An Alternative Low-Cost Process for Deposition of MCrAlY Bond Coats for Advanced Syngas/Hydrogen Turbine Applications

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One of materials needs for advancement of IGCC power plants is to develop low-cost and effective manufacturing processes for application of new TBC/bond coat architectures with enhanced performance and durability in syngas/hydrogen environments.

Bond Coat Choices

- Bond coat choices
  - Diffusion aluminide
  - MCrAlY overlay (M = Ni, Co or a mixture of Ni & Co)
    - More independent of the substrate composition
    - Lower ductile-to-brittle-transition temperature

- Depending on the bond coat choice and fabrication process the TBC failure mode can be quite different.

(Padture et al., Science, 2002)
Processes for MCrAlY Bond Coat Fabrication

- Current fabrication processes
  - Low-pressure plasma spray (LPPS)
  - Air plasma spray (APS) & high-velocity oxy-fuel (HVOF)

- Limitations of thermal spray processes
  - Line-of-sight, requiring complex robotic manipulation for complete coverage
  - Oxide content can be high in APS and HVOF coatings.
  - High porosity level in APS

- Alternative coating processes for bond coat fabrication
  - Electrolytic codeposition
  - Electrophoresis
  - Autocatalytic electroless deposition
Why Electro-codeposited MCrAlY Coatings?

- **Electrolytic codeposition** ("composite electroplating"): Fine powders dispersed in an electroplating solution codeposit with the metal onto the cathode to form a multiphase coating.
  
  - Non-line-of-sight
  - Low cost (capital investment, energy consumption, powder waste)
  - Ability of producing homogeneous and dense coatings

Cr-Al-Y-based particles    Ni, Co or Ni/Co matrix

Superalloy Substrate
Very Limited Research on Electrolytic Codeposited MCrAlY Coatings

• Codeposition of CrAlY powder and a metal matrix of Ni, Co, or Ni-Co, followed by a post-plating heat treatment


• A dense MCrAlY coating of ~125µm thick was reported.

• The process was later patented by Praxair, known as Tribomet, and has been applied as the abrasive tip coating on first stage turbine blades.

• Lack of systematic studies

• No evaluation in syngas/hydrogen turbine environments
Electrolytic codeposition is a more complex process than conventional electroplating

- It is believed that five consecutive steps are engaged during the electrolytic codeposition process:

1. Formation of ionic clouds on the particles
2. Convection towards the cathode
3. Diffusion through a hydrodynamic boundary layer
4. Diffusion through a concentration boundary layer and finally
5. Adsorption at the cathode where the particles are entrapped within the metal deposit

(Guglielmi, J. Electrochem. Soc., 1972)
Synergistic Effects of Codeposition Parameters

- Codeposition parameters
  - Type of electrolyte
  - Current density
  - pH
  - Temperature
  - Agitation
  - **Particle composition/size/volume**
  - Cathode position (plating configuration)
  - Post-plating heat treatment

- Lack of systematic studies, need to establish a knowledge base
Project Objectives

- Develop and optimize MCrAlY bond coats for syngas/hydrogen turbine applications using a low-cost electrolytic codeposition process

- Improve coating oxidation performance by reducing the sulfur impurity levels and by employing reactive element co-doping

- Evaluate the oxidation behavior of the new bond coat in water vapor environments

- Understand the failure mechanism of the new TBC/bond coat architecture
Key Research Components

#1: Selection of Substrate Alloys More Relevant to IGCC Applications
CMSX-486 (a revised version of CMSX-4)

#2: Development & Optimization of Electro-codeposited Coatings
- Electrolyte selection for Ni-/Co-matrix deposition
- Optimization of particle composition & volume
- Control of other codeposition parameters
- Microstructural evolution during post-plating heat treatment

#3: Microstructural Characterization & Property Measurement
- Microstructure
- Surface roughness & hardness measurement

#4: Evaluation of Coating Performance & Failure Mechanism
- Oxidation in water vapor
- Understanding of failure mechanism
- Potential technology transfer
Major Activities Planned in 36 Months

