Program 4 Measurements and Mechanisms of Localized Aqueous Corrosion in Aluminum-Lithium Alloys

Rudolph G. Buchheit, Jr. and Glenn E. Stoner

Objectives

The objective of this research is to characterize the localized corrosion and stress corrosion crack initiation behavior of Al-Li-Cu alloy 2090, and to gain an understanding of the role of local corrosion and occluded cell environments in the mechanisms of pitting and initiation and early-stage propagation of stress corrosion cracks.
Like most heat treatable aluminum alloys, localized corrosion and stress corrosion of Al-Li-Cu alloys is strongly dependent on the nature and distribution of second phase particles. To develop a mechanistic understanding of the role of localized corrosion in the stress corrosion process, bulk samples of T1 (Al2CuLi) and a range of Al-Cu-Fe impurity phases were prepared for electrochemical experiments. Potentiodynamic polarization and galvanic couple experiments were performed in standard 0.6 M NaCl and in simulated crevice solutions to assess corrosion behavior of these particles with respect to the \( \alpha \)-Al matrix.

A comparison of time to failure versus applied potential using a constant load, smooth bar SCC test technique in Cl\(^-\), Cl\(^-\)/CrO\(_4\)\(^{2-}\), and Cl\(^-\)/CO\(_3\)\(^{2-}\) environments shows that rapid failures are to be expected when applied potentials are more positive than the breakaway potential (\( E_{br} \)) of T1 (crack tip) but less than \( E_{br} \) of \( \alpha \)-Al (crack walls). It is shown that this criterion is not satisfied in aerated Cl\(^-\) solutions. Accordingly, SCC resistance is good. This criterion is satisfied, however, in an alkaline isolated fissure exposed to a CO\(_2\) containing atmosphere. Rapid failure induced by these fissures has recently been termed "preexposure embrittlement."

Anodic polarization shows that the corrosion behavior of T1 is relatively unaffected in alkaline CO\(_3\)\(^{2-}\) environments but the \( \alpha \)-Al phase is rapidly passivated. X-ray diffraction of crevice walls from artificial crevices suggests that passivation of \( \alpha \)-Al occurs as Bayerite (Al(OH)\(_3\)) imbibes solvated lithium and carbonate ions to form a hydrotalcite-type compound \([\text{LiAl}_2\text{(OH)}_6]^{2+} \cdot \text{CO}_3^{2-} \cdot n\text{H}_2\text{O}\).
Stress Corrosion of 2090:
The Role of Localized Corrosion
in the Subgrain Boundary Region

R.G. Buchheit
G.E. Stoner

Department of Materials Science
University of Virginia
Charlottesville, Virginia 22901

Sponsored by NASA, Langley Research Center, Hampton, Virginia
Outline

* Microstructural Heterogeneity and Localized Corrosion

* Time to Failure vs. Applied Potential in Cl\(^-\) and Cl\(^-\)/CrO\(_4^{2-}\)

* SCC in CO\(_3^{2-}\) Environments, "Pre-Exposure Embrittlement"
Centered dark field transmission electron micrograph of the subgrain boundary region showing the precipitation of T₈ on boundaries and in subgrains.
Corrosion Behavior in Aerated 0.6 M NaCl

<table>
<thead>
<tr>
<th>Phase</th>
<th>Model Material</th>
<th>Corrosion Potential (mV&lt;sub&gt;sce&lt;/sub&gt;)</th>
<th>Galvanic Couple Current Density (μA/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α - Al</td>
<td>SHT 2090</td>
<td>-720</td>
<td>----</td>
</tr>
<tr>
<td>Al-14Cu</td>
<td>as cast</td>
<td>-620</td>
<td>-0.5</td>
</tr>
<tr>
<td>Al18-Cu-5Fe</td>
<td>as cast</td>
<td>-670</td>
<td>-7.0</td>
</tr>
<tr>
<td>Al-24Cu-5Fe</td>
<td>as cast</td>
<td>-675</td>
<td>-3.0</td>
</tr>
<tr>
<td>T&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Al-26Cu-21Li</td>
<td>-1100</td>
<td>+500</td>
</tr>
<tr>
<td>PA 2090</td>
<td>Al-3Cu-2Li</td>
<td>-720</td>
<td>----</td>
</tr>
</tbody>
</table>
A. Optical micrograph of pitting associated with Al-Fe-Cu impurity particles.

