Program 6 The Effect of Zinc Additions on the Environmental Stability of Alloy 8090 (Al-Li-Cu-Mg-Zr)

Raymond J. Kilmer and G.E. Stoner

Objectives

The objectives for this PhD research are to document and characterize the effects that Zn additions have on the microstructure of alloy 8090 under different aging conditions and to correlate SCC behavioral changes with changes in alloy composition and microstructure. As an extension of this goal, emphasis will be placed on optimizing SCC behavior and alloy density.
Stress corrosion cracking (SCC) remains a problem in both Al-Li and conventional Al heat treatable alloys. It has recently been found that relatively small additions (<1 wt-%) of Zn can dramatically improve the SCC performance of alloy 8090 (Al-Li-Cu-Mg-Zr). Constant load time to failure experiments using cylindrical tensile samples loaded between 30 and 85% of TYS indicate improvements of orders of magnitude over the baseline 8090 for the Zn-containing alloys under certain aging conditions. However, the toughnesses of the alloys were noticeably degraded due to the formation of second phase particles which primarily reside on grain and subgrain boundaries. EDS revealed that these intermetallic particles were Cu and Zn rich. The particles were present in the T3 condition and were not found to be the result of quench rate, though their size and distribution were.

At 5 hours at 160°C the alloys displayed the greatest susceptibility to SCC but by 20 hours at 160°C the alloys demonstrated markedly improved TTF lifetimes. Aging past this time did not provide separable TTF results however, the alloys toughnesses continued to worsen. Initial examination of the alloys microstructures at 5 and 20 hours indicated some changes most notably the S' and δ' distributions. It was further noticed that Zn additions appear to increase the number fraction of S' precipitating out from the alloys. A possible model by which this may occur will be explored.

Polarization experiments indicated a change in the trend of $E_{Br}$ and passive current density at peak aging as compared to the baseline 8090. Initial pitting experiments indicated that the primary pitting mechanism in chloride environments is one occurring at constituent (Al-Fe-Cu) particles and that the Cu and Zn rich boundary precipitates possesses a breakaway potential similar to that of the matrix acting neither anodic or cathodic in the first set of aerated 3.5 w/o NaCl experiments.

Future work will focus on identification of the second phase particles, evaluation of $K_{1SCC}$ and plateau $da/dt$ via both DCB and slow strain rate techniques. A lower Zn content variant will be examined in the near future in the hopes of optimizing toughness, density and SCC performance.
The Effect of Zn Additions on the Microstructure and SCC Performance of Alloy 8090

R.J. Kilmer
G.E. Stoner

Center for Electrochemical Sciences and Engineering
Department of Materials Science
University of Virginia
Charlottesville, Virginia 22901

Sponsored by NASA, Langley Research Center, Hampton Virginia
NASA Contact: B.A. Lisagor

Co-sponsored by Alcoa Technical Center, Alcoa Center PA
Alcoa Contact: J.M. Newman
<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Li</th>
<th>Cu</th>
<th>Mg</th>
<th>Zn</th>
<th>Zr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>2.53</td>
<td>1.22</td>
<td>0.67</td>
<td>1.36</td>
<td>0.12</td>
</tr>
<tr>
<td>Alloy B</td>
<td>2.47</td>
<td>1.23</td>
<td>0.74</td>
<td>0.99</td>
<td>0.12</td>
</tr>
<tr>
<td>Alloy C</td>
<td>2.54</td>
<td>1.23</td>
<td>0.49</td>
<td>1.00</td>
<td>0.12</td>
</tr>
<tr>
<td>Alloy D</td>
<td>2.55</td>
<td>1.16</td>
<td>0.69</td>
<td>0.02</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Alloy C

