SPATIALLY RESOLVED, IN-SITU MONITORING OF CRACK GROWTH VIA THE COUPLING CURRENT IN ALUMINUM ALLOY 5083

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Figure: Anodic Al<sub>2</sub>Mg<sub>3</sub> beta phase formed due to time and temperature exposure causes cracking

OUTLINE

- Introduction /Significance
- Background
  - History of the Coupling Current
  - CEFM
- Material Specs
- Procedures
- Results (per sample)
- Conclusions from Experimentation
- Modeling
  - Lightly Sensitized
  - Adjusting Model fully sensitized (What’s needed?)
- Future Work
LOCALIZED CORROSION & STRESS CORROSION CRACKING

Corrosion Costs US $276 Billion/Year!!
3.1% of GDP


Definition of SCC

Factors contributing to Corrosion in Industry

- Pitting: 22%
- SCC: 18%
- Crevice: 12%
- Erosion: 8%
- Intergranular: 5%
- Fatigue: 4%
- Brittle: 4%
BACKGROUND: DOES A “COUPLING CURRENT” (CC) EXIST FOR STRESS CORROSION CRACKING (SCC)?

**Case for 304SS**

Reactions in Crack Tip Region

- Fe → Fe^{2+} + 2e^{-}
- Cr → Cr^{3+} + 3e^{-}
- Ni → Ni^{2+} + 2e^{-}

Fe + n_{4}H_{2}O → Fe(OH)_{n_{4}}^{(2-n_{4})^{+}} + n_{4}H^{+} + 2e^{-}

Cr + n_{5}H_{2}O → Cr(OH)_{n_{5}}^{(2-n_{5})^{+}} + n_{2}H^{+} + 2e^{-}

Reactions on external Surface

- 2H^{+} + 2e^{-} → H_{2}
- 2H_{2}O + 2e^{-} → H_{2} + 2OH^{-}
- O_{2} + 4H^{+} + 4e^{-} → 2H_{2}O
- O_{2} + 2H_{2}O + 4e^{-} → 4OH^{-}
- Fe^{2+} + 2e^{-} → Fe
- Cr^{3+} + 3e^{-} → Cr
- Ni^{2+} + 2e^{-} → Ni

**Case for AA5083**

Possible anodic reactions leading to negative current

- Al → Al^{3+} + 3e^{-}
- Mg → Mg^{2+} + 2e^{-}

Al + n_{1}H_{2}O → Al(OH)_{n_{1}}^{(3-n_{1})^{+}} + n_{1}H^{+} + 3e^{-}

Mg + n_{2}H_{2}O → Mg(OH)_{n_{2}}^{(2-n_{2})^{+}} + n_{2}H^{+} + 2e^{-}

Reactions on external Surface

- 2H^{+} + 2e^{-} → H_{2}
- 2H_{2}O + 2e^{-} → H_{2} + 2OH^{-}
- O_{2} + 4H^{+} + 4e^{-} → 2H_{2}O
- O_{2} + 2H_{2}O + 4e^{-} → 4OH^{-}
- Al^{3+} + 3e^{-} → Al
- Mg^{2+} + 2e^{-} → Mg

CAN COUPLING CURRENT ALSO BE MEASURED IN AA5083 WITH SPATIAL RESOLUTION?

Measureable coupling current (Macdonald)

SCC CRACK GROWTH CHARACTERISTICS LEADING TO SUDDEN FAILURE

- Zones I and III depend on mechanical factors.
- Zone II is electrochemical in nature (also Temperature and Pressure dependent).
- Weak dependence of CGR on K in Zone II.
COUPLING CURRENT MEASUREMENTS ON 304SS REVEALED PACKETS OF NOISE POSSIBLY LINKED TO MICROFRACTURE EVENTS

Increase of current with $K$ values

Frequency changes in current indicates brittle fracture
MATERIAL SPECIFICATIONS & PROPERTIES
MATERIAL - AA5083 H116 (ALCOA) HEAT TREATED FOR SENSITIZATION

**COMPOSITION OF SHEET AA5083 MATERIAL (WT%)**

<table>
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<tr>
<th></th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
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<td>0.20</td>
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**As-received AA5083:**
Expected DOS ≤ 4 mg/cm²

**Sensitized AA5083:**
Expected DOS ≥ 30 mg/cm²
Continuous Beta

*β is the Mg-rich phase Mg₂Al₃

With different alloys come different mechanisms!