B. Optical micrograph of discontinuous subgrain boundary pitting associated with $T_1$ precipitated on subgrain boundaries.
Anodic polarization in Cl⁻/CrO₄²⁻
Schematic of the cell used for constant load TTF experiments.
Time to failure versus applied potential in Cl⁻/CrO₄²⁻

Aerated 0.1 M NaCl/0.1 M Na₂CrO₄

Eₚ for T₁

(< 150 days)
A. Scanning electron micrograph of the fracture surface of a 2090 tensile specimen subjected to a time to failure experiment at 55% of the S-T yield strength in 0.1 M NaCl + 0.1 M Na₂CrO₄ at an applied potential greater than Eᵦₚ of T₁.

B. Scanning electron micrograph from the rim of the failure initiating pit.
C. Scanning electron micrograph of the SCC propagation region 200 micrometers below the base of the pit.

D. Scanning electron micrograph of the tensile overload region.
Anodic polarization in 0.6 M NaCl solution
Time to Failure vs. Applied Potential in Aerated 0.6 M NaCl

<table>
<thead>
<tr>
<th>Applied Potential (mV$_{sce}$)</th>
<th>Time to Failure (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-720 ($E_{corr}$)</td>
<td>3 @ &gt; 75</td>
</tr>
<tr>
<td></td>
<td>5 @ &gt; 30</td>
</tr>
<tr>
<td>-715</td>
<td>2 @ &gt; 45</td>
</tr>
<tr>
<td>-1150</td>
<td>2 @ &gt; 45</td>
</tr>
</tbody>
</table>
A. Scanning electron micrograph of the fracture surface of a 2090 specimen loaded to 55% of the S-T yield and immersed in 0.6 M NaCl solution under free corrosion conditions for 7 days then removed from solution and pulled to fracture in air.

B. Scanning electron micrograph of the failure initiating pit.
C. Scanning electron micrograph of the overload region directly below the base of the pit.
Necessary Conditions for Rapid SCC Failure
Appear to be:

* $\alpha$ - Al passive (below $E_{br}$)
* $T_1$ - transpassive (above $E_{br}$)
Pre-Exposure Embrittlement

Load Specimen to 55% of S-T yield

Immerse in aerated 0.6 M NaCl for 7 days under free corrosion conditions

Remove to lab air:
Failure in <24 h

Remove to CO₂-free air:
No failures

* Alloy 8090, Holroyd, et al. (1987)

* Alloy 2090, Moran (1989)
Aerated 0.6 M NaCl too aggressive towards subgrain boundaries

Fissures become alkaline

Absorption of CO$_2$
- pH falls
- LiAlO$_2$ precipitates

SCC initiates and propagates

Remove from solution

Continuous SGB corrosion in pits

Li$^+$ and CO$_3^{2-}$-upon removal

Li$_2$CO$_3$ precipitates at pH 10
- [CO$_3^{2-}$] = 1.0 M
- [Li$^+$] = 0.144 M reqd.

