstructural Analysis: Modification A

Process modification A improves the coating’s high temperature stability by successfully constraining aluminum in an enriched sub-surface layer and preserving a protective alumina scale.

As-processed

Post-Oxidation
1000 hours in humidified air at 900°C
Balance of Plant: Process Development

Prototype component developed to demonstrate the feasibility of the coating on an application-specific component

Prototype 2 ft. long 310 SS coated pipe

Dip-coating application
Aerosol spray deposition
Roller coating
Uncoated
Process Simplification/Cost Reduction

Performance verification and process improvement qualification conducted to develop cost-effective, scalable coating process.

**Oxidation: SS316**

- **V2 = alternative source Al-based powder supplier**

<table>
<thead>
<tr>
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<th>Std</th>
<th>V2 -Std</th>
<th>V2 -Mod A</th>
<th>Uncoated</th>
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<td>Uncoated</td>
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<td>0.8</td>
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**Oxidation: SS310**

- **Mod A = compositional process modification A**

<table>
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<th>Std</th>
<th>V2 -Std</th>
<th>V2 -Mod A</th>
<th>Uncoated</th>
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<td>Weight Change @ 500 Hours (mg/cm²)</td>
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Oxidation: 500 hours in humidified air at 900°C
Coating Refinement: Process Simplification

Similar coating microstructures produced via different application processes and the uniformity of aluminide diffusion layer improved with process modification A

As Processed Coating Microstructures with Alternative Powder Vendor (V2): Standard Process

SS316 - Sprayed
SS316 – Roller Coated
SS310 - Sprayed

As Processed Coating Microstructures with Alternative Powder Vendor (V2): Modification A Process
NexTech is developing a cost-effective process for applying protective aluminide coatings to metallic components used in SOFC systems.

Modified co-anneal operation enables successful co-processing of aluminide coating with commercially available manganese cobalt oxide (MCO) active area coating for dual MCO/aluminide coated interconnects.

Critical functionality of the aluminide coating demonstrated on a range of commercially important alloys:
- Enhanced high-temperature oxidation, chromium volatilization, and coking/carburization resistance.
- Enhanced stack performance (improved powder density and fuel utilization) established for dual MCO/aluminide coated interconnects compared to interconnects with a single MCO active area coating (no seal coating) and NexTech’s incumbent CAO seal area coating.

Compositional process modifications identified to improve long-term, high temperature coating stability.

Process improvements (process simplification/cost reduction) identified to further enhance value proposition of coating technology.
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Project Manager: Dr. Seth Lawson