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

A Dissertation in
Materials Science and Engineering

by
Krystaufeux D. Williams

© 2014 Krystaufeux D. Williams

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy

August 2014
The dissertation of Krystaufeux D. Williams was reviewed and approved* by the following:

Digby D. Macdonald  
Distinguished Professor Emeritus of Materials Science and Engineering  
Dissertation Advisor  
Committee Co-Chair

Mirna Urquiri-Macdonald  
Professor Emeritus of Engineering Science and Mechanics

Kwadwo Osseo-Asare  
Distinguished Professor of Metallurgy and Energy and Geo-Environmental Engineering  
Committee Co-Chair

Zi-Kui Liu  
Professor of Materials Science and Engineering

Hojong Kim  
Assistant Professor of Materials Science and Engineering

Gary Messing  
Distinguished Professor of Ceramic Science and Engineering  
Head, Department of Materials Science and Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The work discussed in this dissertation is an experimental validation of a body of research that was created to model stress corrosion cracking phenomenon for 304 stainless steels in boiling water reactors. This coupled environment fracture model (CEFM) incorporates the natural laws of the conservation of charge and the differential aeration hypothesis to predict the amount of stress corrosion crack growth as a function of many external environmental variables, including potential, stress intensity, solution conductivity, oxidizer concentrations, and various other environmental parameters. Out of this approach came the concept of the coupling current; a local corrosion current that flows from within cracks, crevices, pits, etc… of a metal or alloy to the external surface. Because of the deterministic approach taken in the mentioned research, the coupling current analysis and CEFM model can be applied to the specific problem of SCC in aluminum alloy 5083 (the alloy of interest for this dissertation that is highly sought after today because of its corrosion resistance and high strength to weight ratio). This dissertation research is specifically devoted to the experimental verification of the coupling current, which results from a coupling between the crack’s internal and external environments, by spatially resolving them using the scanning vibrating probe (SVP) as a tool. Hence, through the use of a unique fracture mechanics setup, simultaneous mechanical and local electrochemical data may be obtained, in situ.

The SVP is an alternating current device designed to obtain highly localized potential gradients (with a best resolution of microns) in a solution conductivity of 100s of µS/cm. In order to enhance resolution of the SVP maps as much as possible, without being too far away from the desired test conditions of 0.6M saltwater (utilized in the lab as a substitute for seawater), dilution of the saltwater by an order of magnitude (0.06 M) was used throughout all experiments unless otherwise noted. Initial experiments of localized corrosion events from 10s of micron to
mm-sized galvanic couples were first mapped in order to obtain confidence in the ability to map
the current flowing through the solution above a stress corrosion crack. Furthermore, because of
these feasibility studies, the current density that flows between an alloys matrix to or from an
intermetallic compound can be spatially mapped as well.

Standard fracture mechanics of AA5083-H116 bend bars were performed in diluted
saltwater (0.06M) to obtain the critical fracture toughness for cracking in air and in saltwater.
During loading in a bending test setup, standard load and crack mouth opening signals were
obtained until the sample broke, or until the crack arrested. It was discovered that when the data
was analyzed by plotting the load as a function of crack mouth opening displacement, the critical
stress intensity (air), or threshold stress intensity (electrolyte) could be determined by identifying
the decreasing of unload/reload slopes from a constant value. Transitions to and from different
characteristic zones of cracking (different characteristics for different environments) are observed
in the provided light and scanning electron microscopy images.

The posited existence of the coupling current provides a different and more convenient
marker for analyzing stress corrosion cracking, corrosion fatigue, and other forms of localized
corrosion attack involving applied loads. For the first time, through the research in this
dissertation, the positive current flowing from a crack were mapped, in situ, providing the
changes in the anodic current density through the solution as a function of position. A collage of
SVP maps were constructed on a grand scale according to their observed location with the light
microscope by using features (such as the notch, or the growing crack) from the larger SVP maps
taken at lower fracture toughness values with less resolution. These larger maps were then lined
up with the extremes of the same features in smaller, SVP maps taken at a later time with a new
location and higher resolution to keep up with the advancing crack tip. From that collage, a crack
length vs. time graph was plotted to examine the characteristics of the crack growth. Finally, a
crack growth rate vs. fracture toughness trend was constructed to compare with the CEFM and other studies on stress corrosion cracking of AA5083.

In order to accommodate the expansion of the CEFM to predict crack growth in heavily sensitized AA5083 specimens, more electrochemical data (i.e., polarization scans taken from recent literature and compiled in this dissertation) was needed. The experimental findings from this dissertation also contributed to the model’s expansion with the spatial analysis of the crack internal and external environments. Future work will incorporate testing of the more sensitive specimen orientations, acoustic emission analysis for probing micro-fracture processes, and coating effectiveness for SCC mitigation.
TABLE OF CONTENTS

List of Figures ........................................................................................................... viii
List of Tables ............................................................................................................... xiv
Acknowledgements .................................................................................................... xv

Chapter 1 Introduction ................................................................................................ 1
  Themes in this Dissertation ....................................................................................... 3
  Coupling Current Definition ................................................................................... 3
  Determinism vs. Empiricism ................................................................................... 6
  Spatial Resolution vs. Time Resolution .................................................................. 7
  Chapter Outline ......................................................................................................... 9
  References ................................................................................................................ 10

Chapter 2 How the SVP Works (Instrumentation) ....................................................... 12
  Background/Theory .................................................................................................. 12
  Schematics of the SVP .............................................................................................. 16
  Feasibility Studies for Localized Corrosion Events .................................................. 20
  Results ....................................................................................................................... 24
  Conclusions ............................................................................................................... 28
  References ................................................................................................................ 29

Chapter 3 Fracture Mechanics and SEM of LT Bend bars .......................................... 32
  Theory ....................................................................................................................... 33
  Bend-bar Configuration ............................................................................................ 35
  Testing Setup ............................................................................................................. 37
  Results ....................................................................................................................... 42
  Fractography ............................................................................................................ 50
  SEM ........................................................................................................................... 52
  Conclusions ............................................................................................................... 55
  References ................................................................................................................ 56

Chapter 4 Use of SVP for In-Situ Monitoring IGSCC Crack Growth ......................... 58
  Obtaining Spatially-Resolved Potential Information ................................................ 59
  Experimental Setup ................................................................................................. 60
  Image Analysis of Potential Maps ............................................................................ 68
  Crack Growth Monitoring Using SVP ...................................................................... 75
  Conclusion ............................................................................................................... 89
  References ................................................................................................................ 93

Chapter 5 Calibration of the CEFM ......................................................................... 95
  Background for CEFM ............................................................................................. 96
  Findings on Effect of DOS on Crack Growth Rate .................................................. 98
Structure/Architecture of the CEFM ................................................................. 104
CEFM Findings for AA5083 (lightly sensitized) .............................................. 108
Conclusions ......................................................................................................... 112
References ........................................................................................................ 113

Chapter 6 Discussion and Future Work ................................................................ 115

Discussion ........................................................................................................... 116
Coatings and Anodizing: Options for SCC Mitigation? .................................... 118
Calibration of the CEFM .................................................................................... 120
Refined Experimental Path ................................................................................ 120
References ........................................................................................................ 123
LIST OF FIGURES

Figure 1-1: A schematic of the interplay between a corrosive environment, a susceptible alloy, and a tensile stress that combine and leads to SCC [1-2]......................................................1

Figure 1-2: Al-Mg phase diagram highlighting the region where the β phase is prevalent from Ref. [2]. .........................................................................................................................2

Figure 1-3: A schematic of SCC occurring on a specimen where the electron current flows from within the crack to the external surface of the metal based on the availability of the cathodic depolarizers (from Ref. [12]). Positive current flows from the crack ..................................................................................................................4

Figure 1-4: The expected behavior of the CC as a function of position across the external surface away from the crack mouth (on the horizontal axis), or into the crack (vertical axis). The conservation of charge is expected to hold in this SCC scenario (from Ref. [12])...................................................................................................................5

Figure 1-5: Findings from the time-based CC study of 304 stainless steel (SS) showing how the positive current flowing to the external surface through the solution (as acquired by a zero resistance ammeter – ZRA) is connected to the stress intensity (from Ref. [6]). ..................................................................................................................8

Figure 1-6: High acquisition rate of the CC during a load hold on 304 SS is likely connected to the microfracture events within the crack tip region (from Ref. [6])............8

Figure 2-1: Illustrations of the current lines that flow from an anode to cathode (top) and the corresponding potential contours (bottom) [1].........................................................13

Figure 2-2: a.) A physical diagram of a scanning probe in solution and the corresponding potentials measured by the probe in three areas (A, B, and C) of a corroding sample separated by insulating blocks. Region B is the anode in this case and the anodic current/potential flows equally to regions A and C. b.) The polarization potential of B has been raised to equal the open circuit potential of A. Hence, no current flows to region A but it does flow to region C. The potential profile in region A has a baseline potential while the other areas are the same [1].........................................................14

Figure 2-3: A schematic diagram of the SVP along with the associated components. Optional connections to a potentiostat can be made. .................................................................17

Figure 2-4: The electronic components of a typical LIA where a small AC signal is detected after removing the noise component from the signal [37, 38]. ......................18

Figure 2-5: The external components of the SVP in a flow diagram from Ref. [8]..............18

Figure 2-6: An explanation of how the LIA and electrometer interprets signals based on the user inputs from the computer [39].................................................................19
Figure 2-7: Two sample configurations including the AA2024 matrix with an embedded Cu wire in physical contact with the matrix (left) and an AA2024 matrix with an insulated Cu wire (right).

Figure 2-8: A light microscope image of the AA2024 surface with multiple Cu wires embedded in the surface. The AA2024 and the Cu wires were in physical contact with each other.

Figure 2-9: A complementary experimental setup measuring the electron current passing from the Cu to the AA2024 matrix with a potentiostat (ZRA mode).

Figure 2-10: A comparison of the typical electrochemical cell measurement (left) for galvanic currents with a SVP potential map (right) of the current passing through the solution.

Figure 2-11: An SVP potential map taken on the surface of the multiple Cu wire sample. Darker colors are more cathodic and the potentials obtained just above the Cu wires were the darkest obtained for the map.

Figure 2-12: SVP maps obtained in increasing points in time from the earliest map (top left) as the sample corrodes using the same potential scale as Figure 2-11. The colored bar axis represents the local potential gradient in the solution. Most scans were acquired in approximately 30 minute intervals. The post corrosion metallograph image is shown on the bottom.

Figure 3-1: Schematic of a plate of alloy material showing the terminology of their corresponding reference direction and the shorthand for specimens that could be extracted from the plate. Images represent the typical grain structure found on each of the surfaces.

Figure 3-2: A schematic of the mechanical setup for fracture mechanics testing of AA5083 bend bars where the mechanical components or the measurement devices are not exposed to the solution.

Figure 3-3: The load (blue) and extension signal (red) for an as-received/unsensitized specimen immersed in 0.06M saltwater. Load steps were 25 lbs. per step.

Figure 3-4: The load and extension plot versus time for a sensitized specimen immersed in 0.06M saltwater.

Figure 3-5: An example of load vs. extension plot for a sensitized specimen showing how the unload/reload slopes decrease dramatically as the crack started growing.

Figure 3-6: Stress corrosion test performed on a fully sensitized sample (DOS ≈ 45mg/cm²). The loading steps occurring just prior to and following $K_{ISC}$ are shown above.

Figure 3-7: A comparison of the as-received/unsensitized specimen (blue) to the sensitized one. The sensitized specimen not only reached a lower load (the
maximum load value in the trend) for final failure, but crack growth initiates sooner than in the as-received case.

Figure 3-8: UR slopes as a function of CMOD for sample S002. Continuous decreasing in the slopes as a function of CMOD ($\Delta^2P/\Delta E^2$) indicates crack growth.

Figure 3-9: UR slope behavior for sample U004 tested in 0.06M saltwater showing that little or no SCG is expected in this sample until final fracture occurs (the last two data points).

Figure 3-10: S008 UR slope values vs. CMOD for a sensitized specimen tested in air.

Figure 3-11: UR slopes behavior as a function of extension for several samples tested in different loading conditions. $\Delta^2P/\Delta E^2$ for the sensitized specimens in SW decreased much sooner (seen in the continual decrease of the fitted lines) than those tested in air. The trends for sensitized specimens each have two slopes for before (relatively flat) and after the onset of SCG (decreasing).

Figure 3-12: S002 Fracture surface identifying fatigue pre-crack (zone A), flat, low K SCC growth (zone B) and intergranular SCC growth with perpendicular grains opening up (zone C).

Figure 3-13: As-received specimen U006 fracture surface showing.

Figure 3-14: S008 fracture surface tested in air.

Figure 3-15 a-f: (a) U005-top two; fatigue pre-crack with horizontal striations for an unsensitized specimen tested in air and (b) pre-crack to mechanical overload transition for an as-received specimen tested in air. (c) S008 – Pre-crack to transgranular, mechanical crack growth transition in sensitized material tested in air. (d) S005 – Transition zone from flat, low K SCC to IG, higher K SCC zone for a sample tested in 0.06M saltwater. (e) S006 Stress corrosion region on a sensitized specimen in saltwater where the arrow indicates a crevice where corrosion product peels away from the alloy matrix. (f) S005 - transition from pre-crack to low K SCC.