S-T

100 μm

10 μm

ORIGINAL PAGE IS OF POOR QUALITY
Quench Sensitivity

Alloy C  SHT at 545 C for 30 minutes
Aged 5 hours at 160 C

Air quench after SHT

Cold water quench after SHT
<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Aging Condition</th>
<th>Li</th>
<th>Cu</th>
<th>Mg</th>
<th>Zn</th>
<th>$K_{Ic}$ (S-T) (ksi $\sqrt{\text{in.}}$)</th>
<th>TYS (ksi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A</td>
<td>5 hr @ 160°C</td>
<td>2.53</td>
<td>1.22</td>
<td>0.67</td>
<td>1.36</td>
<td>12.8</td>
<td>41.6</td>
</tr>
<tr>
<td></td>
<td>100 hr @ 160°C</td>
<td>2.53</td>
<td>1.22</td>
<td>0.67</td>
<td>1.36</td>
<td>7.2</td>
<td>57.1</td>
</tr>
<tr>
<td>Alloy B</td>
<td>5 hr @ 160°C</td>
<td>2.47</td>
<td>1.23</td>
<td>0.74</td>
<td>0.99</td>
<td>8.0</td>
<td>41.6</td>
</tr>
<tr>
<td></td>
<td>100 hr @ 160°C</td>
<td>2.47</td>
<td>1.23</td>
<td>0.74</td>
<td>0.99</td>
<td>7.8</td>
<td>56.4</td>
</tr>
<tr>
<td>Alloy C</td>
<td>5 hr @ 160°C</td>
<td>2.54</td>
<td>1.23</td>
<td>0.49</td>
<td>1.00</td>
<td>18.3</td>
<td>40.3</td>
</tr>
<tr>
<td></td>
<td>100 hr @ 160°C</td>
<td>2.54</td>
<td>1.23</td>
<td>0.49</td>
<td>1.00</td>
<td>9.0</td>
<td>57.0</td>
</tr>
<tr>
<td>Alloy D</td>
<td>5 hr @ 160°C</td>
<td>2.55</td>
<td>1.16</td>
<td>0.69</td>
<td>0.02</td>
<td>27.9</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td>100 hr @ 160°C</td>
<td>2.55</td>
<td>1.16</td>
<td>0.69</td>
<td>0.02</td>
<td>10.7</td>
<td>55.8</td>
</tr>
</tbody>
</table>
Graph showing the relationship between aging time (hrs) and % TS. The graph compares four different alloys: Alloy A (diamonds), Alloy B (pluses), Alloy C (squares), and Alloy D (circles).
### 8090 and 8090 + Zn Variants

#### Alternate Immersion Testing (ASTM G-49)

30 day tests, 1/4" tensile samples

<table>
<thead>
<tr>
<th>Alloy Code</th>
<th>Aging at 160°C (hrs)</th>
<th>20 ksi</th>
<th>30 ksi</th>
<th>40 ksi</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>F/N Days</td>
<td>F/N Days</td>
<td>F/N Days</td>
<td>F/N Days</td>
</tr>
<tr>
<td><strong>Alloy A</strong></td>
<td>1 3/3 2.2,3</td>
<td>3/3 2.2,2</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 2/3 2.3</td>
<td>3/3 1.1,2</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 0/3 ----</td>
<td>0/3 ----</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 0/3 ----</td>
<td>0/3 ----</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 0/3 ----</td>
<td>N/A 1/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td><strong>Alloy B</strong></td>
<td>1 2/3 3.10</td>
<td>3/3 2.2,2</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 3/3 1.1,2</td>
<td>3/3 1.1,2</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 0/3 ----</td>
<td>3/3 2.3,9</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 0/3 ----</td>
<td>0/3 ----</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td><strong>Alloy C</strong></td>
<td>1 3/3 2.3,3</td>
<td>3/3 3.4,17</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 3/3 2.2,3</td>
<td>3/3 1.2,2</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 1/3 17</td>
<td>2/3 9.17</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 0/3 ----</td>
<td>0/3 ----</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 0/3 ----</td>
<td>N/A 0/3</td>
<td>----</td>
<td></td>
</tr>
<tr>
<td><strong>Alloy D</strong></td>
<td>1 3/3 4.5,17</td>
<td>3/3 4.6,7</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 3/3 3.3,5</td>
<td>3/3 1.2,3</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 2/3 3.4</td>
<td>3/3 2.2,2</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 2/3 3.5</td>
<td>3/3 3.3,4</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 1/3 4</td>
<td>N/A 3/3</td>
<td>2.2,2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 2/3 3.6</td>
<td>N/A 3/3</td>
<td>2.3,3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 3/3 2.2,3</td>
<td>N/A 3/3</td>
<td>1.1,1</td>
<td></td>
</tr>
</tbody>
</table>

