Objective

The objective of this work is to develop a fundamental understanding of the effects of dissolved and trapped hydrogen on the mechanical properties of selected Al-Li-Cu-X alloys. We propose to: (a) distinguish hydrogen induced EAC from aqueous dissolution controlled processes, (b) correlate hydrogen induced EAC with mobile and trapped hydrogen concentrations and (c) identify significant trap sites and hydrides (if any) through the utilization of model alloys and phases.
Hydrogen Interactions in Aluminum Lithium Alloys

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This program seeks to develop a fundamental understanding of the effects of dissolved and trapped hydrogen on the mechanical properties of selected Al-Li-Cu-X alloys. We propose to (a) distinguish hydrogen induced EAC from aqueous dissolution controlled EAC, (b) correlate hydrogen induced EAC with mobile and trapped hydrogen concentrations, and (c) identify significant trap sites and hydride phases (if any) through utilization of model alloys and phases. A review of the literature indicates three experimental factors which have impeded progress in the area of hydrogen EAC for this class of alloys. These are: (i) inter-subgranular fracture in Al-Li alloys when tested in the S-T orientation in air or vacuum make it difficult to readily detect hydrogen induced fracture based on straightforward changes in fractography, (ii) the inherently low hydrogen diffusivity and solubility in Al alloys is further compounded by a native oxide which acts as a hydrogen permeation barrier; these factors complicate hydrogen detection and measurement, and (iii) hydrogen effects are masked by dissolution assisted processes when mechanical testing is performed in aqueous solutions. This program will attempt to circumvent these experimental barriers through the use of novel breaking load, hydrogen analysis, and metallurgical techniques. The intended approach and current program status is reviewed.
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Sponsored by NASA-Langley Research Center. Pending support from the Alcoa Technical Center Foundation Program
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Experimental Problems associated with Investigation of Hydrogen Effects in Al-Li-Cu-X Alloys

1. **Problem:** Low fracture toughness is observed for aged Al-Li-Cu-X alloys stressed in the S-T orientation. Intergranular and inter-subgranular fracture occurs in air or in vacuum making it difficult to detect hydrogen assisted fracture on the basis of fractography. **Solution:** Test specimens in L-T orientation after appropriate aging to produce shear band cracking in air or vacuum.

2. **Problem:** Low hydrogen diffusivity and solubility in aluminum alloys is compounded by an oxide permeation barrier. These factors make hydrogen analysis difficult. **Solution:** Use thermal desorption spectroscopy and Pd coated samples.

3. **Problem:** Aqueous EAC response may be dominated by dissolution assisted processes even during cathodic charging. This tends to mask hydrogen effects. Fractographic features distorted by dissolution. **Solution:** Use modification of method originally described by Gruhl and co-workers or use Pd coated breaking load samples.
Approach

1. Age alloys to produce shear band fracture in air.

2. Perform modified breaking load and slow strain rate tests using pre-charged Al-Li-Cu-X alloys in L-T orientation. Use Pd coated samples with native oxide removed by sputter etching. Use alloy with a known hydrogen response (i.e. 7075-T6) as a control.

3. Analyzed fracture surfaces using "advanced" methods

4. Conduct hydrogen analysis on hydrogenated model alloys as well as Al-Li-Cu-X alloys specimens:
   a) Modified Devanathan-Stuchurski permeation method
   b) Thermal desorption spectroscopy
   c) hydride detection methods
   d) nuclear methods
Fabrication of Flat Tensile Bar in L-T Orientation for Breaking Load Studies
Constant Deflection Apparatus for use in Breaking Load studies
Advantages to Using Palladium Coatings

- Can remove $\text{Al}_2\text{O}_3$ layer, which impedes hydrogen diffusion.

- Surface of specimen will not be affected by cathodic charging.

- Can distinguish between aqueous and hydrogen effects.

ex.

