Investigation of electrochemically-induced repassivation of Al 7075-T6 and Al 2024-T3 as a function of applied stress and galvanic corrosion

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Investigation of Electrochemically - Induced Repassivation of Al 7075-T6 and Al 2024-T3 as a Function of Applied Load and Galvanic Corrosion

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Talking points

- Electrochemically-induced repassivation
  - Halide film vs Oxide film
  - Active phase at grain boundaries: $\beta$ phase ($\text{Al}_3\text{Mg}_2$) in Al-Mg alloys

- Repassivation and bending load: Al 7075-T6 and Al 2024-T3
  - Experimental variables: environment, electrochemical, mechanical

- Galvanic corrosion and bending load
  - Dissimilar metal CRES 304

- Final remarks
Electrochemically induced repassivation

**SCHEMATICS OF PIT INTIATION AND REPASSIVATION**

**Metal halide nucleation and growth**

Very thin oxide film extends over the active surface on the pit bottom and then increases its thickness, resulting in complete repassivation.
Electrochemically induced repassivation

<table>
<thead>
<tr>
<th>Halide film</th>
<th>Oxide film at pit bottom</th>
</tr>
</thead>
</table>

**E_{ptp}** - thermodynamic driving force of Al dissolution on freshly created (filmed) surface

**iptp** \( \propto \) rate hydrolysis equilibrium at \([Al^{3+}]_{\text{crit}}\)

\[
2Al^{3+} + H_2O + OH^- \leftrightarrow 2Al(OH)^{2+} + H^+
\]

**steepness** \( \propto \) \(H^+\) removal for full hydrolysis at \(E_{prot}\) (delayed repassivation constant ?!)
Active phase at grain boundaries: β phase precipitation

Al 5083-H111 as a function of sensitization time at 150 °C

✓ Commercial Al-Mg alloy, strain hardened by 20% of cold work, 10 years Lab. conditions

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Ti</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 5083-H111</td>
<td>0.17</td>
<td>0.32</td>
<td>0.04</td>
<td>0.62</td>
<td>4.32</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

20 mm x 30 mm rectangular sheets, thickness 1.5 mm
Surfaces wet ground up to 1200 grit

- Microstructure/composition (XRD, metallography*, SEM)
- Electrochemical properties (pitting scan, scan rate 0.1667 mV/s, 0.6 M NaCl, pH 6.5, room T)
- Mass loss test (NAMLT, 24-hours immersion HNO₃, ASTM G67)
- Mechanical properties (micro-hardness measurements 0.1 kgf/10 sec, diamond indenter, ISO 14577/DIN 50359)

*Metallography
1) 0.05 μm colloidal Al₂O₃
2) chemical etching
(NH₄)₂S₂O₈ 1g/10 mL, 30 min, room T
Active phase at grain boundaries: $\beta$ phase precipitation

Al 5083-H111 as a function of sensitization time at 150 °C
Active phase at grain boundaries: $\beta$ phase precipitation at grain boundaries

Al 5083-H111 as a function of sensitization time at 150 °C

Pitting Scan (PS)

0.6 M NaCl (pH 6.5)

$i_{\text{rev}} = 2.5 \text{ mA/cm}^2$

scan rate ($\nu$) 0.1667 mV/s

(10 mV/min)
Active phase at grain boundaries: $\beta$ phase precipitation at grain boundaries

Al 5083-H111 repassivation as a function of sensitization time at 150 $^\circ$C

![Average PS curves](image)
Active phase at grain boundaries: $\beta$ phase precipitation at grain boundaries

Al 5083-H111 repassivation as a function of sensitization time at 150 °C
Active phase at grain boundaries: $\beta$ phase precipitation at grain boundaries

Al 5083-H111 as a function of sensitization time at 150 °C
1) Combining in-situ generated by corrosion fresh surfaces and externally applied load?

2) Stress assisted galvanic corrosion?