Figure 4-1: Schematic of the experimental setup demonstrating the approach to concurrent CC monitoring and fracture mechanics testing.

Figure 4-2: Section of the as-received/unsensitized bend bar in test using the orientation of the obtained SVP scans presented in this chapter. The increasing y direction is parallel to the growing crack increasing in the up direction on this page.

Figure 4-3: Initial SVP map obtained with Mg wire implanted in the unsensitized sample to establish signal orientation with active elements on the sample.

Figure 4-4: Loading profile for an unsensitized AA5083 specimen (in blue) in 0.06 M saltwater with a superimposed straight line (red) to give a visual estimate of departure from the linear-elastic regime, or rather the onset of subcritical cracking. CC potential maps were collected before and after the onset of crack growth.
Figure 4-5: Accompanying potential map for the unloaded unsensitized sample in test in Figure 4-4, U003. The map was obtained following the dissolution of the Mg insert....66

Figure 4-6: A follow-up scan of the unsensitized specimen, U003 with no load. The activity in the notch increased since the first scan was acquired. .................................66

Figure 4-7: Load reached a value of approximately 500 lbs. The activity in the notch has decreased, but as the load increases and the crack starts to grow, activity is observed in the region of the crack..............................67

Figure 4-8: At a load of approximately 1750 lbs, the sample has opened up to the position of the pre-crack and the crack-tip has become anodic. b.) The load has increased beyond $K_{ISCC}$ and the crack has arrested and developed a large plastic zone. The sample was warped as a result and the notch was curved rather than straight. The colored local potential gradient scale is the same as in Figure 4-7. .............................67

Figure 4-9: An SVP scan of sensitized specimen S006 at an initial load of about 700 lbs. The precrack has opened up slightly as a result of the load leading to the presence of CC. No crack growth expected at this stage. Note that the CC will exist for intergranular attack (IGA) even though no crack growth is occurring. .................................69

Figure 4-10: SVP scan taken afterwards where the pre-crack that is 2794 um deep is almost fully opened. ........................................................................................................69

Figure 4-11: Decay in the CC is shown at a load of 910 lbs. because there is no crack growth occurring with time when the load under the KISCC value. .............................70

Figure 4-12: SVP scan of sensitized specimen S004 being held at a constant load. ..........72

Figure 4-13: SVP scan captured after a week or more of holding the load. .....................73

Figure 4-14: Digital micrograph of the sensitized specimen held at a constant load. The precrack (region A) was measured to be 2.59 mm with approximately another 2 mm of SCC crack growth (region B). Hence, following the SCC crack growth, the shiny fatigue beachmark zone (zone C) was purposely put in to mark the end of SCC. Zone D was the zone of ductile rupture from loading the sample in moist air until the sample was broken.............................................................74

Figure 4-15: Initial SVP Potential map of the notch and crack-tip region of a sensitized specimen (S007) before the onset of subcritical crack growth. Enhanced activity in the notch region is revealed but little or nothing in the crack-tip/pre-crack region. ........76

Figure 4-16: SVP Potential above the S007 specimen at a higher load. Most of the activity in the crack-tip area is due to the opening of the pre-crack. .........................77

Figure 4-17: An SVP scan capturing the end of the notch on the lower middle portion of the scan along with the growing crack tip. By comparison with the positions of the notch and the crack-tip in the previous image, it can be determined that the crack has grown by approximately 900 µm beyond the pre-crack. ........................................78
Figure 4-18: a-d) A few of the SVP scans collected for sample S007. e) Light micrographs showing the scanning areas in red for the larger scans from Figures 4-14 through 4-15 and f) for the smaller, higher resolution scans 4-16 through 4-17.

Figure 4-19: A collage of most of the SVP scans involving sample S007 showing the crack progression with time. Relative positions were compiled from combined light micrographs and by recording positional changes taken by the SVP for the smaller high-resolution scans.

Figure 4-20: Post-mortem fracture surface of sensitized specimen S007. It was somewhat different than the other samples featured in Ch. 4 in that there was not a strong intergranular section with transverse crevices.

Figure 4-21: Graphs showing the trend of the highest CCs (inferred from the SVP potential) observed in the crack-tip of an unsensitized specimen due to SCC. Three of the strongest potentials from each scans were measured and averaged to represent the crack-tip potential.

Figure 4-22: The crack-tip potentials as a function of load (top plot) and as a function of K (bottom plot) for a sensitized specimen. A series of peaks occur rather than one strong peak near the K_{ISCC}.

Figure 4-23: Crack-tip potentials for a sensitized specimen experiencing incrementally increasing loads (load holds had varying time periods longer than those from the other experimental setup discussed in chapter 4.

Figure 4-24: Comparison of the crack-tip potentials vs. load for sensitized and as-received specimens.

Figure 4-25: Loading profile with time for the sensitized sample S007 from Figures 4-20 and 4-21 with the crack extension as a function of time superimposed.

Figure 4-26: Crack growth rate (CGR during load holds only for a fully sensitized specimen S007 compared to the CGR predicted for lightly sensitized AA5083.

Figure 5-1: Schematic of the coupling current established for SCC of any alloy. The external environment described by the chemical equations help determine the crack growth rate from Ref. [11].

Figure 5-2: Aging curve for AA5083-H116 for samples held at 100°C for various periods of time from Bumiller [13].

Figure 5-3: Results of cyclic polarization scans reported by Bumiller of AA5083-H116 in saltwater [13].

Figure 5-4: Results of cyclic polarization scans reported by Bumiller of AA5083-H116 in 0.1M saltwater [13].

Figure 5-5: Description of β coverage (high>70% coverage, low<70%, or no coverage) for AA5083 samples with varying DOS levels from Reference [16].
Figure 5-6: (Left) Damage depth for various exposure times with different DOS values for samples exposed to 0.6M saltwater held at the breakdown potential [16]. (Right) Damage depth for different DOS levels shown for various periods of time in the same solution [16].

Figure 5-7: Dependence of damage depth on % of β coverage on the grain boundaries from Ref. [16]. Grains oriented in the L direction had the most IGC penetration.

Figure 5-8: Schematic flowchart of the overall CEFM procedure [1].

Figure 5-9: Flowchart of the CEFM process for CGR calculation [1].

Figure 5-10: Flowchart for the internal current calculation [1].

Figure 5-11: Results from the CEFM showing how the CGR vs. ECP varies for different solution conductivities Ref. [11]. A few experimental data points reported in the literature for solution treated (ST) and quenched (Q) AA5083 compact tension specimens.

Figure 5-12: Results of the CEFM showing how the CGR and ECP vary as a function of [O₂] or [H₂O₂] (b.) of [H₂O₂] or [H₂] from Ref. [11].

Figure 5-13: Results of the CEFM showing how the CGR vs. ECP for different solution conductivities from Ref. [11].

Figure 6-1: a.) ECP vs. [O₂] as predicted by the CEFM for AA5083-H321 using various SECD multipliers showing strong inhibition of ORR when the SECD decreases and strong catalysis when the SECD increases. b.) CGR behavior vs. [O₂] for different SECD values from Ref. [2].

Figure 6-2: Two examples of AE information that is obtained from the a.) crack growth and propagation and the b.) failure of steel cables obtained from Ref. [18].
LIST OF TABLES

Table 1-1: Composition of sheet AA5083 material in wt%.................................................................3

Table 2-1: The galvanic series for metals and alloys in seawater from reference [40].
   White boxes indicate active behavior for active-passive alloys..................................................21

Table 3-1: A selection of the room-temperature plain strain and yield strength values of
   some aluminum alloys, showing the anisotropy for the different orientations from
   Ref. [16]............................................................................................................................................37

Table 5-1: Summary of important values from cyclic polarization scans from Bumiller
   [13].....................................................................................................................................................101

Table 5-2: Comparison of polarization results for β phase in 0.1M NaCl from two
   different sources [13].........................................................................................................................101

Table 5-3: Values used in the CEFM for lightly sensitized AA5083-H321 from Ref. [11]....108
ACKNOWLEDGEMENTS

As scientists pursue a doctoral degree, we all have challenges throughout the journey, which could even come down to experiments just not working out. At times, some very talented scientists do not complete the course. Some attribute the success of experimental pursuits to the scientist being lucky. I believe that there is a Spirit who is responsible for bringing me to this point in my career. Hence, I first of all have to thank my LORD Jesus Christ for blessing me to have all of the pieces come together through all of the challenges, to get me to the finish line of completing my doctoral degree.

I am grateful to my advisor, Professor Digby Macdonald, for his guidance through this process. It is a privilege to be instructed by a scientist of such a high caliber. Also, considering his great talent, his accessibility to students is also impressive. I thank my committee: Professor Mirna Urquidi-Macdonald provided amazing insight on bringing my ideas together, Professor Kwadwo Osseo-Asare was instrumental in helping guide me through the graduate program and in terms of helping me to set up the chapters for future publication, Professor Zi-Kui Liu for discussion about the experiments and Professor Hojong Kim for adding his insight to the study considering the short notice. I appreciate the support of my colleagues from the Center for Electrochemical Science and Technology at Penn State: Matthew, Samin, and Sang-Kwon as well as the more senior and younger scientists who have come through the center. This work owes much gratitude to the insight to the great scientists at the Naval Research Laboratory, particularly Drs. Robert Bayles, Paul Natishan, Ronald Holtz, and the entire Center for Corrosion Science and Engineering (one of the world’s best corrosion labs). I would also like to thank the UVA faculty and researchers, particularly, Professor Robert Kelly, Drs. Cortney Crane and Elissa Bumiller, and Mary C. Lynn Lim for providing guidance, encouragement and documents when needed.
GOD has put some great people in my life to help me along the way. In terms of friends and family I first have to thank my beautiful wife, Tara and son, Ocean, whose patience through this process has been severely tested! Yet, they have managed to encourage and help me all along the way. I have also had the support of family and friends (my village) to help encourage me along the way. Thank you Aunt Gene, Uncle Dickey, the entire Williams family, all of my in-laws, Dad, my Partlow family, Albright-Bethune United Methodist Church, Nate, Keisha, Drs. Bowen, Dr. Wilson and family, and Philadelphia AMP to name a few.
Chapter 1

Introduction

Krystaufeux D. Williams
NRL SCEP Student, Code 6134, Chemistry Division, Naval Research Laboratory, Washington, DC 20375

Corrosion costs the US industry sector around $276 billion per year in shutdowns, sudden failures, and lack of production, to name a few [1]. This cost accounts for about 3.1% of the GNP [1]. Advances in technology and the study of this field have led to tremendous savings of this spending, but there remains work to be done. One particular type of damage that involves corrosion is referred to as stress corrosion cracking (SCC). SCC is a local phenomenon that can lead to catastrophic failure as a result of the combination of three factors. These three factors are an applied stress, a susceptible alloy, and a particular corrosive environment. The interplay between the three is schematically shown as in Figure 1-1.

![Diagram of SCC interplay](image-url)

Figure 1-1: A schematic of the interplay between a corrosive environment, a susceptible alloy, and a tensile stress that combine and leads to SCC [1-2].
There has been a considerable amount of effort put into understanding the mechanisms of stress corrosion cracking (SCC) for particular alloys as each one has its own susceptibility. In this dissertation, the focus is on SCC of AA5083. The alloy’s composition is shown in table 1-1. 5XXX series aluminum alloys experience sensitization due to exposure to moderate temperatures (50°C) for long periods of time to high temperatures (175°C) for shorter periods. Sensitization for this alloy occurs as a result of the formation of a Mg-rich β phase – Al₃Mg₂ that forms on the grain boundaries. Upon exposure to the temperature profiles discussed above, the β phase forms as a result of the diffusion of Mg to the grain boundaries where the intermetallic Al₃Mg₂ is formed. The phase appears on the Al-Mg phase diagram shown in Figure 1-2. The β phase dissolves preferentially because it has a more negative corrosion potential than the bulk aluminum matrix.

![Al-Mg phase diagram](image)

Figure 1-2: Al-Mg phase diagram highlighting the region where the β phase is prevalent from Ref. [2].
Themes in this Dissertation

**Coupling Current Definition**

Early in the 20th century, U.R. Evans established the differential aeration hypothesis (DAH) that serves as a guide for all localized corrosion processes including pitting, crevice corrosion, and SCC [3]. Based on the theory of differential aeration set forth by UR Evans, Macdonald and coworkers have posited that a coupling current (CC), which is a current that flows from within a localized corrosion event (e.g., crevice, crack, pit, etc...) to the external surface as a result of the coupling between the internal and external environments. For an alloy or metal that is undergoing stress corrosion cracking, the CC will emanate from a crack-tip (applying to a small crack width= 3.81 cm) [3-11]. This CC was said to flow from the crack tip to the external surfaces of the material, where the cathodic depolarizer is more available. CC flowing from a stress corrosion crack can be described schematically as shown in Figure 1-3.

