Novel Corrosion Protection Methods for Aluminum and Magnesium Alloys

Army Corrosion Summit
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# Novel Corrosion Protection Methods for Aluminum and Magnesium Alloys

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Outline

• Process for increasing the corrosion resistance of Al alloys
  – Novelis Fusion™ Process

• Stannate chemical conversion coatings on Mg alloys
  – Advantages and problems with Mg alloys
  – AZ91D and EV31A-T6 alloys
  – Surface pretreatment and stannate concentrations
  – EIS and linear polarization results
  – Microstructures

• Sacrificial anode design
Mg Alloys

Advantages of Mg alloys

- Specific modulus (E/\rho) similar to Fe, Al, and Ti alloys
- Mg alloys are often superior to plastics for stiffness critical applications

Problems with Mg Alloys

- Chemical Reactivity
  - Corrosion susceptibility of wrought products and castings
  - Complicates liquid metal processing
- HCP crystal structure so fewer slip systems than mild steels (BCC) and Al alloys (FCC)

Design for Corrosion Resistance!

- Alloy Selection
- Service Environment
  - Bare vs. Coatings
  - Coatings vs. Cost Trade Studies
  - Purity Level vs. Corrosion Resistance vs. Cost
Open Circuit Potential of Mg

Potential vs. pH diagram for Mg

Typical Open Circuit Potential value of Mg alloys in aqueous solutions.
Corrosion Mitigation via Conversion Coatings

Stannate-based conversion coatings for AZ91D and EV31A-T6 alloys

- Effect of surface modification prior to stannate coatings
- Effect of stannate concentration

<table>
<thead>
<tr>
<th></th>
<th>AZ91D</th>
<th>EV31A-T6</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy Type</strong></td>
<td>High Pressure Die Cast</td>
<td>Sand Cast</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>1.81 g/cm³</td>
<td>1.82 g/cm³</td>
</tr>
<tr>
<td><strong>Typical Yield Strength</strong></td>
<td>115 MPa</td>
<td>154 MPa</td>
</tr>
</tbody>
</table>
Stannate coated AZ91D (One week in 3.5% NaCl)

Blank  Alkaline  Acidic

Alkaline/Acidic  Directly Treated

Artificial Crevice (0.1mm)

Acrylic cell
Viton® O-ring
Clamp
Specimen
EIS Analysis of Passive Film

Nyquist Plots of AZ91D

10 mV perturbation at OC

EIS after one week of immersion in NaCl solution

\[ Z = Z' - jZ'' \]

\[ \frac{1}{Z} = \frac{1}{R} + \frac{1}{i\omega C} \]

Basic Equivalent Circuit
Effects of Stannate Coating on AZ91D Corrosion Rates

<table>
<thead>
<tr>
<th>Sample Surface Modification</th>
<th>Blank</th>
<th>Alkaline</th>
<th>Acidic</th>
<th>Alkaline/Acidic</th>
<th>Directly treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ecorr (VSCE)</td>
<td>-1.57</td>
<td>-1.56</td>
<td>-1.54</td>
<td>-1.54</td>
<td>-1.59</td>
</tr>
<tr>
<td>Icorr (µA/cm²)</td>
<td>61.3</td>
<td>30.0</td>
<td>1.9</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Rp (KΩ cm²)</td>
<td>0.83</td>
<td>0.86</td>
<td>14.00</td>
<td>11.11</td>
<td>18.1</td>
</tr>
<tr>
<td>Corrosion rate (µm/yr)</td>
<td>350</td>
<td>170</td>
<td>110</td>
<td>130</td>
<td>80.0</td>
</tr>
</tbody>
</table>

Linear polarization measurements after 30 minutes of immersion in 3.5% NaCl solution

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Corrosion Rate (µm/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ91D</td>
<td>254</td>
</tr>
<tr>
<td>EV31A-T6</td>
<td>432</td>
</tr>
</tbody>
</table>

ASTM B117 Salt Spray
SEM Images of Passive Film

Before Corrosion

After Corrosion

Alkaline/Acidic

Directly treated

Porous coating

Self healing

Pores blocking
Effect of Immersion Time

Nyquist plots for directly treated AZ91D samples

EIS of directly treated samples for longer immersion times in NaCl solution
Corrosion protection of EV31A-T6

Stannate coated EV31A-T6 after seven days in NaCl

Blank

Alkaline

Acidic

Alkaline/Acidic

Directly Treated
EIS Analysis of Passive Film on EV31A-T6

Nyquist Plots of Stannate coated EV31A-T6 after seven days in NaCl
Corrosion protection of EV31A-T6

EIS after seven days of immersion in NaCl solution
(The data for the stannate coatings are for the directly treated surface pretreatment)
Hydrogen Reduction Rate on coated and Uncoated Mg Alloys
Results for Stannate Conversion Coatings

- Preliminary results indicate stannate conversion coatings decrease corrosion rates by 1/3 - 1/2 and display some self-healing characteristics.
- Results indicate that surface pretreatments offer no substantial advantage over directly coating, which is advantageous from a coatings manufacturing or processing perspective.
- This is an electroless process that could offer advantages over popular coating methods that use a surface pretreatment anodization step followed by a resin type topcoat.
- Other chemistries to include could be molybdates, tungstates, and vanadates.
Surface Engineering for Corrosion Reduction via a Sacrificial Anode Technique

ASTM B117 Test Results

2195-BT\(^1\) 336 hours Exposure - Bare Metal

2195-BT 1000 hours Exposure
Surface Engineered Material

2519-T87 336 hours Exposure - Bare Metal

\(^1\)BT is the “balanced temper” developed by CTC for optimum combinations of resistance to AP and FSP threats.
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