Anodic Dissolution in AA5083

Hydrogen Embrittlement in AA5083


METALLOGRAPHY (KELLER’S ETCH) AND ORIENTATION CODING

Longitudinal/Rolling direction (L)

Width Long Transverse (T)

1\textsuperscript{st} Letter: Direction of load for tension/Dir. of penetration plane

2\textsuperscript{nd} Letter: Direction of crack growth

LS

TL

ST

TS
SAMPLE DETAILS: AA5083 BEND BAR TL ORIENTATION

0.039-0.0787 in / 1-2mm

10"

SVP location

0.6"

1.5"

0.75"

Exposes the crack to environment, but not parts of the Fracture Mechanics device
Easily exposes closest external surface (Compared to CT and WOL)
ORIENTATION ANISOTROPY LEADS TO LOWER FRACTURE TOUGHNESS FOR S-L AND S-T

<table>
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<th>Alloy</th>
<th>Temper</th>
<th>MPa</th>
<th>Ksi</th>
<th>L-T</th>
<th>ksi/in</th>
<th>T-L</th>
<th>ksi/in</th>
<th>S-L</th>
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New Approaches to the Fracture Mechanics and SCC Analysis

PROCEDURES & EQUIPMENT
SAMPLES FOR FEASIBILITY STUDY

Sample # 1: Galvanic Couple in physical electrical contact

Sample # 2: Galvanic Couple in electrical contact through Pstat/ZRA
4 POINT BEND: MACHINE # 2

**Top View**
AA5083 Specimen (laying on its side)

Applied Load

**Front View**
Waterline in cell

SVP Probe

Load Pins

**Sliding Platform for SVP to monitor crack activity**

Machined Notch and crack-tip

Applied Load

Use this machine to measure the CC.
SVP SCAN AREAS

Growing Crack

Raster Scan Area

Notch
Results for Machine 1 first
**Time-resolved** ZRA current and potential signals after connecting Cu to Al

**Spatially-resolved** SVP Potential Map of Cu rod in Al Alloy Matrix

Ring of potential decreases in spacer region because of current passing from Al to Cu (elec. connection through ZRA)
WE CAN TRACK CATHODIC REGIONS ON SCC SAMPLES WITH TIME

FEASIBILITY STUDY: WE IMPLANT CU WIRES IN AA2024 MATRIX

These results gave us confidence that we could resolve the crack tip coupling current

In green overlay, darker colors are more cathodic. Control Sample: AA2024
Sensitized fracture surface identifying fatigue pre-crack (zone A), flat, low K SCC growth (zone B) intergranular SCC growth with perpendicular grains opening up (zone C).
COMPARISON OF UNSENSITIZED AND SENSITIZED FRACTURE SURFACES

Flat precrack region

Ductile regions with SCC growth w dimples around particles

Flat precrack region w transverse cracking in more susceptible crack growth dir

Flat/ Brittle SCC growth with more pronounced openings

These results U/R testing indicated that intergranular/subcritical crack growth was occurring for sensitized alloys vice the unsensitized alloys experience transgranular ductile tearing.
### SUMMARY OF SAMPLES AND EXPERIMENTS
#### MACHINE #2

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Treatment</th>
<th>Tests</th>
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<tr>
<td>U003</td>
<td>As-received</td>
<td>Continuous Rising load from 200 lbs.</td>
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<tr>
<td>S004</td>
<td>Sensitized at 175°C for 14 days – DOS = 45 mg/cm²</td>
<td>Constant load = 200 lbs, SVP</td>
</tr>
<tr>
<td>S005</td>
<td>Sensitized at 175°C for 14 days – DOS = 45 mg/cm²</td>
<td>Continuous Rising load from 200 lbs.</td>
</tr>
<tr>
<td>S006</td>
<td>Sensitized at 175°C for 14 days – DOS = 45 mg/cm²</td>
<td>Continuous Rising load from 700 lbs.</td>
</tr>
<tr>
<td>S007</td>
<td>Sensitized at 175°C for 14 days – DOS = 45 mg/cm²</td>
<td>Incrementally increasing load starting at 500 lbs., SVP</td>
</tr>
</tbody>
</table>
4 POINT BEND: MACHINE # 2

