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

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Coating Development Need for IGCC  
(Integrated Gasification Combined Cycle)

- 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 are codeposited 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
• 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 generally believed that five consecutive steps are engaged:

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
5. **Adsorption** at the cathode where the particles are entrapped within the metal deposit

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 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
Synergistic Effects of Electro-codeposition Parameters

- Type of electrolyte
- Current density
- pH
- Temperature
- Agitation
- Particle loading
- Particle composition/geometry/size
- Cathode position (plating configuration)
- Post-plating heat treatment
Electro-codeposition Experiments

- **Substrate:**
  Ni-200 or René 80 discs
  (17 mm in diameter, 1.8 mm thick)
  - ground to 600 grit
  - grit blasted with #220 Al₂O₃

- **Anode:** pure Ni plate

- **Temperature:** 50°C

- **pH:** 3.5

- **Time:** 2h

- **Pre-alloyed powder**
  - Laboratory: ball-milled CrAlY-based powder
  - Commercial: atomized CoNiAlY

- **Watts plating solution**

<table>
<thead>
<tr>
<th>Constituent</th>
<th>(g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulfate</td>
<td>210-310</td>
</tr>
<tr>
<td>Cobalt sulfate</td>
<td>0-12</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>45-50</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30-40</td>
</tr>
<tr>
<td>Sodium lauryl sulfate</td>
<td>2.0</td>
</tr>
</tbody>
</table>
Conventional Configurations in Electro-codeposition

**Vertical**
*(Traditional Electroplating)*
- Simple, more literature data
- Limited particle incorporation

**Horizontal**
*(Sediment Codeposition)*
- Increased particle incorporation on the top surface
- Nearly no particles on the bottom surface
Rotating Barrel System

- A semi-permeable barrel that holds the specimen and powder
  - 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
- The barrel rotates along a horizontal axis during plating
  - More uniform coating and particle incorporation

(Honey et al., J. Vac. Sci. Technol., 1986)
Design and Setup of the Rotating Barrel at TTU

- Polypropylene barrel: 52-mm ID, 70-mm length
- Thin nylon membrane: with ~1 μm mesh size
Two-Step Coating Process to Form MCrAlYs

1. **Form a composite coating:**
   CrAlY-based particles are electro-codeposited with Ni/Co

   CrAlY powder: Cr-37Al-1.7Y (wt.%) (Cr$_2$Al, Cr$_5$Al$_8$, & YCr$_4$Al$_8$)

   Need ~40 vol.% in coating

2. **Convert to $\beta + \gamma$:** post-plating diffusion treatment

   16-22 Al, 18-22 Cr, 0.3Y, at.%
   (8-12 Al, 18-22 Cr, 0.5Y, wt.%)

   (Grushko et al., J. Alloys Compd., 2008)
# Commercial Powder vs. TTU Powder

<table>
<thead>
<tr>
<th></th>
<th>Commercial</th>
<th>TTU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt.%)</td>
<td>Co-32Ni-21Cr-8Al-0.8Y</td>
<td>Cr-37Al-1.7Y</td>
</tr>
<tr>
<td>Processing</td>
<td>Atomizing</td>
<td>Ball milling</td>
</tr>
<tr>
<td>Shape</td>
<td>Spherical</td>
<td>Irregular</td>
</tr>
<tr>
<td>Size ((\mu m))</td>
<td>12.9</td>
<td>7.1</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>7.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Powders with desired composition are not commercially available.
Barrel Codeposition Results

Particle loading: 20 g/L
Rotation speed: 7 rpm

Commercial Powder

Laboratory Powder

20 mA/cm²

20 µm

60 mA/cm²
Effect of Barrel Codeposition Parameters

- Higher particle incorporation for atomized powder
- Particle incorporation increased with reduced rotating speed
Effect of Particle Density

- Higher particle incorporation for CrAlY-Ta powder
- Ta (0.5-3.4 wt.%) has been added to some MCrAlY coatings (A. Vande Put et al., Surf. Coat. Technol., 205, 2010, p. 717)

Cr-25Al-1.5Y-12.6Ta (wt.%)
Effect of Plating Current Density

- Decreasing current density led to increased particle incorporation

Particle loading: 20 g/L
Rotation speed: 7 rpm
Powder: CrAlY
Composite Coatings with Ni-Co Matrix

- Powder: 20 g/L CrAlY
- Current density: 5-20 mA/cm²
- Rotation speed: 7 rpm
- Plating time: 2h

- Coating thickness ~55 µm, CrAlY particle incorporation 30-40 vol.%
Post-deposition Heat Treatment

- NiCo-CrAlY composite coatings on René 80
- Temperature: 1000, 1100, 1200°C
- Time: 2h
- Environment
  - Vacuum: $10^{-4}$ Pa
  - Ar: 1 atm
NiCo-CrAlY Coatings after Diffusion Heat Treatment

- More interdiffusion at 1100-1200°C
- Cr evaporation at 1200°C in vacuum
After Heat Treatment in Vacuum: $\beta + \gamma'$

Coatings on René 80

20 30 40 50 60 70 80 90 100

$\gamma'$ (100) $\beta$ (110) $\gamma'$ (110) $\gamma'$ (111) $\beta$ (111) $\gamma'$ (200) $\beta$ (200) $\gamma'$ (220)

1200°C

1100°C

1000°C

As-deposited
After Heat Treatment in Ar: $\beta + \gamma + \gamma'$
NiCo-CrAlY Coatings after Diffusion Heat Treatment