<table>
<thead>
<tr>
<th>Year</th>
<th>Year 1</th>
<th>Year 2</th>
<th>Year 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quarter</td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
</tr>
<tr>
<td>TASK 1.0 – Project Management, Planning, and Reporting</td>
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<tr>
<td>Task 2.0 – Selection of Substrate Alloys More Relevant to IGCC Applications</td>
<td></td>
<td>A</td>
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<td>Task 3.0 – Development and Optimization of Electrodeposited MCrAlY Coatings</td>
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<td>B</td>
<td></td>
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<tr>
<td>Subtask 3.1 Electrolyte Selection for Ni-/Co-Matrix Deposition</td>
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<td>Subtask 3.2 Optimization of Particle Composition and Volume</td>
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<tr>
<td>Subtask 3.3 Control of Other Codeposition Parameters</td>
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<td>C</td>
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<tr>
<td>Subtask 3.4 Microstructural Evolution during Post-Plating Heat Treatment</td>
<td></td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>Task 4.0 – Microstructural Characterization and Property Measurement</td>
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<td></td>
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<tr>
<td>Subtask 4.1 Microstructural Characterization</td>
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<td></td>
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<tr>
<td>Subtask 4.2 Surface Roughness and Hardness Measurement</td>
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<td>E</td>
<td></td>
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<tr>
<td>Task 5.0 – Evaluation of Coating Performance and Failure Mechanism</td>
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<td></td>
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<tr>
<td>Subtask 5.1 Oxidation Study in Water-Vapor Environments</td>
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<tr>
<td>Subtask 5.2 Understanding of the Failure Mechanism of the New TBC/Bond Coat Architecture</td>
<td></td>
<td>G</td>
<td></td>
</tr>
<tr>
<td>Subtask 5.3 Potential Technology Transfer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Task 6.0 – Cost Analysis</td>
<td></td>
<td>F</td>
<td></td>
</tr>
</tbody>
</table>

A. Material Selection/Procurement (02/15/2012):
Complete selection and procurement of substrate alloys as well as electro-codeposition supplies and start initial experiments on electro-codeposition of MCrAlY coatings

B. Initial Coating Process Development (08/15/2012):
Demonstrate initial success of the electrolytic codeposition of the MCrAlY coatings

C. Optimization of Codeposition Process (02/15/2013):
Identify optimized parameters of the codeposition process

D. Post-Plating Heat Treatment (08/15/2013):
Finalize the post-plating heat treatment procedure that produces the desired coating microstructure

E. Property Characterization (02/15/2014):
Complete surface roughness and hardness measurement

F. Cost Analysis (06/15/2014):
Complete cost analysis and provide a cost comparison between the proposed coating technique and the current techniques such as APS and HVOF

G. Performance & Failure Assessment (08/15/2014):
Complete both the oxidation testing and failure mechanism study for the developed coatings

A, B, C, D, E, F, G – Milestones from Milestone Log: 1– Decision Point
Research Progress
(Since Last UTSR Workshop in October 2011)

- Preparation of Cr-Al-Y powder
  - Fabrication of Cr-Al-Y alloy via arc melting
  - Ball milling and sieving

- Electro-codeposition experiments
  - Effect of current density
  - Vertical and horizontal configurations
No commercial Cr-Al-Y powder is currently available with the specific composition required

**Gas Atomized**

- Commercial powder suppliers
  1. CEAC
  2. American Elements
  3. READE Advanced Materials
  4. LPW Technology
  5. Sandvik
  6. ARCMELT
  7. Stellite
  8. Flame Spray
  9. HAI
  10. Shinwa Bussan (Japan)
  11. Sulzer Metco
  12. Praxair
  13. AEE
  14. HC Stark
  15. Powder Alloy Corp

**Ball Milled**

- Arc melting of Cr-Al-Y alloys, followed by ball milling at TTU
- Metals purchased for arc melting
  - Al – 99.99%
  - Cr – 99.995%
  - Y - 99.9%
Fabrication of Cr-Al-Y Alloy — Problems with the Initial Arc Melting Process