**Table 1-1**: Composition of sheet AA5083 material in wt%.

<table>
<thead>
<tr>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
<th>Other (Each)</th>
<th>Other (Total)</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.09</td>
<td>0.20</td>
<td>0.04</td>
<td>0.65</td>
<td>4.5</td>
<td>0.09</td>
<td>0.02</td>
<td>0.02</td>
<td>0.05</td>
<td>0.15</td>
<td>Remaining</td>
</tr>
</tbody>
</table>

Themes in this Dissertation

**Coupling Current Definition**

Early in the 20th century, U.R. Evans established the differential aeration hypothesis (DAH) that serves as a guide for all localized corrosion processes including pitting, crevice corrosion, and SCC [3]. Based on the theory of differential aeration set forth by UR Evans, Macdonald and coworkers have posited that a coupling current (CC), which is a current that flows from within a localized corrosion event (e.g., crevice, crack, pit, etc...) to the external surface as a result of the coupling between the internal and external environments. For an alloy or metal that is undergoing stress corrosion cracking, the CC will emanate from a crack-tip (applying to a small crack width= 3.81 cm) [3-11]. This CC was said to flow from the crack tip to the external surfaces of the material, where the cathodic depolarizer is more available. CC flowing from a stress corrosion crack can be described schematically as shown in Figure 1-3.
For the purposes of prediction via the coupled environment fracture model (CEFM), that also resulted from the research performed by Macdonald and coworkers (discussed in Chapter 5 of this dissertation), an initial mathematical expression for the conservation of charge is described as

\[
i_{\text{crack}} A_{\text{crack-mouth}} + \int_{S} i_{c}^{N} ds = 0, \tag{1.1}
\]

where \(i_{c}^{N}\) is the net cathodic current density resulting from the charge transfer on the external surface \([3-11]\). This current decays to zero asymptotically as the distance coordinate \((ds)\) increases going away from the crack mouth. This behavior is shown schematically in Figure 1-4.
In the past years, some researchers have attempted to describe the mechanisms of SCC as a result of a slip dissolution/film rupture process [13-14]. In their description, crack advance was said to result from increasing strain which lead to oxide film rupture (slip dissolution/film rupture mechanism) [13-14]. Furthermore, no electrochemical reactions were posited to occur, only those that involve chemical oxidation; and these oxidation reactions occur within the confines if the crack (i.e., the transition region between the crack mouth and the crack tip). The purpose of this study was to take the ideas about the CC from the experimental research performed in the past by Macdonald and colleagues and to try resolve them spatially using the scanning vibrating electrode technique (SVET). Hence, it was demonstrated for the first time, that crack advance during (SCC) was indeed electrochemical; meaning that positive ions flowed from the crack tip to the external surfaces of the alloy where there were high concentrations of the cathodic depolarizers.

Figure 1-4: The expected behavior of the CC as a function of position across the external surface away from the crack mouth (on the horizontal axis), or into the crack (vertical axis). The conservation of charge is expected to hold in this SCC scenario (from Ref. [12]).
Due to the presence of positive ions on the external surface, as correctly posited by Macdonald and coworkers, the CC was resolved spatially and analyzed as a function of time and load in order to obtain more insight into mechanisms of SCC for AA5083 [3-11]. While some of the literature reports use of the SVP for mapping potentials near the crack tip none of the literature surveyed attempts to resolve the anodic and cathodic regions or recognizes the role of the external environment on the coupling current, which has a substantial impact on the crack growth rate (CGR) [15-17]. Additionally, the scanning vibrating probe (SVP) maps, which come from the machine that applies the SVET, may be a good way of tracking the crack tip.

**Determinism vs. Empiricism**

Determinism and empiricism are two typical philosophies that exist for modeling. Empiricism is an approach to modeling that is based on experience [18]. An experimenter gathers all of the possible information they could and use that information to predict what would happen in the future. The challenge for creating a model is to take all of the independent variables, such as pH, temperature and solution concentrations, to determine the present and future state of the dependent variables, that may include crack growth rate (CGR), localized potential, etc… If many dependent variables exist, which is usually the case when determining the corrosion evolutionary path (CEP), an enormous database would be needed [18].

Alternatively, determinism is the approach used for the CEFM development. Hence the CEFM is based on an accepted mechanism that connects the dependent variables to the independent ones; and the predictions of which are constrained by the natural laws [18]. Common examples of these include conservation of mass and energy, and Faraday’s Law of mass-charge equivalency. A sufficient number of relationships would be required to account for all of the system’s unknown variables [18]. Deterministic models are typically better suited for
handling systems with a large number of variables because they rely on the governing natural laws (e.g., charge conservation) to compute rather than experimental data that can be too cumbersome to collect. The perfect model, however, does not exist because of the interpretation of phenomena with the limited senses and intellect of the experimenter and equipment [18].

Spatial Resolution vs. Time Resolution

The research in this dissertation attempts to utilize one of the foundational constraints of the CEFM, the conservation of charge via the CC, to monitor the SCC process, *in-situ*, with spatial resolution. Former work validates the CEFM charge conservation approach by resolving the CC in time. Manahan, Macdonald, and Peterson’s research shows that the CC is measureable when external cathodes are mounted within a few tens to hundreds of microns (ideally) from an insulated, pre-cracked fracture mechanics specimen [6]. The work also shows CC behavior that was highly dependent on the loading of the specimen (more specifically, the fracture toughness of the material) [6]. Furthermore, the CC appears to contain components of noise that reveal the nature of the cracking process. These components are shown in Figures 1-5 and 1-6. The behavior of the current with time was in good agreement with the predictions of the CEFM.
Figure 1-5: Findings from the time-based CC study of 304 stainless steel (SS) showing how the positive current flowing to the external surface through the solution (as acquired by a zero resistance ammeter – ZRA) is connected to the stress intensity (from Ref. [6]).

Figure 1-6: High acquisition rate of the CC during a load hold on 304 SS is likely connected to the microfracture events within the crack tip region (from Ref. [6]).
There are also predictions based on the spatial variation of the CC. The flow of current to the external surface as a function of stress intensity and position is explored via the potential maps shown in Chapter 4. Foundational studies found in the literature on localized corrosion of other alloys agree with the Chapter 4 findings that the local crevice or crack is driven to anodic potentials as time increases [8, 19-28]. Based on the experimental findings presented, further insight into the SCC process is determined, such as whether there exists a cathodic region on the external surface and how that region behaves over time for different levels of sensitization.

Chapter Outline

This dissertation divulges the usefulness in mapping the coupling current as a tool for monitoring crack growth and SCC in AA5083. In Chapter 2, the SVP is described in terms of its history and its basic components. Also, a feasibility study is discussed on AA2024, an alloy with a well-known localized corrosion mechanism that involves dissolution of the Al matrix around the Cu particles (added for strengthening). This localized Al dissolution leads to the formation of pits whose coupling currents can be observed using the SVP with a few adjustments to the alloy. Chapter 3 is a review of some of the typical experimental approaches taken for fracture mechanics and SCC analysis. There are some unique aspects of the setup that aims to determine threshold stress intensity (K_{th}) or the critical fracture toughness for SCC (K_{ISCC}) since featured experimentation (in Chapter 4) is not yet setup to do so. Chapter 5 features our unique setup for in-situ CC measurement and SCC crack growth monitoring. Chapter 6 is a discussion of the conclusions and future works.
References


Chapter 2

How the SVP Works (Instrumentation)

The scanning vibrating probe (SVP) has been heavily utilized in the research discussed in this dissertation to provide positional maps of the potential in the region of the crack-tip. Hence, it was necessary to understand the components of the SVP and how they work together to provide the maps. Several feasibility studies were performed to understand the limits of the SVP in terms of the type and the size of the localized corrosion events. One example of the calibration corrosion events was the dissolution of the AA2024 aluminum matrix around copper-rich intermetallic compound (IMC) particles. The particles were a constituent of the alloy for strengthening, however, when the alloy was introduced to an electrolyte such as saltwater, the aluminum dissolved around the copper-rich IMCs.

Background/Theory

The early version of the scanning vibrating electrode technique (SVET) instrument was first introduced for local corrosion studies on metal alloys by H. Isaacs in the late 70’s [1]. Its predecessor, the scanning reference electrode technique (SRET), was built around the idea that an inert reference probe with a small capillary tip would scan around a surface (immersed in an electrolyte) in order to directly obtain the local potentials over that sample [1-4].

Since the probe was composed of an inert material (usually Pt), there was no electrochemical influence on the surface that was being scanned. Theoretically, the local potential gradients are predicted by Laplace’s equation and Ohm’s law as follows $\nabla^2 E = 0$ and $i = -KE$, respectively, where $E$ is the potential, $i$ is the current density and $K$ was the conductivity. The sign convention was taken to be opposite of the normal convention so that anodic regions were plotted as peaks in potential and cathodic regions were plotted as minima (Figure 2-1). Figure 2-1 shows how the local potential and the current
changed between the anode (the source of positive ions) and the cathode (the drain of the positive ions) as a function of position. Figure 2-2 shows a schematic of what type of potential readings to expect from the probe scanning a particular type of sample using the SRET. Hence localized corrosion events were able to be studied in-situ as a result of the SRET.

Figure 2-1: Illustrations of the current lines that flow from an anode to cathode (top) and the corresponding potential contours (bottom) [1].
While the SRET had some success in monitoring localized corrosion events such as pitting on metals, galvanic activity on welds and dissimilar metals, and the differential aeration cells created in crevices and cracks, Isaacs and Vyas found that there were some drawbacks to the technique [1]. While decreasing the size of the tip and the proximity of the probe to the corroding surface resulted in increased resolution, because it was a direct current (DC) application, noise could also be enhanced. Ultimately, these factors had to be adjusted to deliver the best tradeoff for resolution. The early work by Isaacs and

Figure 2-2: a.) A physical diagram of a scanning probe in solution and the corresponding potentials measured by the probe in three areas (A, B, and C) of a corroding sample separated by insulating blocks. Region B is the anode in this case and the anodic current/potential flows equally to regions A and C. b.) The polarization potential of B has been raised to equal the open circuit potential of A. Hence, no current flows to region A but it does flow to region C. The potential profile in region A has a baseline potential while the other areas are the same [1].
Vyas set preliminary experimental courses that are still followed upon today, including local corrosion monitoring of pitting, weld-zones galvanic couples, and SCC of metal alloys [4-13].

The SVET is a device equipped with a vibrating probe that is attached electronically to a lock-in amplifier, which assisted with the probe’s potential detection capability (through AC detection techniques and noise rejection with the lock-in amplifier) [8, 14]. It was developed as an alternative method for the measurements of localized currents rather than the traditional time-based measurements that were made with potentiostats/galvanostats [4-13, 15, 16]. Other scanning modes such as the scanning Kelvin probe (SKP) technique also grew from this useful approach in the analysis of localized corrosion [17-22]. In localized corrosion events, such as those that occur in pits and crevices, the time-based detection by a potentiostat does not give spatial insight to what is happening locally.

More recently, others have utilized the SVP in the investigation of SCC in other alloys [4-13, 15, 16, 23]. Zhang and coworkers, and Teng et al. combined their SVET work with local electrochemical impedance spectroscopy to analyze the solution and passive film characteristics as they related to SCC [24-26]. For example, Zhang and Cheng found that the passive film was less stable at the crack-tip (where the SVP probe is scanning the surface available on the side of the sample) than it was in a region on the external surface ahead of the crack-tip (on the sample’s side relatively far from the crack vicinity) using LEIS, and SVET combined with standard Mott-Schottky and polarization techniques [24, 25]. Their particular alloy of interest was the X70 pipeline steel in basic solutions. It was also determined that local dissolution was enhanced when higher stress intensities were applied to a pre-cracked sample [24]. These findings were in agreement with the findings in previous studies by Macdonald (based on differential aeration) and coworkers, Crane, and with the work published in this dissertation [27-36]. After continued work on these pipeline steels, the crack tip region was discovered to have higher corrosion currents, more negative corrosion and pitting potentials than the material further away from the crack-tip [25].
A recent report by Deshpande [11] demonstrated the importance of the SVET to show the corrosion rate of alloy in a galvanic couple while the two materials were in physical contact. Previously, studies on galvanic couples, like those performed by Battocchi et al., were conducted with the materials in question separated from each other as discussed in the schematics above [10]. With this experimental setup, Deshpande was able to calculate the current density using the equation $j = -\sigma \frac{\Delta E}{A}$, where $j$ is the current density in A/m$^2$, $\sigma$ is the conductivity of the solution and $A$ is the vibration amplitude [11]. Furthermore, the corrosion rate was also calculated for their galvanic couple with the equation $C_R = \frac{M}{z F \rho} j$, where $M$ is the atomic mass, $F$ is Faraday’s constant, $\rho$ is the density and $z$ is the number of equivalents. These experiments and equations explain the important capability of the SVET and were considered throughout all of the SVET studies in this dissertation.

**Schematics of the SVP**

The scanning vibrating probe, which is the device that uses the SVET, consisted of a few basic components. These components included an SVP control unit, a computer for processing data and controlling the experiments, an optional potentiostat and the controllable motors for motion of the probe. The schematic is shown in Figure 2-3. Also, the basic setup of the cell and specimen is shown.
The lock-in amplifier (LIA) is one of the major electronics components of the SVP circuitry. A very basic LIA is shown schematically in Figure 2-4. The devices shown below work together with the SVP to take an AC input, which is taken from the probe that is vibrating/oscillating above the sample to eliminate the noise associated with it. By utilizing the LIA with the SVP, an experimenter is able to distinguish very small potential changes (optimally down to nV’s for some LIAs) locally [37, 38]. A follow-up schematic of how the LIA interacts with the SVP equipment is shown in Figure 2-5.