   Complex design requirements
Repassivation and bending load: Al 7075-T6 and Al 2024-T3

Experimental variables

☑ Environment - Test solution composition ([Cl⁻], pH, viscosity), pre-exposure time, temperature
☑ (Electro)chemical - electrochemical parameters ($i_{rev}$, $E_{rev}$, $n$), galvanic coupling (joint with CRES 304)
☑ Mechanical - Static bending load (side in tension and compression), also followed by unload (residual tensile and compressive stress)
Materials, loaded specimens and electrochemical setup

Al 7075-T6 & Al 2024-T3 (Aviometal Spa, Italy)

Chemical composition (wt.%)

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Zn</th>
<th>Ti</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 7075-T6</td>
<td>0.06</td>
<td>0.13</td>
<td>1.70</td>
<td>0.02</td>
<td>2.60</td>
<td>5.80</td>
<td>0.04</td>
<td>0.20</td>
</tr>
<tr>
<td>Al 2024-T3</td>
<td>0.07</td>
<td>0.12</td>
<td>4.40</td>
<td>0.46</td>
<td>1.50</td>
<td>0.08</td>
<td>0.08</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Mechanical properties (Stress - Strain curves)

<table>
<thead>
<tr>
<th></th>
<th>Al 7075-T6</th>
<th>Al 2024-T3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (mm)</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Elastic Modulus E (GPa)</td>
<td>74.5</td>
<td>75.7</td>
</tr>
<tr>
<td>Yield strength YS, Rp02 (MPa)</td>
<td>510</td>
<td>354</td>
</tr>
<tr>
<td>Ultimate tensile strength UTS (MPa)</td>
<td>583</td>
<td>499</td>
</tr>
</tbody>
</table>
Materials, loaded specimens and electrochemical setup

Flat four-point bent-beam (4PPB) specimens (ASTM G39-99)

\[
\sigma = \frac{12Et y}{(3H^2 - 4A^2)}
\]

\[
y = \frac{\sigma(3H^2 - 4A^2)}{12Et}
\]

- \( t \) – thickness of specimen
- \( y \) – maximum deflection (between outer supports)
- \( Y' \) – deflection between inner supports
- \( h \) – distance between inner supports
- \( H \) – distance between outer supports
- \( A \) – distance between inner and outer supports

Constant load mostly below the elastic limit
Materials, loaded specimens and electrochemical setup

Flat four-point bent-beam (4PPB) specimens (ASTM G39-99)

side in tension

side in compression

Laminae dimension: 165 x 25 x 2 mm (Al 7075)
165 x 25 x1.5 mm (Al 2024)

Laminae dimension: 248 x 38 x 2 mm (Al 7075)
248 x 38 x1.5 mm (Al 2024)
Materials, loaded specimens and electrochemical setup

Flat four-point bent-beam (4PPB) specimens (ASTM G39-99)

LOAD LEVELS

![Strain gauges](image)

**Graphs:**
- **Stress vs. Strain** for Al 7075-T6 and Al 2024-T3.
  - Al 7075-T6:
    - Stress (MPa) vs. Strain (mm/mm)
    - Strain gauge (mm/mm) vs. Average strain (mm/mm)
  - Al 2024-T3:
    - Similar graphs as above.
Materials, loaded specimens and electrochemical setup

Electrochemical setup

Double walled Pyrex O-ring cell (bi-adhesive tape)
WE – Al alloy
CE – Pt
RE – SCE (Luggin)

1 cm² exposed Al surface
3 μm finish

Luggin Probe
Materials, loaded specimens and electrochemical setup

Electrochemical setup

Computer-driven Gamry Multipotentiostat

Parallel experimental runs in random order
At least 2 replications for each exp. condition
Repassivation and applied load Al 7075-T6 Static bending load - side in tension

Pre-exposure time $t_{\text{exp}}$

0.6 M NaCl pH 6.5, room T, $i_{\text{rev}}$ 2.5 mA/cm$^2$
Repassivation and applied load

Al 7075-T6 Static bending load - side in tension

Test solution viscosity

0.6 M NaCl pH 6.5/3.5, room T, $i_{rev}$ 2.5 mA/cm²

<table>
<thead>
<tr>
<th>% Glycerol</th>
<th>η (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.06</td>
</tr>
<tr>
<td>10</td>
<td>1.43</td>
</tr>
<tr>
<td>20</td>
<td>2.65</td>
</tr>
<tr>
<td>30</td>
<td>5.87</td>
</tr>
<tr>
<td>40</td>
<td>9.25</td>
</tr>
<tr>
<td>50</td>
<td>20.0</td>
</tr>
<tr>
<td>60</td>
<td>21.5</td>
</tr>
</tbody>
</table>