SCC initiates and propagates
Corrosion Behavior in Cl⁻ and Cl⁻/CO₃²⁻

<table>
<thead>
<tr>
<th>phase</th>
<th>i_{pass} (ua/cm²)</th>
<th>E_{br} (mV_{sce})</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Al (0.6 M NaCl, pH = 7-8)</td>
<td>1.0</td>
<td>-690</td>
</tr>
<tr>
<td>T₁</td>
<td>200</td>
<td>-720</td>
</tr>
<tr>
<td>α-Al (0.6 M NaCl + 0.1 M Li₂CO₃, pH = 10)</td>
<td>0.75</td>
<td>-590</td>
</tr>
<tr>
<td>T₁</td>
<td>550</td>
<td>-720</td>
</tr>
</tbody>
</table>

-590 mV > Rapid Failure Window > -720 mV
Aerated 0.6 M NaCl/0.1 M Li₂CO₃ pH 11.2

Time to failure versus applied potential in Cl⁻/CO₃²⁻
Open circuit potential versus time in Cl⁻/CO$_3^{2-}$
A. Scanning electron micrograph of the film that forms in the SCC region of a 2090 tensile specimen where the specimen is immersed in aerated 0.6 M NaCl for 7 days then removed to CO₂-free air.

B. Scanning electron micrograph of the film that forms in the SCC region of a 2090 tensile specimen that is immersed in aerated 0.6 M NaCl for 7 days then removed to laboratory air.

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ALUMINUM HYDROXIDE / BAYERITE, SYN

20-11

LITHIUM ALUMINUM CARBONATE HYDROXIDE HYDRATE

37-728

* hydrotalcite-type compound \([\text{LiAl}_2(\text{OH})_6]^+ \cdot \text{CO}_3^{2-} \cdot n\text{H}_2\text{O}\)

* derived from bayerite \(\text{Al(OH)}_3\)
Hydrotalcites

* Alumina Gels + Lithium Salts $\rightarrow (\text{LiX}_x)_y \cdot 2(\text{AlOH})_3 \cdot n\text{H}_2\text{O}$

* Several anions produce isomorphous compounds

\[ \text{OH}^- \quad \text{Cl}^- \]

* Passivating effects associated with its presence (Perrota, 1990)

* Insoluble in alkaline solutions
Ammended Pre-Exposure Embrittlement Mechanism

Constituent Particle Pitting

- H\(^+\) consumption in crevice increases pH
- \([\text{Li}^+]\) increases due to \(T_1\) dissolution
- \(\text{CO}_2\) is absorbed dissociates to \(\text{CO}_3^{2-}\)

pH favors Bayerite formation
imbibes 2\(\text{Li}^+\) \(\text{CO}_3^{2-}\) salt

Film is stable at high pH
\(T_1\) is active

Rapid Failure
Summary

* In order of increasing nobility:
  \[ T_1 < \alpha - Al < Al-Cu-Fe \]

* Rapid SCC ensues when:
  \[ E_{br\, T_1} > E_{applied} > E_{br\, \alpha - Al} \]

* In 0.6 M NaCl, \( E_{br\, T_1} = E_{br\, \alpha - Al} \)
  rapid SCC criterion is not satisfied

* In isolated fissures, rapid SCC criterion is satisfied

* \( \alpha - Al \) is passivated by a hydrotalcite-type compound
The following pages are from a presentation given at the CORROSION/90 Meeting, April 23-27, Las Vegas, Nevada
The Role of Hydrolysis in Crevice Corrosion of Aluminum-Lithium-Copper Alloys

R.G. Buchheit
J.P. Moran
G.E. Stoner

Center for Electrochemical Sciences and Engineering
Department of Materials Science
University of Virginia
Charlottesville, VA 22903

Overview

* Background
* Objectives
* Approach
* Results
* Summary
Background

**Crevice coupled to Bulk Solution**

- pH
- Time (min)
- dissolution in the crevice
- reduction reactions outside the crevice

**Isolated Crevice**

- pH
- Time (min)
- dissolution in the crevice
- reduction reactions inside crevice
Objectives

Separate and identify the roles of:
* Al\(^3+\)
* Li\(^+\)
* Cu\(^2+\)
* hydrolysis
* an external cathode
Approach

Simulated crevice technique
* in situ measurement
* avoid the size constraint associated with real crevices

Measure pH versus Time for:

**Materials**
- 99.99 Al
- SHT Al-3Li
- SHT Al-3Cu
- SHT Al-3Cu-2Li

**Environments**
- Aerated Bulk Solution
- Isolated Crevice
Approach

Interpret steady state pH using Distribution Diagrams for monomeric hydrolysis products and knowledge of where electrochemical reduction reactions are occurring.