Figure 2-3: A schematic diagram of the SVP along with the associated components. Optional connections to a potentiostat can be made.
Figure 2-4: The electronic components of a typical LIA where a small AC signal is detected after removing the noise component from the signal [37, 38].

Figure 2-5: The external components of the SVP in a flow diagram from Ref. [8].
In terms of the interaction between the experimenter with the SVP and its computer, settings are chosen to optimize the LIA and electrometer signals for the particular experiment. This is shown below in Figure 2-6. Using the SVP software package, the user sets the gain, sensitivity, time constant, amplitude and phase of the probe’s electrometer and parameters are adjusted until the probe output is steady.

Calibration can be performed with a point-in-space sample which consists of a wire embedded in epoxy or any other insulated medium. Beyond the typical calibration, a further calibration should be done for the sample and the exact type of local corrosion being monitored. An example of this further calibration is the experiment discussed in the following section where the AA2024 sample is embedded with an insulated Cu wire to understand how currents pass from bulk alloy to an IMC particle.
Feasibility Studies for Localized Corrosion Events

As briefly discussed earlier, several experiments were devised to assess the use of the SVP for the type of SCC experienced with AA5083 because the presence of the β phase. The scanning probe technologies in general proved useful in understanding the influence of IMCs on their parent alloy [6, 9]. Due to the Mg content of this phase that existed at the grain boundaries, the potential in these zones were pushed down (towards more negative potentials with respect to the bulk α phase) resulting in anodic dissolution (see Table 2-1). The first experiment devised was a SVP scan of a bare AA2024 surface that has micron-sized Cu-rich IMCs, as mentioned earlier. According to the relative corrosion potentials of the two alloys, it was expected that the Al would preferentially corrode when in physically or electrically connected the Cu. This was supported by the appearance of pits surrounding the IMC after the sample was exposed to saltwater for a period of time. Further evidence can be determined by viewing the galvanic series chart shown in table 2-1.
The galvanic series chart indicates that Cu has a less negative range of potentials than the aluminum alloys’ range (for the different alloys available). Hence, it was expected that Al would be the anode and Cu would be the cathode. Also highlighted are the major constituents of AA5083 (i.e., Mg and Al).
Initial studies on the bare AA2024 specimens revealed peaks of enhanced activity that appeared as a close collection of mountain peaks on a plain of noisy background signal (not shown). Inspection of this bare specimen with a light microscope showed that the IMCs in the AA2024 alloy specimen appeared in linear arrays. However, it was difficult to conclude from the mentioned SVP scans that there was a separation of anodic (from the bulk Al-rich phase) and cathodic processes. Consequently, an experiment was created where the influence of the Cu was exaggerated by introducing a mm-sized Cu wire (insulated and uninsulated) into the matrix. The samples are shown in the figures below. By using an insulated sample, the positive ions/anodic current and the negative ions/cathodic current can be accounted for via an external potentiostat in zero resistance ammeter (ZRA) mode. The ZRA is a device consisting of a potentiometer and galvanometer circuitry that is used to measure small currents flowing between two points at different potentials. The ZRA measures these small currents by first balancing the IR potential drop via a potentiometer; consequently, the true current flowing between the points of interest can be measured by the galvanometer. A Cu wire in physical contact with the specimen is more representative of a localized corrosion scenario on the AA2024 surface. The samples are schematically shown below in Figure 2-7.

An iteration of this sample with a wire in physical contact arrangement resulted in the sample configuration shown in Figure 2-8. There were three micron-sized Cu rods mechanically inserted into the AA2024 specimen which was polished gradually to a maximum of 1200-grit paper. Final polishes were obtained with alumina slurry of about 0.5 microns.
A final setup was made to complement the insulated Cu wire experiment. The surface of the specimen (with the embedded insulated wire) was exposed in an electrochemical cell designed for testing flat samples. This experiment, which included the typical potentiostat connections, was set up as illustrated in Figure 2-9.
Results

Results for the two insulated wire experiments (one obtained with the SVP and the other done separately with a potentiostat) are as shown in Figure 2-10. One of the advantages of utilizing the SVP with this particular study to monitor galvanic corrosion was an opportunity to monitor both positive ion flow (inferred from potential maps) with the SVP (from the dissolution of Al) and negative electron flow (from the electrons passing through the metal to the cathode using the ZRA). Furthermore, the SVP potential maps allow for spatially resolved activity (Figure 2-10, right) whereas the measurements made by the potentiostat in the ZRA mode (Figure 2-10, left) were time-resolved and did not necessarily suggest the source of that current.
An SVP scan from the AA2024 sample (with the multiple implanted Cu wires) is shown in Figure 2-11. The darker green regions of the map (appearing in the SVP map in Figure 2-11 as three larger circular regions) were more cathodic and the lighter green regions (the remaining area outside of the three larger circles) were more anodic. The SVP maps revealed that the cathodic regions on the sample corresponded with the copper surface on the SVP scan. The anodic regions from the SVP map corresponded to the AA2024 matrix. This experiment gave us the confidence that coupling currents from galvanic couples could be detected with the SVP.

Figure 2-10: A comparison of the typical electrochemical cell measurement (left) for galvanic currents with a SVP potential map (right) of the current passing through the solution.

**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)
Observing a series of maps over a period of a few days revealed that the AA2024 matrix was dissolving around the implanted Cu wires, dissolving around its own IMCs and passivating (See Figure 2-12). This result was confirmed by observing the optical micrograph shown at the bottom of Figure 2-12.

Figure 2-11: An SVP potential map taken on the surface of the multiple Cu wire sample. Darker colors are more cathodic and the potentials obtained just above the Cu wires were the darkest obtained for the map.
Figure 2-12: SVP maps obtained in increasing points in time from the earliest map (top left) as the sample corrodes using the same potential scale as Figure 2-11. The colored bar axis represents the local potential gradient in the solution. Most scans were acquired in approximately 30 minute intervals. The post corrosion metallograph image is shown on the bottom.
Conclusions

In this chapter, a description of the components of the SVP was given. Also, the history of the device was explained with how the device evolved over the last several decades. Although these pivotal studies laid the basis for the work described later in this dissertation as well as briefly exploring the SCC experiments themselves, the current work attempted to approach the problem of SCC in AA5083 considering the description of the coupling current set forth by Macdonald and other colleagues [16, 23, 27-33, 35, 36]. Hence, if Macdonald’s description is correct, it was expected that anodic current flowing from crack-tips to the external surface could possibly be mapped by the SVP (if the cathodic region was within the region being scanned). Initial studies on AA2024, which has a well-known corrosion mechanism, gave confidence for the measuring positive current flow through the solution. Therefore, due to the theoretical and experimental foundations laid by Isaacs and coauthors for the SVET, as well as the approach to prediction of SCC based on the presence coupling current, a course for mapping and fully interpreting SCC of AA5083 was set [1, 27, 29].
References

13. H N Mcmurray, J.R.S., *The Use Of Svet For Investigating Changes In The Corrosion Mechanism Induced By Forming Galvanised Steel Samples The Use Of Svet For Investigating Changes In The Corrosion Mechanism Induced By Forming Galvanised Steel Samples*. 2000.


Chapter 3
Fracture Mechanics and SEM of LT Bend bars

There have been several approaches to studying fracture mechanics of metal alloys and identifying their critical fracture toughness values [1-10]. Scientists and materials engineers have to consider not just their understanding of the strength of the material, but various combinations of environments that will interact with the material in such a way to produce catastrophic failure where it would not normally occur based on knowledge of the materials strength alone. In this chapter, a more traditional experimental approach is taken as opposed to the unique approach discussed in Chapter 4 of the dissertation where fracture mechanics and localized electrochemistry is performed together.

Fracture mechanics experiments were performed on AA5083 bend-bar specimens in 0.06M saltwater (used to match key experiments performed in the next chapter) to obtain the critical fracture toughness values using the load and crack mouth opening displacement. The primary concern was to acquire the critical fracture toughness values for stress corrosion cracking ($K_{ISCC}$). With these values, which are independent of the loading configuration, the relationship between the increase in coupling current and crack propagation was evaluated. The results are presented in the next chapter. In this chapter, the results of the typical fracture mechanics experiments, where crack length is measured with a clip gauge that measures the crack mouth opening with knowledge of the compliance of the specimen, with the same specimens as discussed in the next chapter, are explored. The SEM images from both experimental setups helped to determine the fracture surface characteristics and to give insight to the fracture mechanisms (see also Chapter 4).
Theory

As mentioned in the previous section, the goal of testing the specified AA5083 fracture mechanics specimens was to determine the critical stress intensity factor for the stress corrosion cracking scenario, $K_{\text{ISCC}}$, where the subscript “I” indicates mode I loading and is related to only the normal/perpendicular stresses on a solid. First, a few aspects of the theory behind finding $K_I$ and $K_{IC}$, which are the stress intensity for mode one loading and the critical stress intensity for failure (fracture toughness), respectively, are discussed. Above the $K_{IC}$, a flaw embedded in a member will stably propagate with a velocity that is a fraction of the velocity of sound through the material causing failure [7-8, 11]. This parameter can be derived by first considering the stress field at the crack-tip of an infinite plate with a through-thickness crack [7-8]. Taking an element $dx\,dy$ at a distance $r$ from the crack-tip and an angle $\theta$ from the plane of the crack, it can be shown that

$$\sigma_x = \sigma \sqrt{\frac{a}{2r}} \cos \frac{\theta}{2} \left[ 1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right]$$  \hspace{1cm} 3.1

$$\sigma_y = \sigma \sqrt{\frac{a}{2r}} \cos \frac{\theta}{2} \left[ 1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right]$$  \hspace{1cm} 3.2

$$\tau_{xy} = \sigma \sqrt{\frac{a}{2r}} \sin \frac{\theta}{2} \cos \frac{\theta}{2} \cos \frac{3\theta}{2}$$  \hspace{1cm} 3.3

$$\sigma_z = 0 \text{ (plain stress)}$$  \hspace{1cm} 3.4

$$\sigma_z = \nu (\sigma_x + \sigma_y) \text{ (plain strain)}$$  \hspace{1cm} 3.5

in the more general form,

$$\sigma_{ij} = \frac{K_I}{\sqrt{2\pi r}} f_{ij}(\theta)$$  \hspace{1cm} 3.6

where $K_I = \sigma \sqrt{\pi a}$, where $a$ is defined as the crack length [8]. The $K_I$ term is referred to as the stress intensity factor [8].
$K_{\text{ISCC}}$ or $K_{\text{IHC}}$ is defined as the threshold for the onset of unstable crack growth in a corrosive environment, or for a susceptible material. In an experimental setup, $K_{\text{ISCC}}$ can be determined using a variety of samples in adapted fracture mechanics setups (e.g., in corrosive environments such as saltwater) [11-12]. For the purposes of this study, we focus on the bend bar specimen of AA5083 in the pure bending arrangement where the sample is immersed in 0.06M saltwater (details in the following section). In the analysis published by Tada et al., as well as in work published by a few other authors, it was demonstrated how to obtain the compliance relationship using the crack mouth opening for this setup as well as how to obtain the $K$ values from the experimental load and the material specifications [10, 13-14]. The compliance relationship is also useful for determining the onset of subcritical crack growth (SCG).

Specimen size requirements are established by ASTM E399-12 that ensures that plane strain conditions exist at the crack tip when performing fracture mechanics experiments which are important for keeping the crack front straight [4]. The standard describes that both the thickness $W$ and the crack length $a$ of the specimen should be $> 2.5 \left( K_{\text{IC}} / \sigma_y \right)^2$. For the specimens used in this study, $\sigma_y = 228$ MPa and an estimate of $K_{\text{IC}}$ for the T-L specimen orientation used in these experiments is between 19.2 and 21.7 MPa√m (estimated as the $K_{\text{IC}}$ and $K_{\text{JIC}}$ values for AA5083, S-L orientation, single edge notch tension specimens in Crane’s dissertation as calculated from experimental results using the direct current potential difference voltage and displacement signals and computed using corrected 3-dimensional finite element analysis) [15]. Hence, the minimum thickness requirement by the upper end of the range, $K_{\text{JIC}}$, $B=22.6$ mm, is not met (the starting crack length, $a=19.05$ mm for the specimens used in this study); however, if the full range of allowed crack lengths/thicknesses, $17.7 \geq B \geq 22.6$ mm, based on the range of fracture toughness values (from $K_{\text{ISCC}}$ to up to $K_{\text{IC}}$) is considered, the thickness dimension appears acceptable.
Hence, these experiments were considered valid $K_{IC}$ tests for plain strain fracture toughness testing.

The general approach used to determine $K_{ISCC}$ involved acquiring the load and crack mouth opening displacement (CMOD) signals as a function of time. Next, a plot was made of the load as a function of CMOD which resulted in step-like load and extension trends (shown in detail in the “Testing setup” section, Figure 3-3) with 10% unloading and reloading interruptions (also discussed in the “Testing Setup” section). The slopes of the load vs. CMOD curve, similar to computing the derivative ($\Delta P/\Delta \delta$, where $P$ is the load and $\delta$ is the CMOD), are then evaluated against the CMOD to determine when the CMOD continuously decreases. A report published by Gross and Srawly demonstrates how to obtain $K$ from $P$ just before the onset of subcritical crack growth, where $\Delta P/\Delta \delta$ just begins to decrease [10]. Hence, the fracture toughness can be computed from the load, the initial crack length and a few other properties of the alloy.