* indicates sample fracture at threads
Microstructure

5 hr @ 160C
* small or no δ' free zones
* no S' apparent
* boundary ppt

20 hr @ 160C
* well developed δ'-FZ
* S' well developed
* boundary ppt

* solute distribution (?)
S' distribution in alloy A after 20 hr at 160°C

δ' distribution in alloy A after 20 hr at 160°C
Alloy A
20 hrs at 160°C
Precipitate D.F.
Effects of alloying on the corrosion behavior of Aluminum

Al solid solution more noble

Al solid solution more active

Potential (volts)

$E_{br}$

$i_{pass}$

Log $i$ (amps/cm$^2$)
Alloy B-T3

3.5 w/o NaCl
Aerated

0 min

30 min

75 min

* Alloy was lightly etched in Keller's etchant
Future Work

* DCB Samples to evaluate $K_{1\text{sc}}$ and plateau da/dt
* Compare/Contrast with slow strain rate approach
  ** Environmental changes
* Scanning auger spectroscopy
* Identification of precipitates via CBED
  ** Casting
* Different 8090 + Zn variant(s) to attempt improving:
  ** toughness
  ** maintain improved SCC performance
  ** Correlation between microstructure and SCC behavior **
SCC Testing of 8090 + Zn Alloys

**Approach**

* Evaluate SCC performance of 8090 and 8090 + Zn alloys in S-T orientation

**Method**

* Using a constant displacement rate technique, determine, rank and quantify pertinent SCC characteristics of these alloys and correlate the results with associated microstructure. These techniques should allow for determination of $K_{th}$ and the plateau cracking velocities.

**Experimental**

* (See attached figures)

* Sample will be a cylindrical S-T specimen with a EDM induced chord across the edge of the sample followed by fatigue pre-cracking via stepped load shedding (decreasing $K$) so that final $K_{max} < K_{1scc}$.

* The test will be run under free corrosion potential.

* Grips will be pin loaded to allow for rotation.

* Displacement rates will be varied.

* $da/dt$ will be continuously measured via a DC potential drop technique.

* $K_{th}$ vs. displacement rate will be plotted for air and 3.5 NaCl environment to aid in determining appropriate displacement rate.

* $K$ vs. $da/dt$ will be plotted for a number of microstructures (i.e. vs. aging time and temp.). Plateau cracking velocities and threshold $K$'s will be determined.

* $K_{th}$ and plateau cracking velocities can be compared/contrasted with DCB tests.
connection to air pump

external connection to sample

extensor bar

reference electrode

da/dt measured via a dc potential drop technique

overflow and air out

platinum mesh electrode (counter electrode)

electrode

external connection to platinum electrode

bubbler device to provide aeration

fatigue pre-cracked S-T SEN sample

eelliptical fatigue crack

Sample cross-section

Figure 1. Schematic of load cell for constant displacement rate and constant load experiments
S' and T₁ Distribution in Alloys A-C after 100 hrs at 160°C

Alloy A

Alloy B

Alloy C
* Zn incorporated into delta prime increasing the interfacial mismatch

* area adjacent to delta prime enriched in vacancies, Cu and Mg, creating environment conducive to $S'$ nucleation

* heterogeneous nucleation site whose competitiveness increases as the degree of stretch decreases and the degree of solute supersaturation increases