Monomeric Hydrolysis

\[ xM^{2+} + yH_2O \leftrightarrow M_x(OH)_y^{(x-z)} + yH^+ \]

* Rapid \[ 10^5 < k < 10^{10} \text{ moles}^{-1}\text{sec}^{-1} \]
* Reversible
* An equilibrium treatment is applicable
Reactions Considered

**Aluminum**

\[ \text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{Al(OH)}^{2+} + \text{H}^+ \]  
\[-\log K_{xy} = 4.97\]

\[ \text{Al}^{3+} + 2\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_2^{+} + 2\text{H}^+ \]  
\[-\log K_{xy} = 9.3\]

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_3^- + 3\text{H}^+ \]  
\[-\log K_{xy} = 15.0\]

\[ \text{Al}^{3+} + 4\text{H}_2\text{O} \leftrightarrow \text{Al(OH)}_4^{2-} + 4\text{H}^+ \]  
\[-\log K_{xy} = 23.0\]

**Lithium**

\[ \text{Li}^+ + \text{H}_2\text{O} \leftrightarrow \text{LiOH} + \text{H}^+ \]  
\[-\log K_{xy} = 13.86\]

**Copper**

\[ \text{Cu}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{CuOH}^+ + \text{H}^+ \]  
\[-\log K_{xy} = 8.0\]

\[ \text{Cu}^{2+} + 2\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_2 + 2\text{H}^+ \]  
\[-\log K_{xy} = 17.3\]

\[ \text{Cu}^{2+} + 3\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_3^- + 3\text{H}^+ \]  
\[-\log K_{xy} = 27.8\]

\[ \text{Cu}^{2+} + 4\text{H}_2\text{O} \leftrightarrow \text{Cu(OH)}_4^{2-} + 4\text{H}^+ \]  
\[-\log K_{xy} = 39.6\]

\[ \text{Cu}^{2+} + \text{H}_2\text{O} \leftrightarrow \frac{1}{2}\text{Cu}_2(\text{OH})_2^{2+} + \text{H}^+ \]  
\[-\log K_{xy} = 10.36\]

**Electrochemical Reactions**

\[ \text{M} \rightarrow \text{M}^{n+} + \text{ne}^- \]  
internal

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]  
external

\[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]  
internal

\[ \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H} + \text{OH}^- \]  
internal
Construction of Distribution Diagrams

Formation Quotients (Baes and Mesmer, 1986.)

\[ \log Q_{xy} = \log K_{xy} + \frac{a I^{1/2}}{1 + I^{1/2}} + b I \]

\[ I = \frac{\sum z_i^2[i]}{2} \]

Mass Action Expressions

\[ Q_{11} = \frac{[\text{AlOH}^2+][H^+]}{[\text{Al}^{3+}]} \]

\[ \ldots \]

\[ F_{\text{AlOH}^2+} = \frac{[\text{AlOH}^2+]}{\Sigma [\text{species}]} \]
Results for Pure Aluminum

Electrochemical Reactions:
\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \text{internal} \]
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad \text{external} \]

Hydrolysis Reaction:
\[ \text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlO}^2+ + \text{H}^+ \quad \text{internal} \]

pH determined by \( [\text{Al}^{3+}] / [\text{AlO}^2+] \) in this range
Results for Aluminum

Electrochemical Reactions:

\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \]

\[ 3\text{H}^+ + 3e^- \rightarrow \frac{3}{2}\text{H}_2 \]

dissolution of 1 Al consumes 3 H⁺

Hydrolysis Reactions:

\[ \text{Al}^{3+} + \text{H}_2\text{O} \rightarrow \text{Al(OH)}^2^+ + \text{H}^+ \]
\[ \text{net loss of 2 H}^+ \]

\[ \text{Al}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{Al(OH)}_2^+ + 2\text{H}^+ \]
\[ \text{net loss of 1 H}^+ \]

\[ \text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + 3\text{H}^+ \]
\[ \text{no net loss of H}^+ \]

\[ \text{Al}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Al(OH)}_4^- + 4\text{H}^+ \]
\[ \text{net gain of 1 H}^+ \]
Results for SHT AI-3Li

Electrochemical Reactions:
\[ \text{Al} \rightarrow \text{Al}^{3+} + 3e^- \quad \text{internal} \]
\[ \text{Li} \rightarrow \text{Li}^+ + e^- \quad \text{internal} \]
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \quad \text{external} \]

Hydrolysis Reactions:
\[ \leftrightarrow \text{AlOH}^2^+ + \text{H}^+ \]
\[ \leftrightarrow \text{Al(OH)}_2^+ + 2\text{H}^+ \]
\[ \leftrightarrow \text{Al(OH)}_3 + 3\text{H}^+ \]

Reduction kinetics are slowed at the external cathode.
Results for SHT Al-3Li

Electrochemical Reactions:

\[ \text{Li} \rightarrow \text{Li}^+ + e^- \]  
\[ \text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2 \]  
\[ \text{H}_2\text{O} + e^- \rightarrow \text{H} + \text{OH}^- \]

Dissolution of 1 Li consumes 1 H⁺

Hydrolysis Reactions:

\[ \text{Li}^+ + \text{H}_2\text{O} \leftrightarrow \text{LiOH} + \text{H}^+ \]

No net loss of H⁺

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Results for SHT Al-3Cu

Aerated Bulk Solution
Consistent with $\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlOH}^{2+} + \text{H}^+$ equilibrium.

Isolated Crevise

Electrochemical Reactions:
$$\text{Cu} \rightarrow \text{Cu}^{2+} + 2e^-$$ internal
$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$$ internal
dissolution of 1 Cu atom form the alloy consumes 2 H$^+$.

Copper oxidation can not discharge H$^+$. 

In RRDE experiments with Al$_2$Cu at potentials below $E_R \text{Cu/Cu}^{2+}$, copper deposits have been observed. (Mazurkiewicz and Piotrowski, 1983).

$[\text{Cu}^{2+}] > 10^{-9} \text{ M}$ not detected in these crevices.
Results for SHT 2090

Aerated Bulk Solution
Consistent with $\text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlO}^2^+ + \text{H}^+$ equilibrium.

Isolated Crevice
$\text{Li} \rightarrow \text{Li}^+ + e^-$
$\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$

assisted by elemental Cu on walls

$\text{Li}^+ + \text{H}_2\text{O} \leftrightarrow \text{LiOH} + \text{H}^+$

replaces $\text{H}^+$ and inhibits further pH increase.
Summary

* In aerated bulk solutions, crevice pH is consistent with:

\[ \text{Al}^{3+} + \text{H}_2\text{O} \leftrightarrow \text{AlOH}^{2+} + \text{H}^+ \]

dependent on reduction kinetics at the external cathode.

* \( \text{Al(OH)}_{2}^{+}/\text{Al(OH)}_{4}^{-} \) system point defines the pH in pure Al, isolated crevices.

\[ \begin{align*}
\text{Li} & \rightarrow \text{Li}^+ + e^- \\
\text{H}^+ + e^- & \rightarrow \frac{1}{2}\text{H}_2 \\
\text{Li}^+ + \text{H}_2\text{O} & \leftrightarrow \text{LiOH} + \text{H}^+ 
\end{align*} \]

gives an alkaline crevice replaces \( \text{H}^+ \)

* Elemental Cu on walls of crevices may assist in generating alkaline crevice solutions.