**Bend-bar Configuration**

AA5083 material was obtained from Alcoa, Inc. in Pittsburgh, PA., as 1.905 cm (0.75 in.) thick rolled plates. Bend bars were cut from the plate that were the same thickness of the plate, 25.4 cm (10 in.) long and 3.81 cm (1.5 in.) thick. Specimens were in the T-L orientation with respect to the wrought plate. Figure 3.1 shows the different rectangular specimen orientations that can be extracted from the extruded material and their respective letter coding as they relate to the applied load for tension (the first letter in the coding) and the direction of crack growth (the second letter in the coding). The sample was lightly etched with Keller’s reagent (a mixture of hydrochloric, hydrofluoric, and nitric acid) to show grain structure as a function of surface orientation, which depends on the 3 indicated directions. The orientations are important because of the microscopic anisotropy that has an influence on crack propagation as it relates to the
fracture-toughness. Fracture in the particular orientation mentioned above (T-L orientation) would represent cracking through thickness and along the length of a plate of Al alloy that could be utilized in building a major structure such as the fuselage of an airplane, or a major member in the body of an automobile. Table 3-1 shows how $K_{IC}$, the critical fracture toughness, changes as a function of the specimen orientation. Because of the grain structure and the associated orientation anisotropy, it is evident that most aluminum and other alloys with grain structure similar to that shown in Figure 3-1, are most susceptible to fracture when the applied load for tension is in the short-transverse (S-L and S-T) orientations. The reason for higher sensitivity to cracking along the short transvers orientations is a crack propagating in these orientations encounters more grain boundary area than any of the other orientations.

Figure 3-1: Schematic of a plate of alloy material showing the terminology of their corresponding reference direction and the shorthand for specimens that could be extracted from the plate. Images represent the typical grain structure found on each of the surfaces.
Testing Setup

Stress corrosion cracking testing in an electrolyte can be challenging because of the specimen’s configuration. For example, the compact specimen designed to be loaded in tension (referred to as the C(T) specimen) under plain strain conditions typically utilizes loading pins to apply the force/bending moment to the specimen. Because the specimen is compact, there is not much room left for a solution chamber if the experimenter wants to avoid galvanic coupling of the sample and the load bearing components. Some groups have employed the strategy of coating the load bearing components before closing both the sample and the loading grips in the solution [17-19]. Another way to overcome the problem of galvanic coupling is to have the testing components (i.e., the load frame, loading pins or barrels) be of the same material as the test specimen. In most cases, the test machine components need a higher toughness value than that of the specimen. For the purposes of the fracture mechanics experiment, this galvanic coupling issue is addressed by using the typical vertical loading frame with a bend bar sample where the

Table 3-1: A selection of the room-temperature plain strain and yield strength values of some aluminum alloys, showing the anisotropy for the different orientations from Ref. [16].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Temper</th>
<th>Yield Strength at 0.2% offset</th>
<th>Plain strain fracture toughness, $K_{IC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>MPa</td>
<td>Ksi</td>
</tr>
<tr>
<td>2014</td>
<td>T651</td>
<td>440</td>
<td>64</td>
</tr>
<tr>
<td>2024</td>
<td>T351</td>
<td>325</td>
<td>47</td>
</tr>
<tr>
<td>2024</td>
<td>T851</td>
<td>455</td>
<td>66</td>
</tr>
<tr>
<td>7075</td>
<td>T651</td>
<td>505</td>
<td>73</td>
</tr>
<tr>
<td>7075</td>
<td>T7651</td>
<td>470</td>
<td>68</td>
</tr>
<tr>
<td>7075</td>
<td>T7351</td>
<td>435</td>
<td>63</td>
</tr>
<tr>
<td>7050</td>
<td>T7651X</td>
<td>495</td>
<td>72</td>
</tr>
<tr>
<td>7050</td>
<td>T7351X</td>
<td>459</td>
<td>65</td>
</tr>
</tbody>
</table>
load bearing components are far from the growing crack (See Figure 3-2). In addition, a unique and possibly more sensitive approach (than the typical identification of load drops) to determining the start of subcritical cracking is discussed later in this section.

During the loading of the bend-bar specimen, the load signal as a function of time is recorded by using a standard load cell. The crack mouth opening signal vs. time is also recorded using a standard clip gauge. The loading procedure was performed according to the incremental step loading technique that included unloading/reloading at the end of each step to determine a compliance relationship at each step; an adjustment to the procedure discussed in reference [20]. Periodic unloading and reloading was extremely important to determine the occurrence of incremental crack growth based on periodic and strictly elastic slopes. Otherwise, there is no valid point of reference for the change in crack mouth opening measured from the load vs. displacement curve [21]. This compliance relationship was used to determine the $K_{\text{ISCC}}$ values for specimens in different testing conditions. The procedure can be outlined as followed:
1. Acquire load and clip gauge signals vs. time using the standard load cell and clip gauge. The signals from these devices should be recorded with a data acquisition system and computer (See Figure 3-3).

2. Utilize a programmable motor to employ the incremental step loading scheme with periodic unload/reload (UR) sequences (Figures 3-3 and 3-4).

3. Ensure that load and clip gauge signals follow each other for initial $K < K_{ISCC}$. If this requirement is met, acquire signals until final failure of the sample, remove solution from container while the sample is still under load and apply DI water to rinse the corrosion product from the crack, remove sample from test setup, rinse specimen, and form a plot of the load signal as a function of the gauge signal that include these periodic unload/reload sequences (Figure 3-3).

4. Measure each of the UR slopes from step 3 (starting with the final UR slope value and working backwards) and determine when the slopes start to decrease from a constant value when plotted versus the extension value (Figure 3-5).

5. The UR slope obtained just before the rapid decrease can be used to identify the critical load, and hence, the critical fracture toughness after which subcritical crack growth (SCG) is initiated, may be computed.

Figure 3-3: The load (blue) and extension signal (red) for an as-received/unsensitized specimen immersed in 0.06M saltwater. Load steps were 25 lbs. per step.
Figure 3-4: The load and extension plot versus time for a sensitized specimen immersed in 0.06M saltwater.
Sections of the specimens were cut from the main bend-bar specimen using a cut-off wheel to examine the fracture surfaces post-mortem. Actual final and initial crack lengths can be determined by using a calibrated digital microscope provided by Anmo Electronics Corp, Hsinchu, Taiwan (headquarters). A three point average was taken across a relatively straight change in texture that indicated the end of the pre-crack zone on the sample. There was good agreement between the expected pre-crack length (in terms of the $a/W$ ratio) calculated in-situ via compliance relationships for the three-point bend loading arrangement and the pre-crack length determined using SEM micrographs of the fracture surface following the experiment. Similar
measurements were made with the other sections on the fracture surface including the transition from electrochemically dominated to mechanically dominated crack growth, and finally the fatigue benchmarked section was placed in the sample to indicate the end of all crack growth during the test. Benchmarking by fatigue would either continue until the sample was split in two or in some cases the sample would experience a mechanical overload before breaking. Hence, all the data reported in this chapter pertain to samples tested in the more traditional pure bending fracture mechanics setup.

**Results**

Based on the procedure discussed in the previous section, the $K_{ISCC}$ values were determined for as-received and sensitized specimens both in air and in 0.06 M saltwater. Although loading conditions varied with the fracture mechanics device used in this chapter and the device discussed being used in the next chapter, which was especially designed for simultaneous loading and localized electrochemical testing, the technique discussed for this chapter was useful for determining the $K_{ISCC}$ with the aid of CMOD measurements and hence, to know, according to the hypothesis, at what critical values of $K$ to expect spikes in the coupling current for the experiments discussed in the next chapter. These same measurements were much more difficult, if not impossible (for reasons similar to those mentioned in the previous sections of this chapter) in the customized setup because of the sample being totally immersed in the 0.06 M solution. The slope changes of the sensitized sample in solution are shown in the Figure 3-6 below.
In the loading and extension signals of the sensitized specimen in 0.06 M saltwater, both load and extension increase in sequence until $K_{\text{ISCC}}$ is reached. Following this critical step, occurring at a load of 3207 N (721 lbs.) and at an extension of about 0.279 mm (approx. 0.11 inches), the load started to decrease while extension increased. The physical reason for the changes in the mentioned signals, as shown in Figure 3-7, is that as the load increased beyond $K_{\text{ISCC}}$ and was subsequently held stationary on the load step, the crack grew by some amount $\Delta a$, and smaller load was applied to the sample as a result. As the crack grew, a corresponding amount of crack mouth opening increase occurs. Before passing the $K_{\text{ISCC}}$ any random increases in load and extension are attributed to physical changes in the specimen unrelated to crack growth such as the device taking up slack as the experiment began.

Figure 3-6: Stress corrosion test performed on a fully sensitized sample (DOS $\approx 45\text{mg/cm}^2$). The loading steps occurring just prior to and following $K_{\text{ISCC}}$ are shown above.
Following the acquisition of the data for load and extension, the load was plotted as a function of the extension as mentioned in the previous section. Figure 3-8 shows the results for the sensitized sample that led to the time based signals in Figure 3-7. Extending from the bottom of the load as a function of extension curve were the unload/reload slopes from which the $K_{ISCC}$ was calculated. It is apparent from the figure that the slopes, $\Delta P/\Delta E$, are decreasing going from left to right because less load is required for the same extension before the crack started growing. Prior to reaching the $K_{ISCC}$, the UR slopes are proportional to the elastic modulus of the material. Hence, the importance of using the UR slope approach, again, was to observe purely elastic changes to the sample as the crack was growing. Any other changes above the elastic limit may be attributed to plastic deformation where a more complicated calculation must be made [21-22].
When the value of each slope was plotted vs. the average extension value the resulting plot was as shown in Figure 3-8. Initially, the UR slope values obtained with lower extension values ($\Delta^2P/\Delta E^2$) are relatively constant. When the slope values as a function of CMOD/extension continuously decreased, as shown in the data in Figure 3-8 at a CMOD value of 0.3048 mm, crack growth has been initiated. Due to the amount of random relative uncertainty in the $\Delta^2P/\Delta E^2$
trend (about 2.5% in Figure 3-8), finding the exact onset of crack growth presented some challenge. This uncertainty, which was likely due to a slight shifting or vibration of the sample while in test, could have created the appearance of a decreasing trend (around a CMOD). However, utilizing the visual evidence, such as that provided in Figure 3-6 where a simultaneous load drop with a change in inflection during a load hold occurs with an increasing extensometer signal, we determined a value of $K_{ISC}$ from the CMOD and the corresponding load. When an as-received sample was tested in the same manner as the previous sensitized sample, the results were as shown in Figure 3-9. When moving from left to right on the plot, initially the slope appears to increase. However, this is attributed to random fluctuation of the mechanical components, especially when the experiment begins and any slack of the mechanical components is eliminated. The onset of SCG occurs between 0.3175 and 0.3937 mm.

Figure 3-8: UR slopes as a function of CMOD for sample S002. Continuous decreasing in the slopes as a function of CMOD ($\Delta^2 P/\Delta E^2$) indicates crack growth.
The final slope vs. CMOD plot was obtained for a sensitized specimen tested in air. The results are shown in Figure 3-10. As with the others, initially, there is some noise in the trend. Between about 0.254 and 0.432 mm of extension, the signal levels out. Beyond 0.432 inches, subcritical cracking began to occur and the slopes decrease while the sample was breaking.

Figure 3-9: UR slope behavior for sample U004 tested in 0.06M saltwater showing that little or no SCG is expected in this sample until final fracture occurs (the last two data points).
In order to gain a better perspective of the UR slopes, they were all plotted on the same scale with each sample’s UR slopes normalized with respect to the initial slope obtained (on the far left). The normalization accounted for samples having different starting pre-crack lengths, leading to slightly different initial UR slopes. It should be expected that for the same material, the initial UR slopes should be about the same (i.e., proportional to the elastic modulus of the alloy).

Figure 3-10: S008 UR slope values vs. CMOD for a sensitized specimen tested in air.

No evidence of SCG
The results in Figure 3-11 represent a new means of obtaining the $K_{ISCC}$ without having to use the strenuous mathematical compliance relationships for determining the actual crack length from the crack mouth opening displacement (CMOD) measurement from the clip gage. This is the first time the discussed slope analysis was employed to determine the $K_{ISCC}$.

Figure 3-11: UR slopes behavior as a function of extension for several samples tested in different loading conditions. $\Delta^2 P/\Delta E^2$ for the sensitized specimens in SW decreased much sooner (seen in the continual decrease of the fitted lines) than those tested in air. The trends for sensitized specimens each have two slopes for before (relatively flat) and after the onset of SCG (decreasing).
Fractography

In the light micrographs shown below, Figures 3-12 through 3-14, general loading zones can be identified on the crack surface of the specimens. Moving from left to right on the image in Figure 3-12 zone A, the zone of fatigue crack growth was encountered. This zone was characterized by a flat and shiny surface. The fatigue section could only be verified at a higher magnification via the SEM (See next section). The next section crack growth encountered was a flat region of crack growth that had a tunneling aspect that grew faster in the middle than it did on the sides. The final section was less flat and intergranular with crevices growing in a direction perpendicular to the crack growth direction (zone C).

