A NON-CHROMATE CONVERSION COATING PROCESS FOR CORROSION PROTECTION OF AL 2024-T3 ALUMINUM ALLOY

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Outline

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  Corrosion protection of the alloy
  Significance of study and Objectives,
  Reason for choosing titanates

- Corrosion resistance of a titanate conversion coating on Al 2024-T3 alloy
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  Surface characterization (SEM, AES)
  Potentiodynamic studies
  Electrochemical Impedance Spectroscopy (EIS)
  Conclusions

- The effect of surface treatments on the fatigue life of Al 2024-T3 alloy
Microstructure and Corrosion of Al 2024-T3

- Al 2024-T3 is a high strength, heat treatable aluminum alloy with combination of good mechanical properties and light weight
- It is formed by precipitation hardening, it consists of substitutional solid solution of copper in aluminum and precipitate particles

**Schematic of Corrosion Cell**

\[
O_2 + 2H_2O + 4e^- \rightarrow 4OH^-
\]

Anodic Sites:
\[
Al \rightarrow Al^{3+} + 3e^-
\]

Initially Anodic → Cathodic
After Cu left behind
\[
Cu^{2+} + 2e^- \rightarrow Cu
\]

Al\textsubscript{2}O\textsubscript{3} Passive film

Al 2024-T3 (Al-93.5%, Cu-4.4%, Mg-1.5%, Mn-0.6%)
Corrosion protection of Al 2024-T3

- Chromate conversion coating (CCC)

- Immersion of aluminum alloy in an anodic solution containing dichromate, cyanide and fluoride ions, pH 1.5 - 3

- \[ 6e^- + 8H^+ + Cr_2O_7^{2-} \rightarrow 2Cr(OH)_3 + H_2O \]
  
  \[ 2Al - 6e^- \rightarrow 2Al^{3+} \text{ (in presence of F-)} \]

- Coating thickness \( \sim 10-60 \text{ nm} \)

- Excellent corrosion protection, have a self healing mechanism
Significance of study

- Toxic and carcinogenic effects of chromates

- Personnel Exposure Limit (PEL) for hexavalent chromates has gradually been reduced to levels difficult for industry to handle and further reductions are expected

- PEL is 1µg/m³ (8 hour time weighted average shift) as per OSHA regulations

- Alternates to chromate conversion coatings are needed. A titanate based process developed between URI and NUWC
Objectives

- To develop conversion coating to replace chromates based on titanium ion chemistry for Al 2024-T3 alloy and study the corrosion behavior of the alloy after conversion coating.

- To investigate the mechanism and formation of this conversion coating system.

- To study the fatigue properties of the alloy after the conversion coating to see whether the chemical and mechanical surface treatments have altered or affected it.
Why? Titanium based solutions

<table>
<thead>
<tr>
<th>Feature</th>
<th>Chromium</th>
<th>Titanium</th>
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</thead>
<tbody>
<tr>
<td>Multiple Valence</td>
<td>6+or 3+</td>
<td>4+ or 2+</td>
</tr>
<tr>
<td>Passive Film</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Low Passivation potential</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Ionic Form</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Similar Pourbaix diagrams</td>
<td></td>
<td></td>
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</tbody>
</table>
Simple corrosion testing

Bare sample in 0.5N NaCl

Bare sample in 0.5N NaCl in presence of titanate ion
Conversion coating formulation

The titanium bath formulation for all samples consisted of:
- 6g/L of K$_2$TiO$_3$
- 4g/L of NaF
- pH adjustment with nitric acid to either 2 or 5.5 at 60 °C
- No cyanide additions were used

**Process Conditions**

- 10 minutes in NaOH for uniform surface
- 10 minutes in SmutGo for uniform surface
- 3 minutes in conversion bath – longer leads to a powdery deposit on surface
Titanate conversion coating process

- Solvent cleaning with acetone
- Rinse in de-ionized water
- Chemical cleaning with sodium hydroxide at pH 12.5 for 10 minutes at 40 °C
- Rinse in de-ionized water
- Deoxidize in proprietary solution of Smut-Go
- Rinse in de-ionized water
- Conversion coating in titanate solution at 60 °C for 3 minutes
- Rinse in de-ionized water
- Air dry
Titanate conversion coatings

(Left to Right) Digital images of samples after NaOH treatment, after Smut-Go treatment and after conversion coating
5.5 pH, Titanate conversion coating

(a) SEM image of 5.5pH conversion coating on Al 2024-T3, (b) EDS spectra taken at the intermetallic region, (c) EDS spectra taken over the entire matrix of the alloy
2.0 pH, Titanate conversion coating
Auger electron spectroscopy analysis for 5.5 pH coating
Depth profile for 5.5 pH conversion coating for 3 min.
Auger electron spectroscopy analysis for 2.0 pH coating
Depth profile for 2.0 pH conversion coating for 3 min.
Electrochemical test apparatus (Flat cell)
Potentiodynamic scans in 0.5N NaCl with and without titanate
Electrochemical Impedance Spectroscopy

- Reference electrode
- Counter electrode (Pt)
- Clamps
- O ring
- Working electrode

- Gamry Instrument PC 4
- 10mV AC Voltage perturbation
- Open circuit potential measured for 100 sec
- Frequency range from 100,000 Hz to 0.01 Hz
Bode plots for bare and conversion coated samples
Bode plot for time dependence for 5.5 pH coating for 3 min.
Conclusions

- Simple corrosion testing and potentiodynamic studies revealed that the titanate ion protects the alloy surface.
- Titanate conversion coatings gave a good impedance magnitude at low frequencies.
- Auger analysis revealed that the layer of coating formed on the surface has intensities of Ti and O in the ratio that is most likely to be a titanium oxide layer.
- Thickness of the coatings were greater compared to chromate conversion coatings.
- The titanate coatings at pH 2.0 were thick compared to coatings at pH 5.5 but mud cracked while the coatings at pH 5.5 were cohesive.
- Titanate coatings at pH 5.5 for 3 minutes at 60 °C were found to be the optimum coating conditions for best corrosion protection.
Fatigue

- **Fatigue** = failure under cyclic stress

- Key points: Fatigue...
  - can cause part failure, even though $s_{\text{max}} < s_c$
  - causes $\sim 90\%$ of stress induced failures

- Many of the applications of this alloy are in aerospace

- In this application, they will undergo cyclic stressing or fatigue

- One of the properties required is that in addition to corrosion resistance, the fatigue properties should not be degraded
Fatigue testing machine, set up and test conditions

**Test conditions**

- Tension Tension cycle
- 3 Hz
- Load Controlled until failure

Note: All dimensions are in mm
Fatigue changes due to mechanical surface treatments on the alloy

Bare sample subjected to stress

![Diagram showing intermetallics, slip lines, rolling direction, and cracks with a scale of 10 μm with points plotted on a graph showing Log(N) vs Stress in kpsi.]
Effect of mechanical & chemical surface treatments on fatigue

- bare sample
- scotch brite abraded sample
- conversion coated sample

Stress in Kpsi vs. Log (N)

- ballotini glass bead treatment
- conversion coated sample
- bare sample
Conclusions

- Surface finishing with Ballotini glass beads was detrimental and was the main factor responsible for decrease in fatigue life.
- Surface finishing with mechanical abrasion of Scotchbrite also affected the fatigue life but to a lower extent.
- Conversion coating after mechanical treatments didn’t affect and was not detrimental to the fatigue life.
- Crack initiation sites in the alloy are most likely at the intermetallics.
Thank you