![Diagram showing hydrogen assisted cracking and film rupture with aqueous effect]
Etching of an Aluminum Alloy Substrate by dc Sputter Etching
Deposition of Palladium by dc Sputtering
Tensile Specimen for Modified Breaking Load Studies

Notched Surface:
- Uncoated.
- Exposed to lab air and/or vacuum.

Back Surface:
- Coated with Pd.
- Cathodically charged.
# Test Matrix for Breaking Load Studies

<table>
<thead>
<tr>
<th>Material</th>
<th>Orientation</th>
<th>Treatment</th>
<th>Fractography at Applied Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>7075 - T6</td>
<td>L - T</td>
<td>Glove Box / Lab Air</td>
<td>slip band      slip band    slip band</td>
</tr>
<tr>
<td>2090 -</td>
<td>L - T</td>
<td>Glove Box / Lab Air</td>
<td>slip band      slip band    slip band</td>
</tr>
<tr>
<td>8090 -</td>
<td>L - T</td>
<td>Glove Box / Lab Air</td>
<td>slip band      slip band    slip band</td>
</tr>
<tr>
<td>7075 - T6</td>
<td>L - T</td>
<td>Cathodic Charging</td>
<td>to be determined</td>
</tr>
<tr>
<td>2090 -</td>
<td>L - T</td>
<td>Cathodic Charging</td>
<td>to be determined</td>
</tr>
<tr>
<td>8090 -</td>
<td>L - T</td>
<td>Cathodic Charging</td>
<td>to be determined</td>
</tr>
</tbody>
</table>
# Hydrogen Analysis Methods Pertinent to Aluminum-Lithium Alloys

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantage</th>
<th>Facility</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Devanathan</td>
<td>Inexpensive</td>
<td>U.Va-CESE</td>
<td>Favors alloys with permeability and mobile H</td>
</tr>
<tr>
<td>Stuchurski Permeation</td>
<td>Significant Experience</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nuclear Reaction</td>
<td>Absolute conc. depth profile</td>
<td>Sandia</td>
<td>Not readily avail. trapped+mobile D must use D₂O</td>
</tr>
<tr>
<td>³He(d,p)⁴He</td>
<td>used for Al</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal Desorption</td>
<td>relative conc. Spectroscopic</td>
<td>U.Va-CESE</td>
<td>proven for Al-Li must use D₂O</td>
</tr>
<tr>
<td>Spectroscopy</td>
<td>assess trap strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neutron Act.</td>
<td>thick samples</td>
<td>U. Va.-Nuclear</td>
<td>quantitative qualitative</td>
</tr>
<tr>
<td>Neutron Rad.</td>
<td>&quot; &quot;</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Hydrogen Concentration Profile During Hydrogen Permeation Studies

Charging side:

hydrogen reduction

\[ C_H = f(n_c) \]

\[ H^+ + e^- \rightarrow H \]

Exit side:

hydrogen oxidation

\[ C_H \rightarrow 0 \]

\[ H \rightarrow H^+ + e^- \]
Schematic of Devanathan–Stachurski Permeation Cell
Schematic of Differential Permeation Cell

charging side

exit side

control cell

CE  RE  WE
potentiostat/galvanostat

WE2

WE1  RE  CE
bipotentiostat
Hydrogen Transport in Endothermic Hydrogen Absorbers (Fe) is a Strong Function of The Nature and Density of Traps

\[ K = N_i k_r / p_r = \exp(-E_B / RT), \quad k \text{ is the trap rate, } p \text{ is the release rate} \]

\( N_i \) (lattice sites) = \( 2.6 \times 10^{23} \) octahedral sites/cm\(^3\) for BCC iron

\( E_B > E_s \) Strong Trap (~29 KJ/mole)
A Series of Permeation Rise and Decay Transients is Utilized to Separate Reversible from Irreversible Trapping

\[ \text{DECAY: } \frac{\log (1-l_2)}{\log (1-l_1)} = 1 - \frac{2}{\sqrt{\pi t}} \cdot \exp \left( \frac{-1}{4\tau} \right) \]

\[ \text{RISE: } \frac{\log (l_2/l_1)}{\log (l_2/l_1)} = \frac{2}{\sqrt{\pi t}} \cdot \exp \left( \frac{-1}{4\tau} \right) \]