Figure 3-12: S002 Fracture surface identifying fatigue pre-crack (zone A), flat, low K SCC growth (zone B) and intergranular SCC growth with perpendicular grains opening up (zone C).
In an as-received specimen tested in the same environment, the fracture surface was exposed and examined (Figure 3-13). The fatigue region was the same as in the sensitized sample as well as most of the stress corrosion region. However, there were no perpendicular crevices as there was with the sensitized sample. Hence, the rest of the fracture process was attributed to transgranular ductile rupture.

![Figure 3-13: As-received specimen U006 fracture surface showing.](image)

The final micrograph shows a sensitized specimen tested in air. The flat pre-crack region is shown in zone A of Figure 3-14. Zone B is characterized by a mixture of intergranular perpendicular crevices as well as transgranular fracture on the main surface. Zone C was the overload region where the sample was broken after removing it from the test setup.
SEM micrographs of the samples were collected to identify the nature of the different fracture zones discussed in the previous section. All of the samples tested were pre-cracked by fatigue loading a notched sample in 3-point bending arrangement at a frequency of 20 Hz, according to ASTM E399-12e2 [4]. Evidence of the fatigue striations (oriented horizontally) are shown in Figure 3-15 a. Considering the crack grows from the top of each image to the bottom, a transition to another ductile, dimply, overload region was observed as shown in Figure 3-15 b. This particular second type of fracture character was observed because the as-received sample was tested in air. The result of testing a sensitized sample in a similar environment (air) was a

Figure 3-14: S008 fracture surface tested in air.

SEM

SEM micrographs of the samples were collected to identify the nature of the different fracture zones discussed in the previous section. All of the samples tested were pre-cracked by fatigue loading a notched sample in 3-point bending arrangement at a frequency of 20 Hz, according to ASTM E399-12e2 [4]. Evidence of the fatigue striations (oriented horizontally) are shown in Figure 3-15 a. Considering the crack grows from the top of each image to the bottom, a transition to another ductile, dimply, overload region was observed as shown in Figure 3-15 b. This particular second type of fracture character was observed because the as-received sample was tested in air. The result of testing a sensitized sample in a similar environment (air) was a
flat fatigued region just like in image b, but with crevices perpendicular to the crack growth direction (into the page/material). They appeared because of the high susceptibility of the ST plane grain boundaries to intergranular corrosion (IGC) and possible additional modes of loading during crack growth (Figure 3-15 c) [15, 23-25]. There was also a transition from fatigue to ductile dimples as there was in Figure 3-15b. Instead of transitioning immediately to ductile dimples, the transitions for a sensitized sample in 0.06 M saltwater were a flat, typical pre-crack zone (not shown in the image), then a flat, low K SCC or hydrogen induced cracking (HIC) zone with closed crevices, that left a curved crack front (Figure 3-15 d). Finally, there is a sharp transition, as indicated by the black arrow in 3-15 d to a flat region, which led to a slightly less flat, intergranular stress corrosion crack growth with opened crevices. That IGSCC growth was shown magnified in Figure 3-15e, where to the left of the image, more detail within the crevice was shown. The last Figure 3-15f showed the less obvious transition from fatigue to low K crack growth where the closed crevices mostly appeared after the transition indicated by the black arrows.
Figure 3-15 a-f: (a) U005-top two; fatigue pre-crack with horizontal striations for an unsensitized specimen tested in air and (b) pre-crack to mechanical overload transition for an as-received specimen tested in air. (c) S008 – Pre-crack to transgranular, mechanical crack growth transition in sensitized material tested in air. (d) S005 – Transition zone from flat, low K SCC to IG, higher K SCC zone for a sample tested in 0.06M saltwater. (e) S006 Stress corrosion region on a sensitized specimen in saltwater where the arrow indicates a crevice where corrosion product peels away from the alloy matrix. (f) S005 - transition from pre-crack to low K SCC.
Conclusions

A standard fracture mechanics test setup was created with the same environmental conditions that were intended for the unique setup discussed in the next chapter. Hence, critical information about our sample, such as the $K_{\text{ISCC}}$ for the sensitized and as-received, notched AA5083 bend bar, was gathered. Furthermore, the $K_{\text{ISCC}}$ was needed for the as-received and sensitized bars in environmental conditions of saltwater and the $K_{\text{IC}}$ was needed for testing in air. These values were also determined from these experiments and are reported in the next chapter of this dissertation.

Upon examination of the fracture surfaces, the fatigue pre-crack generated an ideally straight crack front. The texture of the fracture surface in that region includes fatigue striations that could only be viewed with the SEM when the sample was tested in air. Corrosion products prevented any observation of this region and made further interpretation of the crack growth process difficult. The fracture surface of samples exposed to 0.06 M saltwater, surprisingly, appeared to have another flat zone that was attributed to SCC crack growth at low K values. It was determined that during the low K stage the crack grew faster in the middle than it did on the sides, leaving a nearly parabolic/concave crack front during this time. One possible reason for accelerated growth in the center may be a result of the specimen not meeting the necessary requirements for plain-strain conditions at the crack tip as discussed in the theory section of this chapter.

Ultimately, this set of fracture mechanics experiments helped to establish behavior of the bend-bars to help interpret the localized electrochemical maps (while the sample is immersed in solution) that were coupled with fracture mechanics in a different set of experiments. These experiments are discussed in the next chapter where more about the crack growth mechanism was examined via localized in-situ electrochemical mapping.
References

Chapter 4

Use of SVP for In-Situ Monitoring IGSCC Crack Growth

Seminal research performed by Macdonald, et al. demonstrated the ability to make a time-based measurement of the coupling current (CC) by mounting external cathodes within a few microns of an electrically insulated fracture mechanics test specimen [1-6]. Once the load was applied to the specimen exceeding the critical fracture toughness for mode I loading ($K_{fSCC}$), they observed that current flowed from the freshly exposed alloy in the crack-tip to the cathode. In the absence of a surface coating, Macdonald and coworkers [1-6] posited that CC should flow from the crack tip to the nearest external surface to the growing crack. On the other hand, other researchers posited that if this CC exists, some or all of it can be extinguished within the confines of the crack mouth [7-8]. CC extinguishing in the confines of the crevice, according to the referenced authors, is based on the dynamics in the interior of the crevice geometry over long periods of time leading to micro-crevice formation in the internal environment of the crevice, or even a reverse crevice corrosion phenomenon where the external surfaces, in the case of non-passive metals such as Cu, corrode and the crevice is passive [7-8]. Because of the existence of CC in alloys subject to SCC as reflected in these seminal studies, a testing apparatus was created to determine if this CC may be measured with spatial resolution.

The work in this dissertation expands on the recent research efforts on AA5083 through in-situ positional potential maps of the CC measured by the SVP device discussed in Chapter 2. Once it was determined whether the CC can be resolved spatially, then differences in the CC between the sensitized and the as-received specimens were sought. Further, there was also a wealth of information for the fracture mechanics community as a result of the experiments.
performed including the ability to monitor stress corrosion, corrosion fatigue, and other types of crack growth, \textit{in-situ}.

\textbf{Obtaining Spatially-Resolved Potential Information}

Due to the presence of the CC and having the ability to resolve it spatially using the SVP, as shown later in this chapter, it was discovered that localization of the anodic and cathodic regions appeared on the scanning plane the surface of the specimen as the sample approached $K_{\text{ISCC}}$. One hypothesis was that local CC flowing from an anodic crack-tip to some cathodic space on the surface near the notch (see the following figures in this section) would be greater in heavily sensitized specimens (Degree of Sensitization-DOS $\geq 30\text{mg/cm}^2$) than the CC shown by localized potential scans of the as-received samples (DOS $\leq 4\text{mg/cm}^2$), possibly indicating a more dominant anodic dissolution (AD) mechanism than hydrogen induced cracking (HIC) for stress corrosion crack growth. Although both mechanisms were posited occur simultaneously, in S.K.-Lee’s recent summary of reports on crack growth mechanisms, he explained the consensus of those authors researching SCC of Al-Mg alloys that the HIC mechanism strongly influences growth through the alloy matrix (between discrete $\beta$ particles) in lightly sensitized alloys (low DOS values) [9-10]. As the crack propagates through the $\beta$ phase itself, the AD mechanism was more prevalent since the $\beta$ phase has a more negative potential than the Al matrix [9-10]. Based on these observations from previous studies, intergranular stress corrosion crack (IGSCC) growth through a fully sensitized specimen with complete coverage of $\beta$ phase on the grain boundaries should result in more continual AD mechanism. A more dominant HIC mechanism for crack advance may not experience the same increase in the CC [9-10]. Nevertheless, in either mechanism of crack advance, failure still occurs sooner for sensitized materials due to the presence of the continuous $\beta$ phase particles along the grain boundaries of the alloy (shown in the
later sections). Furthermore, it was expected that at the onset of subcritical crack growth, a sharp increase in the coupling current/potential should be observed because of the introduction of newly exposed alloy to the solution. It was also likely that the combination of these mechanisms depends on the degree of sensitization as put forth by Holtz et al., Gao and Crane [10-12]. One of the main ideas supported by Lee and Macdonald that is different from others is that hydrogen diffuses ahead of the crack-tip in the alloy matrix to enhance the IGSCC crack propagation for lightly sensitized AA5083 specimens [9, 13]. Since the fatigue pre-crack length of fracture mechanics specimens was known (bend bars were pre-cracked in a separate 3-point bend arrangement) from the compliance relationships in ASTM E399, as well seen in the light and scanning electron micrographs of post-mortem fracture surfaces, that length was used in the present study to determine the $K_{ISCC}$ [14]. Furthermore, evidence of crack growth and insight into the crack growth mechanisms can be gathered from the potential maps and the images from the digital light microscope obtained from Anmo Electronics Corp and scanning electron microscope.

**Experimental Setup**

As-received and sensitized AA5083 bend bars (0.75” thick x 10” long x 1.5” wide) were prepared for testing to determine the fracture toughness for stress corrosion cracking in a four point bending (pure bend) arrangement using a loading scheme as suggested by either ASTM E399-90 or ASTM F1624-12, as well as to simultaneously monitor the CC utilizing the SVP [14-15]. Sensitized bend bars were heat-treated by holding them at a temperature of 175 °C for 14 days and the effect of the heat treatment can be measured and analyzed using the techniques from ASTM G-67 [16]. The corresponding DOS value for the mentioned heat treatment was 40-50 mg/cm². The experimental setup also involves a four-point bending fracture mechanics testing apparatus to apply a load through a pure bending moment. The apparatus has been uncommonly
arranged to lie on its side (horizontally) such that the direction of crack growth is perpendicular to the lab bench surface area normal. Figure 4-1 shows the arrangement of the sample and the critical apparatus components. More traditional fracture machines are arranged vertically so that the load is applied in a direction parallel to the surface of the lab bench surface.

**4 Point Bend: Machine # 1**

![Diagram of 4 Point Bend Machine](image)

**Top View**
- AA5083 Specimen (laying on its side)
- Applied Load
- Machined Notch and crack-tip
- Applied Load

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

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

Figure 4-1: Schematic of the experimental setup demonstrating the approach to concurrent CC monitoring and fracture mechanics testing.

Bend bars were arranged on the side with the largest surface area parallel to the lab bench in order to examine the surface with the SVP. A 0.06 M solution was placed in a plastic container such that only the sawed chevron notch, the crack and the immediate middle section of the bar (approx. 2”) was exposed.

Initial experiments were performed to understand the signal orientations as they related to the actual surface that was scanned by the SVP probe. An as-received specimen of AA5083 bend-bar was prepared for simultaneous loading and localized electrochemical testing. A thin wire (on the order of mm) of Mg was inserted in the scanning area to establish the nature of the
signals (anodic/cathodic) measured by the SVP (Figure 4-2). Although, for the sake of real-world applications the typical seawater equivalent of saltwater, 0.6 M, is ideal for the experiments, the samples were immersed in 0.06M salt water because the SVP requires lower conductivities (about 6mM) for its best resolution. Since Mg is the more active species, measurements taken above the Mg wire will be anodic as compared to the potentials obtained above the bulk alloy (Figure 4-2). Therefore it was concluded, that any additional, similarly oriented potentials (depending on the settings of the SVP as they can be set as negative or positive) from the same sample were also anodic. For the remaining experiments performed, anodic signals were set (utilizing the software to set the SVP’s electrometer) to be negative (darker colors in the SVP potential maps show).

Figure 4-2: Section of the as-received/unsensitized bend bar in test using the orientation of the obtained SVP scans presented in this chapter. The increasing y direction is parallel to the growing crack increasing in the up direction on this page.
Following dissolution of the Mg wire (Figure 4-3), anodic signals appeared in the region of the notch and pre-crack of the unsensitized specimen as illustrated in Figure 4-5. The more electronegative signals are located towards the opening of the notch as opposed to the crack-tip, which had not started growing yet. The load was continuously increasing at a rate of about 50 lbs./hr. (see Figure 4-4). A few scans were performed before the load ramping began and there was already increasing activity within the notch of the specimen due to the crevice corrosion (see Figures 4-5 and 4-6). When the load reached about 500 lbs., a cathodic region (brighter colors on the local potential gradient scale) was observed in the upper right corner of the scan (Figure 4-7). The appearance of this region indicates the flow of current from the notch to the external surface of the specimen.