- Target alloy composition: Cr-37Al-1.7Y (wt.%)  
  - High weight loss of ~4% in initial arc melting  
  - Britteness of the intermetallic phases leads to cracking & loss of material into the arc melter chamber if the turn-over speed is not well controlled.
Improvement in the Arc Melting Process

- Careful control of the turn-over speed to prevent material loss
- Instead of using pure Y, an Al-Y master alloy was made first for Y incorporation.
  - Reduce oxidation of Y
  - More accurately control the Y level in the Cr-Al-Y alloy

![Al-Y Master Alloy Diagram](image)

Al-Y Master Alloy
Al-66.7Y (wt.%)  
(AI-37.8Y in at.%)
Weight loss of < 0.5% was achieved for the arc-melted Cr-Al-Y alloys

- Weight loss of the new alloys is in the range of 0.04 to 0.44%.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Total Weight (g)</th>
<th>ΔW (g)</th>
<th>ΔW%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
<td></td>
</tr>
<tr>
<td>#1 (initial)</td>
<td>75.00</td>
<td>71.70</td>
<td>-3.30</td>
</tr>
<tr>
<td>#2</td>
<td>99.96</td>
<td>99.89</td>
<td>-0.07</td>
</tr>
<tr>
<td>#3</td>
<td>79.99</td>
<td>79.72</td>
<td>-0.27</td>
</tr>
<tr>
<td>#4</td>
<td>79.97</td>
<td>79.94</td>
<td>-0.03</td>
</tr>
<tr>
<td>#5</td>
<td>79.97</td>
<td>79.62</td>
<td>-0.35</td>
</tr>
</tbody>
</table>
Accurate Composition Control of Cr-Al-Y Alloy

- The concentrations of major alloying elements are very close to the target composition.
- The levels of impurity elements (S and O) are extremely low.

<table>
<thead>
<tr>
<th>Element</th>
<th>Target Composition (wt.%)</th>
<th>DIRATS Analysis (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>61.3</td>
<td>61.25</td>
</tr>
<tr>
<td>Al</td>
<td>37.0</td>
<td>37.07</td>
</tr>
<tr>
<td>Y</td>
<td>1.7</td>
<td>1.6</td>
</tr>
<tr>
<td>Fe</td>
<td>—</td>
<td>0.02</td>
</tr>
<tr>
<td>W</td>
<td>—</td>
<td>0.02</td>
</tr>
<tr>
<td>Si</td>
<td>—</td>
<td>0.02</td>
</tr>
<tr>
<td>P</td>
<td>—</td>
<td>0.005</td>
</tr>
<tr>
<td>C</td>
<td>—</td>
<td>0.0008</td>
</tr>
<tr>
<td>S</td>
<td>—</td>
<td>&lt;0.0001</td>
</tr>
<tr>
<td>O</td>
<td>—</td>
<td>0.0021</td>
</tr>
<tr>
<td>N</td>
<td>—</td>
<td>0.0035</td>
</tr>
</tbody>
</table>
Characterization of the Cr-Al-Y Alloy

- XRD analysis shows that the Cr-Al-Y alloy (Cr-37Al-1.7Y, wt.%) consists of $\text{Cr}_2\text{Al}$, $\text{Cr}_5\text{Al}_8$, and $\text{YCr}_4\text{Al}_8$ three phases.
- X-ray mapping also indicates that there are three distinct phases.

![Image of XRD analysis](image1)

![Image of X-ray mapping](image2)

![Diagram of phase diagram](diagram)
Procedure of Cr-Al-Y Powder Preparation

1. The arc-melted alloy was crushed into small pieces using a mortar and pestle.

2. Sieved through #10 mesh (2 mm) to exclude large pieces

3. Ball milling for 1-3 hours

4. Sieving (wet vs. dry)

5. SEM examination

6. Particle analysis
Wet Sieving vs. Dry Sieving

- Wet sieving was first selected due to agglomeration of particles (<44 $\mu$m) during dry sieving.
- Contamination was found in the powder after wet sieving.