REARRANGING:

\[ \text{DECAY: } \log (1-l)\sqrt{t} = \log \frac{2F \sqrt{D} (C_1 - C_2)}{\sqrt{\pi}} - \frac{L^2 \log e \times \frac{1}{4D} t}{t} \]

\[ \text{RISE: } \log (l-l_1)\sqrt{t} = \log \frac{2F \sqrt{D} (C_2 - C_1)}{\sqrt{\pi}} - \frac{L^2 \log e \times \frac{1}{4D} t}{t} \]

WHERE: \( \tau = Dt/L^2 \)
Diffusion coefficient of Hydrogen in various Al alloys

Temp. (K)

$D \text{ (cm}^2/\text{sec)}$ vs. $1/T \times 10^4 (1/\text{K})$

- ○ Al–1% Li
- □ Al–2% Li
- ▲ Al–3% Li
- 99.99% Al
- Al–2Li extrapolated to RT

Anyalebechi

Watson & Meshii

for 99.99% Al
Design of Thermal Desorption Spectroscopy system

Thermal Desorption Spectroscopy Offers Several Advantages

Constant Temperature

Temperature Ramp
Solubility of Hydrogen in Al alloys at 10,000 atm.

Temp. (K)

Hydrogen Solubility
mol H/cm metal

\(1/T \times 10^4 \, K^{-1}\)

- Al 99.99%
- Al - 1% Li
- Al - 2% Li
- Al - 3% Li
# Hydrogen Trapping

<table>
<thead>
<tr>
<th>Model Alloy</th>
<th>Exploitable Trap Site</th>
<th>Possible Trapping - Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al - 3Li</td>
<td>$\delta$, $\delta^\prime$, Li$_{ss}$</td>
<td>$\delta^\prime$-interphalal; $\delta$, $\delta^\prime$-hydride; Li-solute</td>
</tr>
<tr>
<td>Al - 3Cu</td>
<td>$\theta^\prime$, $\theta^\prime^*$, $\theta$, Cu$_{ss}$</td>
<td>$\theta^\prime$, $\theta^\prime^*$-interphalal; $\theta$-void</td>
</tr>
<tr>
<td>Al - Li- Cu</td>
<td>$\delta^\prime$, $T_1$, $T_2$</td>
<td>$\delta^\prime$, $T_1$, $T_2$-hydride; $T_1$-interphalal; $T_2$-void</td>
</tr>
<tr>
<td>T$_1$</td>
<td>T$_1$</td>
<td>T$_1$-hydride</td>
</tr>
<tr>
<td>Al</td>
<td>g.b., vacancies, voids, microvoids</td>
<td>interfacial, point defects, voids</td>
</tr>
<tr>
<td>Al - Zr</td>
<td>$\beta$, $\beta^\prime$</td>
<td>$\beta$-void; $\beta^\prime$-interphalal; $\beta$, $\beta^\prime$-hydrides</td>
</tr>
<tr>
<td>Al$_3$Zr ($\beta^\prime$)</td>
<td>$\beta^\prime$</td>
<td>$\beta^\prime$-hydride</td>
</tr>
<tr>
<td>Al - Li - Zr</td>
<td>$\delta^\prime$ coats $\beta^\prime$</td>
<td>interphalal; $\delta^\prime$, $\beta^\prime$-hydride</td>
</tr>
</tbody>
</table>
Program Status - June 1991

1. Hydrogen permeation cells assembled. Thin foils must be prepared.

2. Breaking load configuration built and tested. Specimen exposures to begin this summer.

3. Thermal desorption system in design stages. Equipment purchases to follow.

4. Hydrogen evolution reaction kinetics studies to be undertaken in July to ascertain hydrogen production capability of model alloys and phases.