Viscosity cup (2 mm)
ASTM D1200 Ford

pH 6.5 open symbols
pH 3.5 filled symbols
Repassivation and applied load

Al 7075-T6 Static bending load - side in tension

[Cl\textsuperscript{−}] and pH

NaCl pH 6.5

\[
\log i_{\text{pdc}} (i \text{ in A/cm}^2) = \log [\text{Cl}] ([\text{Cl}] \text{ in M})
\]

90% YS
-0.5
\( (R^2 = 0.961) \)

% YS
- 0
- 25
- 50
- 70
- 80
- 90 (430 MPa)
- 98
- 100 (510 MPa)

NaCl pH 3.5

\[
\log i_{\text{pdc}} (i \text{ in A/cm}^2) = \log [\text{Cl}] ([\text{Cl}] \text{ in M})
\]

90% YS
-0.55
\( (R^2 = 0.997) \)

% YS
- 0
- 25
- 50
- 70
- 90 (430 MPa)
- 98
- 100 (510 MPa)
Repassivation and applied load: Al 7075-T6 Static bending load - side in tension

[Cl\textsuperscript{-}] and pH

Microyielding?
Bending thin specimen
Repassivation and applied load Al 7075-T6 Static bending load - side in tension [Cl⁻] and pH

room T, $i_{rev}$ 2.5 mA/cm²

Graph showing the effect of Cl⁻ concentration and pH on the repassivation and applied load. The graph includes three lines for different pH levels (6.5 and 3.5) and three concentrations of Cl⁻ (0.6 M, 0.3 M, and 0.1 M) with error bars indicating variability.
Repassivation and applied load

Al 7075-T6  Static bending load - side in tension

[Cl⁻] and pH

90% YS

100% YS
Repassivation and applied load

\[ \text{Al 7075-T6 Static bending load - side in tension} \]

\[ \text{room T, } i_{\text{rev}} 2.5 \text{ mA/cm}^2 \]

\([\text{Cl}^-]\) and pH

90% YS

Hair line crack

90% YS

\(0.6 \text{ M}, 0.3 \text{ M}, 0.1 \text{ M}\)

\(\text{pH 6.5}, \text{pH 3.5}\)

\(i_{\text{corr}} (\text{in mA/cm}^2)\)

\(\epsilon (\text{mm/mm})\)
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Amount of promoted corrosion $i_{\text{rev}}$ (red) 1 (blue) 2.5 (green) 5 mA/cm$^2$

Static bending - side in tension

0.6 M NaCl pH 6.5/3.5, room T

Al 7075-T6 0.6 M NaCl pH 6.5

characteristic potentials

$E$ vs SCE (mV)

iptp

steepness

90% YS

Average Epit

$E_{\text{ptp}}$  $E_{\text{prot}}$
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Amount of promoted corrosion $i_{\text{rev}}$ ( ) 1 ( ) 2.5 ( ) 5 mA/cm$^2$

Al 7075-T6 0.6 M NaCl pH 3.5

Static bending - side in tension 0.6 M NaCl pH 6.5/3.5, room T

+ Average Epit  x Average Eptp

Red  Blue  Green  Eprot
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Amount of promoted corrosion $i_{\text{rev}}$ (■) 1 (▲) 2.5 (▲) 5 mA/cm$^2$

Al 2024-T3 0.6 M NaCl pH 6.5

characteristic potentials

$i_{\text{ptp}}$ (mA/cm$^2$)

steepness
Repassivation and applied load Al 7075-T6 and Al 2024-T3

Amount of promoted corrosion $i_{\text{rev}}$ ( ) 1 ( ) 2.5 ( ) 5 mA/cm$^2$

Al 2024-T3
pH 6.5

Static bending - side in tension
0.6 M NaCl pH 6.5/3.5, room T
Repassivation and constant applied load: Al 7075-T6 & Al 2024-T3

Bending load: sides in tension and compression
sides in tension and compression followed by unload