Figure 4-3: Initial SVP map obtained with Mg wire implanted in the unsensitized sample to establish signal orientation with active elements on the sample.
A straight line is superimposed on the load vs. time graph (Figure 4-4) matching the slope of the linear elastic region of the curve, to give an estimate of the onset of subcritical crack growth. As the $K_{\text{ISCC}}$ is reached, the stronger anodic currents than the previous SVP at lower load values were observed in the crack-tip region in the SVP maps. The reason for the progression of the CC has to do with the release of ions from the freshly exposed metal at the crack-tip as well as the differential aeration hypothesis [1-6, 9-10, 13, 17]. In other words, the crevice that was created in the notch and growing crack leads to a drop in pH because of the lack of oxygen and hydrogen and the hydrolysis of $\text{Al}^{3+}$, and as the crack grows from the notch, a more anodic region within the confines of the crack. For sensitized specimens, there should also be a contribution to the overall crack-tip potential from the dissolution of the $\beta$ phase at the grain boundaries [10, 18]. Other reasons for increases in the CC appear to be related to temporary arresting and resumed growth of the crack. The evidence that periodic decay and increase again of the crack front occurs is supported by the digital light micrographs that reveal puckers (places where the crack front was curved rather than straight) on some the samples’ surfaces, possibly due to plastic zone formation, before the crack started growing again.
Figure 4-4: Loading profile for an unsensitized AA5083 specimen (in blue) in 0.06 M saltwater with a superimposed straight line (red) to give a visual estimate of departure from the linear-elastic regime, or rather the onset of subcritical cracking. CC potential maps were collected before and after the onset of crack growth.
Figure 4-5: Accompanying potential map for the unloaded unsensitized sample in test in Figure 4-4, U003. The map was obtained following the dissolution of the Mg insert.

Figure 4-6: A follow-up scan of the unsensitized specimen, U003 with no load. The activity in the notch increased since the first scan was acquired.
Figure 4-7: Load reached a value of approximately 500 lbs. The activity in the notch has decreased, but as the load increases and the crack starts to grow, activity is observed in the region of the crack.

Figure 4-8: At a load of approximately 1750 lbs, the sample has opened up to the position of the pre-crack and the crack-tip has become anodic. b.) The load has increased beyond $K_{ISCC}$ and the crack has arrested and developed a large plastic zone. The sample was warped as a result and the notch was curved rather than straight. The colored local potential gradient scale is the same as in Figure 4-7.
Image Analysis of Potential Maps

Regions of coupling current originate from an anodic crack-tip (distinguishable from the other scanned regions by a darker brown section extending from the top of darker slit in the center of Figures 4-8 a and b where the notch was located) and are adjacent to a highly cathodic region. However, any additional consistently dark zones (i.e., anodic regions), such as the notch or other sensitized patches of grains on the surface of the sample (see next section) were also assumed to produce coupling current (Figures 4-4 and 4-5). Other topological features on the sample were expected not to have affected the scan since the probe does not make contact with the specimen and since the top surface was sanded down with 600-grit sandpaper and rinsed before testing. The results for the initial sensitized specimens studied are shown in Figures 4-9 to 4-11. The sensitized AA5083 specimens were characterized by highly localized and sharp anode and cathode at the meeting at the crack-tip. The CC is discovered to grow to a peak for the opening of the notch and pre-crack and then diminish with time. Afterwards, the CC grew again after the $K_{ISCC}$ value was reached. This growth occurred much sooner (at a lower value of the load) than in the unsensitized counterparts. Furthermore, it was found that even at stationary, low loads, a coupling current potential difference was still observed (discussed later in this section). SEM micrographs of this specimen revealed a relatively small region of crack growth (compared to sensitized samples where the load is continuously increasing) (Figure 4-9).
Figure 4-9: An SVP scan of sensitized specimen S006 at an initial load of about 700 lbs. The precrack has opened up slightly as a result of the load leading to the presence of CC. No crack growth expected at this stage. Note that the CC will exist for intergranular attack (IGA) even though no crack growth is occurring.

Figure 4-10: SVP scan taken afterwards where the pre-crack that is 2794 um deep is almost fully opened.
On the other hand, the SVP scans of unsensitized specimens revealed a less localized cathodic potential region near the crack tip (Figures 4-5 to 4-8). The crack-tips also appear to be less sharp when the crack experiences the highest value of stress intensity than the sensitized counterparts. The reason for the blunted crack-tip could have been related the development of a plastic zone that arrested the crack. Ultimately, some of these crack-tip shapes based on the SVP scans appeared to be connected to the different crack growth mechanisms between sensitized and as-received specimens.

Potentials in the crack-tip were measured by using a data marker from the OriginPro software by the OriginLab, Corporation and averaging three to six points (depending on the resolution of the scan) within the crack-tip area. A baseline signal was established by acquiring three (in the maps with wider scanning areas where not many potentials in the crack-tip were obtained) or six (in the maps with a higher number of points acquired in the crack-tip region)

Figure 4-11: Decay in the CC is shown at a load of 910 lbs. because there is no crack growth occurring with time when the load under the KISCC value.
potentials in the regions away from the crack-tip and adjacent notch area that did not appear to be extremely affected by the CC. Using the load value during the scan acquisition the dependence of coupling current/potential on K and crack length was determined. The Figures below, 4-18 and 4-19, were the results of those studies for each alloy tested in the unique fracture mechanics and SVP device.

In a second set of experiments, maps were acquired from a sample that was held at a constant load level of 200 lbs. The acquired scan is shown in the figures below (Figures 4-12 and 4-13). Even at a $K_1$ value less than $K_{ISCC}$, a coupling current was measured. However, the magnitude of the potential difference between the anodic and cathodic regions was not as significant as the potential difference in the same zone for samples loaded near $K_{ISCC}$. Furthermore, the sample was exposed to solution for a long period of time (until the onset of crack growth discussed later in this chapter) before a coupling current was observed.
Figure 4-12: SVP scan of sensitized specimen S004 being held at a constant load.
Light and electron microscopy was used to help analyze the fracture surface. The SCC regions, after the crack had progressed through the entire thickness of the specimen, usually displayed a few types of zones when viewed with the aforementioned digital light microscope. Following the triangular shape of the sawed chevron notch, a flat, shiny region of fatigue is observed (Figure 4-14, region A).
Next, a darker, more textured, and somewhat shaded region was observed that was a result of corrosion products as the crack propagated in a stress corrosion zone (Figure 4-14, region B). The crack was grown at least an additional 2 mm after about a week. Following the stress corrosion zone is a region of benchmarked fatigue placed purposely to indicate the end of the period of experimentation (Figure 4-14, region C). Lastly, is the region of mechanical overload characterized by the broken alloy at rapidly changing height, which was a result of physically breaking the sample open to examine the fracture surface (Figure 4-14, region D). The changing regions could only be verified and identified with the JEOL variable pressure, field emission Scanning Electron Microscope (SEM).

Figure 4-14: Digital micrograph of the sensitized specimen held at a constant load. The precrack (region A) was measured to be 2.59 mm with approximately another 2 mm of SCC crack growth (region B). Hence, following the SCC crack growth, the shiny fatigue benchmark zone (zone C) was purposely put in to mark the end of SCC. Zone D was the zone of ductile rupture from loading the sample in moist air until the sample was broken.
Crack Growth Monitoring Using SVP

SVP maps were collected for a sensitized fracture mechanics specimen (exposed to a temperature of 175°C for 14 days as before) in order to monitor the crack growth more closely. Further experimentation involved incrementally increasing the load on a sensitized bend bar while using the SVP to monitor the potential around the crack tip (Figures 4-15 and 4-16). The general finding was that the loading scheme led to incremental increases in the resistance to crack growth (i.e., plastic zone formation). Additional support to the increasing crack growth resistance was found on the fracture surface (apparent blunting and sharpness) as shown in Figure 4-16. Also, the result of incremental loading was a rounded-looking, anodic crack front shape in the region scanned above the crack tip coupled with an adjacent cathodic region. Sharper anodic region appeared at higher K values.

This particular set of experiments followed the crack-tip more closely by a setting a reduced scan area of the SVP probe and an increased resolution within the scan window (via the number of points taken per scan line and by decreasing the overall scan window). Hence, the cathodic zones of the map, in terms of their location, position were cut off from the anodic crack-tip location.
Figure 4-15: Initial SVP Potential map of the notch and crack-tip region of a sensitized specimen (S007) before the onset of subcritical crack growth. Enhanced activity in the notch region is revealed but little or nothing in the crack-tip/pre-crack region.
Once the crack started to grow beyond the pre-crack, the mentioned smaller scans of higher resolution were acquired. Consistency in the relative positional measurements after positions and resolutions changed were obtained by lab notes (i.e., the size of the scan and location of the probe at the origin and resolution of the raster region was recorded before changing location and resolution to follow the crack tip) as well as by keeping a known, slowly active or passive region related to a physical feature on the sample (to serve as a fiducial mark), in the view of the new scan. These newer scans, shown in Figures 4-17 through 4-18, followed the crack.

Figure 4-16: SVP Potential above the S007 specimen at a higher load. Most of the activity in the crack-tip area is due to the opening of the pre-crack.
as it grew. Hence, a tradeoff was sought between resolution, total scanning time and accurate

crack-growth tracking.

Figure 4-17: An SVP scan capturing the end of the notch on the lower middle portion of the scan
along with the growing crack tip. By comparison with the positions of the notch and the crack-tip
in the previous image, it can be determined that the crack has grown by approximately 900 µm
beyond the pre-crack.
Figure 4-18: a-d) A few of the SVP scans collected for sample S007. e.) Light micrographs showing the scanning areas in red for the larger scans from Figures 4-14 through 4-15 and f.) for the smaller, higher resolution scans 4-16 through 4-17 d.
Eventually, the scans were combined on a grand scale from the earlier shown large map (Figure 4-15) to track the position of the crack-tip as a function of time. The SVP potential map collage shown in Figure 4-19 was created to aid in determining relative positions of the crack tip.
Figure 4-19: A collage of most of the SVP scans involving sample S007 showing the crack progression with time. Relative positions were compiled from combined light micrographs and by recording positional changes taken by the SVP for the smaller high-resolution scans.
Acquiring multiple maps per load step have allowed for the computation of the crack length as a function of time during the load holds and the crack growth rate as a function of $K$ (shown in later figures). The fracture surface of this particular sample (S007- shown in Figure 4-20) did not have as much of an intergranular dissolution as other sensitized specimens using a continuous rising loading profile (e.g., Figure 3-13 in the previous chapter).

The fracture surface of the sample from the last few figures was somewhat different than the prior sensitized samples. One of the main differences in this experimental procedure for this particular sample was the prolonged load holds. As a result, the fracture surface, shown in Figure 4-20, did not reveal an abrupt intergranular section (like section C in Figure 3-13 from the previous chapter). After the electrochemical tunneling (section B in Figure 3-13 from the previous chapter) portion of the surface, a flat transgranular surface was revealed. To get a better understanding of the fracture processes the coupling current was measured as a function of load and fracture toughness in addition to the positional potential measurements.

Figure 4-20: Post-mortem fracture surface of sensitized specimen S007. It was somewhat different than the other samples featured in Ch. 4 in that there was not a strong intergranular section with transverse crevices.
It was discovered that CC behavior for an unsensitized AA5083 specimen in 0.06M saltwater revealed sudden CC increases of about 10 mV ± 3 mV that corresponded to or occurred just before the onset of subcritical crack growth.

Figure 4-21: Graphs showing the trend of the highest CCs (inferred from the SVP potential) observed in the crack-tip of an unsensitized specimen due to SCC. Three of the strongest potentials from each scans were measured and averaged to represent the crack-tip potential.
Sensitized samples however, did not show sudden peaks in potential. Figures in 4-22 display the continuously increasing (in the negative/anodic direction) behavior of the coupling current. There are several localized peaks within the increasing trend. The first peak may have been related to the onset of subcritical cracking ($K \approx 17 \text{ MPa} \sqrt{\text{m}}$). Another sensitized sample experiencing an incrementally increasing load for extended periods of times when compared to those tested in the previous chapter was tested. The results of the potential vs. $K$ plots for this sample (S007) are shown in Figure 4-23. While the trend was similar to that of Figure 4-22 for the potentials obtained soon after the load was applied, a stronger, more sudden local maximum in potential was identified in the other overarching data points when considering only those potentials obtained during the load plateau (unfilled data points) rather than soon after the applied load (filled data points). The reason for the multiple maxima in the sensitized CC trends was likely related to the crack arresting and starting to grow again rather than continuous crack growth of the sample. Differences in the peak on potential vs. $K$ had to do with the $K_{\text{ISCC}}$ for AA5083 in saltwater being substantially lower than the $K_{\text{IC}}$ in air (See Figure 4-24 where the potential units were normalized and the more anodic potentials were positive for the sake of comparison). The acceleration and deceleration of the crack growth previously mentioned suggests a slip dissolution re-passivation (SDR) or hydrogen-induced cracking (HIC) mechanism of crack growth. SDR has been accepted as the description of the crack growth process for this sensitized alloy undergoing SCC. Where the theory of Scully, and of Gangloff and of Crane differs from the approach of Macdonald and of Lee is in the dimension of slip in lightly sensitized AA5083 and the role of $H$ in that process [10, 19-21]. While Macdonald shows that the slip dimension is on the order of microns through his modeling approach based on the experimental work of Jones, et al., Scully, Gangloff and Crane assert that the slip dimension is on the order of 100s of nanometers, which is still too large as the slip dimension should be on the order of the Burger’s vector (a few nanometers) [10, 19-22].
Figure 4-22: The crack-tip potentials as a function of load (top plot) and as a function of $K$ (bottom plot) for a sensitized specimen. A series of peaks occur rather than one strong peak near the $K_{ISCC}$. 