Impurity elements (Mg, Cl, K, and Ca) were introduced during wet sieving.

- Dry sieving (up to 44 $\mu$m) was used in powder preparation.
Effect of Ball Milling Time

- Ball milling followed by dry sieving
- Sieving through #170 mesh (90 µm) and #325 mesh (44 µm)
Particle Size Analysis by ImageJ

- High-contrast SEM images were taken at various locations to include >10,000 particles for quantitative particle analysis.
- Particle size analysis was conducted using ImageJ.
- The projected area of each particle was measured and converted to the diameter by assuming the particles as spheres.
Particle Size Distribution Table

- The majority of particles are < 5 \( \mu m \) after 1-3h of ball milling.

<table>
<thead>
<tr>
<th>Size (( \mu m ))</th>
<th>Percentage Frequency</th>
<th>Percentage Cumulative Under</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1h</td>
<td>2h</td>
</tr>
<tr>
<td>&lt;1</td>
<td>0.37</td>
<td>0.30</td>
</tr>
<tr>
<td>1-2</td>
<td>0.30</td>
<td>0.36</td>
</tr>
<tr>
<td>2-3</td>
<td>0.17</td>
<td>0.21</td>
</tr>
<tr>
<td>3-4</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>4-5</td>
<td>0.04</td>
<td>0.03</td>
</tr>
<tr>
<td>5-6</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>6-7</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>7-8</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>8-9</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>9-10</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>&gt;10</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
The Probability Density Function

- To obtain the probability density function, the cumulative under vs. particle size curve was fitted using bimodal Weibull distribution.

\[
F(x) = 1 - \alpha_1 e^{-\left(\frac{x}{\lambda_1}\right)^{k_1}} - \alpha_2 e^{-\left(\frac{x}{\lambda_2}\right)^{k_2}}
\]

\[
f(x) = \alpha_1 \left(\frac{k_1}{\lambda_1}\right) \left(\frac{x}{\lambda_1}\right)^{k_1-1} e^{-\left(\frac{x}{\lambda_1}\right)^{k_1}} + \alpha_2 \left(\frac{k_2}{\lambda_2}\right) \left(\frac{x}{\lambda_2}\right)^{k_2-1} e^{-\left(\frac{x}{\lambda_2}\right)^{k_2}}
\]
Summary of Particle Size Analysis

- Out of 100 g powder, ~90 g exhibited a particle size of
  - < 6.0 \(\mu\)m after 1h ball milling
  - < 5.2 \(\mu\)m after 2h
  - < 3.4 \(\mu\)m after 3h

- 1h milling time was selected for fabrication of Cr-Al-Y powder from arc-melted alloys.

### Table:

<table>
<thead>
<tr>
<th>Milling Time (h)</th>
<th>Mean ((\mu)m)</th>
<th>STD ((\mu)m)</th>
<th>Number</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(D_{10}) ((\mu)m)</td>
<td>(D_{50}) ((\mu)m)</td>
<td>(D_{90}) ((\mu)m)</td>
<td>(D_{90}) ((\mu)m)</td>
</tr>
<tr>
<td>1</td>
<td>1.65</td>
<td>1.62</td>
<td>0.2</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>1.67</td>
<td>1.37</td>
<td>0.3</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>1.45</td>
<td>0.90</td>
<td>0.4</td>
<td>1.3</td>
</tr>
</tbody>
</table>
Electro-codeposition Experiments

- **Substrate:** René 80 discs (~17 mm in diameter, ~1.6 mm thick)
  - ground to 600 grit
  - grit blasted with #220 grit
- **Watts plating solution**
- **Anode:** pure Ni plate
Electro-codeposition Parameters

- **Temperature**: 50°C
- **Current density**: 2.0-4.0 A/dm²
- **pH**: 3.0-3.5
- **Time**: 2h