TAGUCHI ORTHOGONAL DESIGN L9

<table>
<thead>
<tr>
<th>EXP</th>
<th>% YS</th>
<th>Scan rate (mV/s)</th>
<th>Erev vs SCE (mV)</th>
<th>T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>0.1667</td>
<td>-550</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>5</td>
<td>-450</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>10</td>
<td>-350</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>0.1667</td>
<td>-450</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>5</td>
<td>-350</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>10</td>
<td>-550</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>0.1667</td>
<td>-350</td>
<td>60</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>5</td>
<td>-550</td>
<td>80</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>10</td>
<td>-450</td>
<td>40</td>
</tr>
</tbody>
</table>

Example: Al 7075-T6 (tension side, load)
Average reverse curves

Test solution: 0.6 M NaCl pH 6.5
Potentiostatic polarization at Erev (10 min) followed by potential scan into the active region
PARTIAL LEAST SQUARES ANALYSIS

Al 7075-T6

Al 2024-T3

Y responses: Eptp, iptp, steepness, Eprot
Galvanic corrosion and load of Al 7075-T6 and Al 2024-T3

Preliminary experiments (0.6 M NaCl, pH 6.5, room T)

RATIO BETWEEN ANODE AND CATHODE AREAS ($A_a/A_c$) ≈ 10:1
Galvanic corrosion and load  Al 7075-T6 and Al 2024-T3

Static bending - side in tension  dissimilar metal: passing through CRES 304 screw

0.6 M NaCl pH 6.5, room T

Macrocouples

- Al – Pt
- Al/Fe – Pt

dissolved O₂ reduction comparable contribution

(Auxiliary) Cathode Pt

WE – Al alloy (WE1) or Al alloy/CRES 304 (WE2)

RE – SCE

two laminae connected with CRES 304 screw

tightening torque 3 Nm

Aa/Ac ≈ 2 : 1

Schematics of Al alloy/CRES 304
Galvanic corrosion and load Al 7075-T6 and Al 2024-T3

Static bending - side in tension dissimilar metal passing through CRES 304 screw

WE1: Al 7075

WE2: Al 7075 / CRES 304
Galvanic corrosion and load  
Al 7075-T6 and Al 2024-T3

Static bending - side in tension  
dissimilar metal passing through CRES 304 screw
Galvanic corrosion and load  Al 7075-T6 and Al 2024-T3

Static bending - side in tension  dissimilar metal passing through CRES 304 screw

WE2: Al 7075 / CRES 304

Higher maximum stress because bending stresses increased by the notch and thread effect
Stress-oriented dissolution enhanced with %YS

mounting resin  0 %YS  100 %YS

100µm  100µm
Galvanic corrosion and load  Al 7075-T6 and Al 2024-T3

Static bending - side in tension  dissimilar metal passing through CRES 304 screw

WE2: Al 7075 / CRES 304

Higher maximum stress because bending stresses increased by the notch and thread effect
Stress-oriented dissolution enhanced with %YS

contact between two laminae

100 %YS

mounting resin

300µm 100µm
Galvanic corrosion and load Al 7075-T6 and Al 2024-T3

Static bending - side in tension

WE2: Al 2024 / CRES 304

dissimilar metal passing through CRES 304 screw
The stress concentration is higher on the top surface of both laminae due to the presence of the hole.
Final remarks

- Electrochemically-induced repassivation in combination with bending load has indicated a critical condition for Al 7075-T6, suggesting inter-relation between local environment, electrochemical and mechanical states.

- Stress-oriented IG dissolution of Al 7075-T6 in contact with CRES 304 is enhanced with YS.

- Microstructural corrosion of Al 2024-T3, presenting less negative pitting potential than Al 7075-T6, could be responsible of the less evident effect of bending load on the repassivation and galvanic behaviors.

- Experiments under dynamic conditions (SSRT) and/or the use of lamina with stress concentration could help to understand better present findings.
Lamina with stress concentration (artificial notch)

Static bending - side in tension

**FEM ANALYSIS**

- Stresses field in x direction (s11)
- von Mises stresses

Depth of the notch = 0.4 mm
Diameter of the notch at the top surface = 0.2 mm

The notch allows to extend the high level of stress from the top surface of the sheet along the lamina thickness
Thank you for the attention