- Phases such as $\beta$, $\gamma'$, and $\gamma$ were observed

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Vacuum</th>
<th>Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C</td>
<td><img src="image1" alt="Vacuum 1000°C" /></td>
<td><img src="image2" alt="Ar 1000°C" /></td>
</tr>
<tr>
<td>1100°C</td>
<td><img src="image3" alt="Vacuum 1100°C" /></td>
<td><img src="image4" alt="Ar 1100°C" /></td>
</tr>
<tr>
<td>1200°C</td>
<td><img src="image5" alt="Vacuum 1200°C" /></td>
<td><img src="image6" alt="Ar 1200°C" /></td>
</tr>
</tbody>
</table>
Heat Treatment in Vacuum - NiCoCrAlY

René 80: Ni-3.0Al-14.1Cr-9.3Co-4.0W-3.9Mo-5.1Ti-0.16C-0.016B-0.02Zr, wt.%

- Coating: 8-9 Al, 11-14Cr, 15-18Co (wt.%)  
- Cr evaporation at 1100-1200°C  
- 3% Cr and 2% Ti at surface 2h at 1200°C
Heat Treatment in Ar - NiCoCrAlY

- Coating: 8-10 Al, 13-15 Cr, 14-18 Co (wt. %)
- Less Cr evaporation; 14-17 at 1100-1200°C
- 1-2% Ti at surface after 2h at 1200°C
Coating Phase Constituents

Typical MCrAlY composition: 16-22 Al, 18-22 Cr, 0.3Y, at.%
(8-12 Al, 18-22 Cr, 0.5Y, wt.%)

- Co destabilizes $\gamma'$ phase and also improves ductility (>20 wt.% Co)
- Need to increase Cr and Co contents
Approaches to Increase Co and Cr Contents in Electrodeposited NiCoCrAlY Coatings

- **Co**: increase CoSO$_4$ in the plating solution

- **Cr**: (1) increase the Cr level in Cr-Al-Y powder;
  
  (2) reduce Cr evaporation during heat treatment
Characterization of Coating Surface Roughness

- In order to provide optimum adherence for an APS TBC top coat, a surface roughness of >10 µm Ra is desirable.

\[ Z(x) = y(x) - \bar{y} \]

\[ Ra = \frac{1}{n} \sum_{i=1}^{n} |Z_i| \]
### Roughness of As-deposited Coatings

**Horizontal setup (TTU powder, particle loading: 10 g/L)**

<table>
<thead>
<tr>
<th>Current density (mA/cm²)</th>
<th>Stirring (rpm)</th>
<th>Particle (vol.%</th>
<th>Ra (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>80</td>
<td>26</td>
<td>6.3±0.6</td>
</tr>
<tr>
<td>60</td>
<td>80</td>
<td>20</td>
<td>10.3±3.9</td>
</tr>
<tr>
<td>20</td>
<td>300</td>
<td>21</td>
<td>3.4±1.6</td>
</tr>
<tr>
<td>60</td>
<td>300</td>
<td>32</td>
<td>7.4±0.6</td>
</tr>
</tbody>
</table>

**Barrel setup (particle loading: 20 g/L, current density: 20 mA/cm²)**

<table>
<thead>
<tr>
<th>Powder</th>
<th>Rotating (rpm)</th>
<th>Particle (vol.%</th>
<th>Ra (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>4</td>
<td>54</td>
<td>3.6±0.4</td>
</tr>
<tr>
<td>Commercial</td>
<td>7</td>
<td>47</td>
<td>4.5±0.7</td>
</tr>
<tr>
<td>Commercial</td>
<td>10</td>
<td>30</td>
<td>3.6±0.6</td>
</tr>
<tr>
<td>TTU</td>
<td>4</td>
<td>33</td>
<td>6.0±1.0</td>
</tr>
<tr>
<td>TTU</td>
<td>7</td>
<td>35</td>
<td>4.1±0.7</td>
</tr>
<tr>
<td>TTU</td>
<td>10</td>
<td>30</td>
<td>2.9±0.2</td>
</tr>
</tbody>
</table>
Characterization of NiCrAlY Coating Hardness

- As-deposited specimens (35-40 vol.% CrAlY in Ni)
- After heat treatment (2h in vacuum at 1000-1200°C)

- Hardness of as-deposited coating was measured in the Ni matrix
- Hardness is lower than thermal sprayed Ni-22Cr-10Al-1Y coating (380-530 HV). (Mishra, et al., J. Tribol., 2006;
## Future Work

- **Evaluation of Coating Performance**
  - Oxidation testing in water vapor at ORNL
  - Understanding of failure mechanism

- **Coatings for oxidation testing (1100°C, air + 10% H₂O)**

<table>
<thead>
<tr>
<th>Coating Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pack cementation NiAl</td>
</tr>
<tr>
<td>HVOF MCrAlY</td>
</tr>
<tr>
<td>Electro-codeposited NiCrAlY</td>
</tr>
<tr>
<td>Electro-codeposited NiCoCrAlY (current composition)</td>
</tr>
<tr>
<td>Electro-codeposited NiCoCrAlY (increased Cr &amp; Co)</td>
</tr>
</tbody>
</table>
Summary

• A rotating barrel system was established and utilized to synthesize Ni-CrAlY & NiCo-CrAlY composite coatings with uniform particle incorporation.
  – Particle incorporation was affected by particle shape and density
  – Decreasing current density led to increased particle incorporation
  – 25-40 vol.% CrAlY particles were incorporated

• Post-deposition heat treatments were conducted in vacuum and Ar at 1000-1200°C.
  – High Cr evaporation in vacuum at ≥1100°C
  – Co and Cr contents need to be further increased

• Coating hardness and surface roughness were evaluated.
  – Electro-deposited coatings showed Ra <10µm
  – Hardness was lower than thermal sprayed coatings
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