**Top View**
- AA5083 Specimen (laying on its side)
- Applied Load
- Sliding Platform for SVP to monitor crack activity
- Machined Notch and crack-tip
- Applied Load

**Front View**
- SVP Probe
- Waterline in cell
- Load Pins

**Load Pins**

**Front View**

**Load Pins**
SVP OF AA5083 SPECIMENS

Raster Scan Area
Growing Crack
Mg Insert
Notch

Dissolving Mg dominates Map

Initial SVP scan

Anodic
SVP POTENTIAL MAPS OF UNSENSITIZED SAMPLE WITH MG INSERT (CONTINUING RISING LOAD)

Notch is active; most of Mg dissolves before crack grows

About 2 hours after exposure, Load≈100 lbs.
SVP POTENTIAL MAPS OF UNSENSITIZED SAMPLE WITH MG INSERT (CONTINUING RISING LOAD)

Active notch and initial crack signals appear

Approximately 20 hours after exposure, load ~3300 lbs.

Coupling Current exists in notch and growing crack due to pH drop and exposure of fresh Al at crack tip.
ANALYSIS OF CRACK-TIP POTENTIALS
DOES IT HELP WITH MECHANISMS?

Global peak of CC vs load/K. CC peaks or near $K_{ISCC}$

Unsensitized $K_{ISCC} \approx 31$ MPa$\sqrt{m}$
SVP OF SENSITIZED SPECIMEN IN 0.06 M SW (CONTINUOUSLY LOADING)

Initial load ≈ 700 lbs., ≈ 2hrs after exp.  

Load ≈ 750 lbs., 2.75 hours after exp.

More local Coupling Current in early scans exists from more activity at anodic grain boundaries
COMPARISON REVEALS CRACK GROWTH IN LOADS BELOW $K_{\text{ISCC}}$.

Load held @ 200 lbs.

Continuously Rising Load
THE CRACK LENGTH CAN BE TRACKED ELECTROCHEMICALLY VIA THE CC!!

Increasing Load & Time

Approx. pre-crack location

µm 2000 4000 6000 8000 10000 12000 14000

µm 0 500 1000 1500 2000 2500 3000 3500 4000 4500

Increasing Load & Time

THE CRACK LENGTH CAN BE TRACKED ELECTROCHEMICALLY VIA THE CC!!
DO THE SVP MAPS CORRESPOND WITH REALITY?

Increasing Load & Time

Area of the 1st scan

Area of the Final scan

Crack propagation
Sanity Check:

The initial crack extension occurs with the increase in load.

At higher loads, extension occurs during the load plateau. This is environmental influence.
This is the first time SCC measured in-situ via the coupling current.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Summary of results</th>
</tr>
</thead>
</table>
| U003   | Mg inserts served as fiducial marker  
       | Established orientation of notch signals |
| S005   | Initial experiment performed for sensitized sample to establish parameters |
| S004   | Crack growth occurred below K-ISCC |
| S006   | Coupling current revealed anodic region and cathodic region  
       | At lower K, the crack front appears to bow  
       | Transition from pre-crack to IGSCC is less obvious in continuously rising  
       | load conditions (See air samples for verification) |
| S007   | Series of Load plateaus resulted in CC monitoring of crack growth |
| U007   | Peak of CC close to K-ISCC |
CONCLUSIONS
CONCLUSIONS

- Fracture Mech. & SVP analysis good for other alloys
- Modeling predicted a CGR and ECP for sensitized AA5083 in saltwater for different environmental conditions (lightly sensitized)
- Framework laid for describing fully sensitized specimens (see dissertation)
- New fracture mechanics device w/ SVP more fully describes SCC
- Verified coupling current flows from an anodic crack-tip
CONCLUSIONS

- SVP maps identified differences in sensitized and as-received crack tip CC (still interpreting)?
- Mg inserts served as fiducial markers and helped establish potential changes
- Showed that both the notch and crack signals were anodic
- Machined notch also anodic possibly because of pH drop in crevice
ACKNOWLEDGMENTS!!!

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QUESTIONS?