<table>
<thead>
<tr>
<th>Constituent</th>
<th>(g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate</td>
<td>310</td>
</tr>
<tr>
<td>Nickel Chloride</td>
<td>50</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>40</td>
</tr>
<tr>
<td>Cr-Al-Y powder</td>
<td>30</td>
</tr>
</tbody>
</table>

G. A. DI BARI, Modern Electroplating, John Wiley & Sons, Inc., 2010
Effect of Current Density

- The roughness increased as the current density increased.
The current density should be controlled in the range of 2.0-3.0 A/dm².
Effect of Sedimentation

- The particle incorporation was much higher on the top edge of the specimen than on the flat surface.
- The coating was also much thicker on the top edge.
Specimens Coated in a Horizontal Position

- An increase of 10% particle incorporation than the vertical position
- The process becomes more line-of-sight.
Future Work: Electro-codeposition Configuration

- **Vertical**: more literature data
- **Horizontal**: a transitional setup
- **Rotating barrel**: a semi-permeable rotating barrel that holds the specimen and powder
  - Ultimate design
  - The electrolyte can diffuse through the membrane wall, while the powder is maintained in suspension in the barrel.
  - Uses significantly less powder, allowing a higher concentration if needed
Future Work: Effect of Interactive Parameters

- A Design-of-Experiment (DoE) approach will be used to understand and optimize codeposition parameters

- Central Composition Design
  - A total of twelve experiments (including four replicates at the center point)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Low</th>
<th>Intermediate</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>A       Current density (A/dm²)</td>
<td>1</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>B       Stirring rate (magnetic stirrer)</td>
<td>3</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>C       Particle loading</td>
<td>10</td>
<td>30</td>
<td>50</td>
</tr>
</tbody>
</table>
**Future Work: Sulfur-Free Ni Plating Solution**

- **Fluoborate electrolyte** typically used for heavy nickel applications & electroforming.

<table>
<thead>
<tr>
<th>Constituent (g/L)</th>
<th>Watts</th>
<th>Sulfamate</th>
<th>High Chloride</th>
<th>All Chloride</th>
<th>Fluoborate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate (NiSO₄·6H₂O)</td>
<td>180-300</td>
<td>—</td>
<td>240</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nickel Sulfamate Ni(SO₃NH₂)₂·4H₂O</td>
<td>—</td>
<td>300</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Nickel Chloride (NiCl₂·6H₂O)</td>
<td>45</td>
<td>15</td>
<td>90</td>
<td>240</td>
<td>—</td>
</tr>
<tr>
<td>Nickel Fluoborate [Ni(BF₄)₂]</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>— 220</td>
</tr>
<tr>
<td>Boric Acid (H₃BO₃)</td>
<td>30-40</td>
<td>30</td>
<td>30-40</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>pH Range</td>
<td>4.0-5.0</td>
<td>3.5-4.5</td>
<td>2.0-2.5</td>
<td>0.9-1.1</td>
<td>3.0-4.5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>25-65</td>
<td>25-65</td>
<td>40-70</td>
<td>40-65</td>
<td>25-65</td>
</tr>
<tr>
<td>Current Density (A/dm²)</td>
<td>1-6</td>
<td>2-15</td>
<td>1-6</td>
<td>5-11</td>
<td>4-11</td>
</tr>
</tbody>
</table>
Summary

- **Milestone A “Material Selection/Procurement”** (02/15/12)
- **Milestone B “Initial Coating Process Development”** (08/15/12)
  - Cr-Al-Y alloys with accurate composition control and low impurity level were fabricated via arc melting
  - Pre-alloyed **Cr-Al-Y powder of particle size <5 µm** was prepared via ball milling and subsequent dry sieving
  - Electro-codeposited coatings containing **12-30 vol% Cr-Al-Y particles** were synthesized, depending on the current density and the sample position.
- **Milestone C “Optimization of Codeposition Process”** (02/15/13)
  - Effect of electro-codeposition configuration
  - Effect of interactive codeposition parameters
  - Sulfur-free plating solution
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