$K_{ISCC} \approx 16 \text{ MPa}\sqrt{\text{m}}$
Figure 4-23: Crack-tip potentials for a sensitized specimen experiencing incrementally increasing loads (load holds had varying time periods longer than those from the other experimental setup discussed in chapter 4.

\[ K_{\text{SCC}} \approx 16 \text{ MPa}\sqrt{\text{m}} \]
Judging by the positional monitoring of the coupling current and the generally stable current transients (inferred from the SVP potentials), crack length was measured after growing increments of microns. Though the ultimate positional resolution of the SVP is limited to tens of microns, over longer durations of time and during no applied load increase, average nanometer/s crack growth rate can be measured. The finding in this set of experiments for fully sensitized specimens shows that most crack growth occurs during the load step increases until $K \approx 22\text{ Mpa}^{\sqrt{m}}$ (see Figure 4-25). Near this value of $K$, the strongest local maximum (in terms of the highest peak of anodic activity) is observed. The growth rate also reaches a maximum at this point and levels off. This observation is shown graphically in Figure 4-26.
Figure 4-25: Loading profile with time for the sensitized sample S007 from Figures 4-20 and 4-21 with the crack extension as a function of time superimposed.

\[ K_{th} \approx 16 \text{ MPa} \sqrt{\text{m}} \]

\[ K \approx 22 \text{ MPa} \sqrt{\text{m}} \]
Conclusion

Considering the scans of the active crack-tips and their periodically polar nature, it is possible to attract or repel and to promote or arrest, crack growth electrochemically in the external environment. Furthermore, if one can stop crack growth by adjusting the voltage of the specimen, then during stress corrosion cracking, it should be possible to predict the crack growth rate because of the deterministic nature of SCC [9, 13]. Hence, one of the goals of the CEFM, not explored in this work, is to predict and verify with experiments (Chapter 6) electrochemical crack growth as a function of environmental parameters.

Figure 4-26: Crack growth rate (CGR during load holds only for a fully sensitized specimen S007 compared to the CGR predicted for lightly sensitized AA5083.
Additional conclusions that can be drawn from the experiments discussed in this chapter are as follows:

1. Stress corrosion crack-tips are anodic in nature, which is confirmed by the Mg wire experiment previously discussed (see initial SVP maps of as-received specimens from Figure 4-5 to 4-8).

2. Sensitized crack growth is usually characterized by a sharp crack tip where the SVP reveals a sharp anodic tip with an accompanying sharp cathodic region during subcritical crack growth (after the alloy in test has surpassed the $K_{ISCC}$ value). The exception may be in the case of an incrementally increasing load where a plastic zone can develop ahead of the crack tip and slightly hinder continuous crack growth as was the case in the as-received specimen (see the blunted crack tip in the SVP maps of Figure 4-8 compared to those in Figures 4-9 through 4-12). The crack propagates along the anodic grain boundaries in the sensitized specimen more easily than it would through the grains of the as-received specimen.

3. Crack growth in an unsensitized AA5083 specimen is characterized by more blunted appearing anodes in the SVP potential maps of crack tips with similar cathodic regions ahead of them in the increasing direction of crack growth. This cathode became localized just ahead of the crack tip (the brightest regions in the SVP maps ahead of the crack tip) during the onset of subcritical crack growth, which occurred at a much higher load than that of the sensitized counterpart.

4. There was correspondence between the initial onset of crack growth with a peak in anodic potential measurements by the SVP as demonstrated in the plot in Figure 4-21. The unsensitized cases actually appeared to have more sharp increases in anodic current density current, as interpreted from the local potential gradients measured by the SVP, which was unexpected. However, the sharp increases may have been due to the larger
resistances to crack propagation because of plastic zone formation. The initial opening of the pre-crack and any further crack growth required a more substantial amount of mechanical energy, which in turn led to a sudden burst of anodic. With the sensitized specimens, the crack propagated more easily at lower loads and the electrochemical contribution to crack growth and surrounding β dissolution resulted in a less sudden spike in the anodic current density (vs. load) and several spikes being clustered together.

5. During subcritical cracking, the crack tip in the center is further ahead than on the edges for low $K_I$ values. This finding was not expected because although the center crack tip is the most occluded from oxygen and hydrogen from the atmosphere, it is the furthest away from the external cathodes. According to the CEFM, the crack should grow more slowly in the center and faster closer to the edges based on the proximity of the edges to the external cathodes (see Figure 4-20). The deviation of the crack shape from the expected results from the CEFM, or the more typically straightened to just slightly bowed crack fronts, is either due to the non-existence of plain strain conditions that results in straighter cracks (See explanation in the Theory section of Chapter 3), or the evolution of internal hydrogen damage produced by the dissolution of β.

6. The advancing of crack growth between $K_{th}$ and 22 MPa√m appears to be due to a slip-dissolution-repassivation (SDR)/anodic dissolution (AD) and hydrogen induced cracking (HIC) mechanism of α and β phase evidenced by a flat, transgranular fracture surface, tunneling (the region of higher growth) near the middle of the specimen, where the pH is likely higher and a lower coupling current was observed during the load plateau. Anodic current density/CC spikes after $K \approx 22$ MPa√m are likely due to additional β phase dissolution (as shown in Figures 4-22 and the dark data points in Figure 4-23) and/or the resuming of crack growth.
Thus far, the local potential gradient change between anodic and strongest cathodic regions in an as-received specimen near the $K_{\text{ISCC}}$ value is estimated to be approximately double that of sensitized specimens at their $K_{\text{ISCC}}$. This finding of stronger CCs in as received specimens may suggest a stronger AD and HIC mechanisms at work in the sensitized specimens. Hence, it was concluded that the enhanced CC in the sensitized specimen was likely due to $\beta$ dissolution in the material.
References


Chapter 5

Calibration of the CEFM

In the previous chapter, the experimental approach to measuring the coupling current was discussed. The concept of the coupling current served as the basis for the coupled environment fracture model (CEFM) developed by Macdonald and Urquidi-Macdonald to predict stress corrosion cracking (SCC) for different alloys [1]. The model has gone through several iterations as it was applied to different environments and alloys [1-9]. Recently, The CEFM was adjusted for prediction of crack growth in AA5083 by S-K Lee and colleagues [10, 11]. Lee, et al., considered the case of lightly sensitized aluminum alloys where both the mechanisms of anodic dissolution (AD) and hydrogen-induced cracking (HIC) play roles [10, 11]. Because each material has its unique mechanism for SCC, the model needed calibration to take this into account.

In this chapter, the history of the CEFM is explored and some results from the recent findings are presented for the lightly sensitized case. The model will also need to accommodate other intermediate sensitization values. To complete the accommodation, this chapter also shows the electrochemical parameters obtained from the polarization scans and observations from the physical changes in the crack-tip and in the bulk of the material (e.g., DOS, electrochemical potential). These are parameters that serve as inputs to the CEFM model. Based on the data presented, a foundation can be laid for expanding the model.
Background for CEFM

The CEFM was first created to address the need for prevention and prediction of SCC given certain electrochemical parameters. Macdonald and Urquidi-Macdonald followed by other collaborators and students developed the model that accounted for the variety of conditions that could occur on stainless steel components in a boiling water reactor (BWR) [2-6, 8]. There were other models developed at the time, however, the CEFM was the first to take into account the influence of the external environment on stress corrosion crack growth [2-6, 8, 10, 11]. The foundations of the CEFM are the conservation of charge, Faraday’s Law of the equivalence between charge and mass, and the differential aeration hypothesis (DAH). The latter, DAH, is the basis for analyzing localized corrosion events [12]. Hence, by knowing the positive current flowing from the crack tip equals the negative current that results from the reduction processes on the specimen surface, or by accounting for the coupling current (i.e., the crack propagation rate/mass loss in the crack tip for the electrochemical portion of the crack growth) and combining that with the amount of expected crack growth due to mechanical contributions, the crack growth rate can be deterministically calculated. The application of the DAH to the CEFM is illustrated in Figure 5-1.
Figure 5-1: Schematic of the coupling current established for SCC of any alloy. The external environment described by the chemical equations help determine the crack growth rate from Ref. [11].
Findings on Effect of DOS on Crack Growth Rate

It was not until more recent periods that the effect of DOS on crack growth rate (CGR) has been assessed. These findings first analyzed the occurrence of intergranular corrosion (IGC) in AA5083. For example, Bumiller sought to understand the motivations for IGC propagation as it related to a discontinuous path of β coverage on the grain boundary [13, 14]. Her work explored the electrochemical analysis and motivations for the IGC penetration, which tended to grow faster parallel to the depth dimension rather than the width. Electrochemical data were reported as a function of DOS level. The relationship between DOS and sensitization aging time was reported for samples aged at 100°C (see Figure 5-2). Some of the polarization scans results for AA5083-H116 in ASTM seawater and 0.1M saltwater (SW) were also reported and are shown in Figures 5-3 and 5-4. Other polarization scan results (not shown in this dissertation) were also reported for AA5083 in various pH levels and for different solutions that simulated the crack environment as well as for the β phase alone.

![Figure 5-2: Aging curve for AA5083-H116 for samples held at 100°C for various periods of time from Bumiller [13].](image-url)
Figure 5.3: Results of cyclic polarization scans reported by Bumiller of AA5083-H116 in saltwater [13].
Lastly, tables that summarized the important parameters obtained from the polarization curves (for AA5083 and a separate table for the polarization scan result for β phase alone) are shown in tables 5-1 and 5-2, where OCP is the open circuit potential, \( E_{\text{bd}} \) is the breakdown or pitting potential, \( E_{\text{rp}} \) is the repassivation potential, \( R_p \) is the polarization resistance, and \( I_{\text{pass}} \) is the passive current density. These parameters are important to the CEFM to predict CGR and other electrochemical parameters for higher DOS levels.

Figure 5-4: Results of cyclic polarization scans reported by Bumiller of AA5083-H116 in 0.1M saltwater [13].
The electrochemical characterization research by Bumiller was complimented by Jain, et al. and Lim, et al. [16, 17]. Jain theorized that the spreading of IGC was based on the continuity of the β particles. The factors governing the spreading were thought to be controlled by metallurgy, electrochemistry and β morphology [16, 17]. Therefore, a portion of their research was dedicated to determining how much β-phase was present on the grain boundaries for particular DOS values. Samples were polished and exposed to a Baker’s etching solution (a mixture of phosphoric, acetic and nitric acid) that dissolved the phase. Results shown in Figure 5-5 divided β coverage into three subsets using above and below 70% coverage as a separating
parameter. Figures 5-6 and 5-7 were the reported damage depths as a function of exposure times for the samples that were set at the breakdown potentials where the samples were most susceptible to IGC.

Figure 5-5: Description of β coverage (high>70% coverage, low<70%, or no coverage) for AA5083 samples with varying DOS levels from Reference [16].

Figure 5-6: (Left) Damage depth for various exposure times with different DOS values for samples exposed to 0.6M saltwater held at the breakdown potential [16]. (Right) Damage depth for different DOS levels shown for various periods of time in the same solution [16].
The body of research discussed extended from the initial foundational findings by Goswami, et al., which showed continuous coverage of $\beta$ on the grain boundaries of AA5083 H131 specimens heat treated at 100°C for investigating of $\beta$ morphology with the TEM studies of sensitized AA5083 [18, 19]. Bernstein, Goswami, and Holtz determined that fracture in sensitized AA5083 was energetically favorable to occur within the $\beta$ phase rather than at the $\alpha/\beta$ interface [20]. Thus when dealing with AA5083 in the CEFM model, the beta coverage on the grain boundaries should increase linearly with the DOS and the annealing exposure time. Also, the electrochemical crack growth rate should reflect the penetration depth of IGC. The final consideration is that upon stress corrosion crack propagation of a fully sensitized specimen, primary crack propagation, and thus the primary dissolution (followed by $\alpha$), would likely occur within a thin layer (on the order of 10’s of nanometers) of $\beta$ [20, 21].

Figure 5-7: Dependence of damage depth on % of $\beta$ coverage on the grain boundaries from Ref. [16]. Grains oriented in the L direction had the most IGC penetration.

![Graph showing dependence of damage depth on % of $\beta$ coverage on the grain boundaries.](image-url)
Structure/Architecture of the CEFM

From a grand perspective the CEFM determines the electrochemical potential (ECP) of the material using mixed potential theory. This calculated ECP is the potential of the sample far away from the growing crack. Equipotential contours are visualized by drawing the perpendicular contours to the current lines shown in Figure 5-1 or by using Figures 2-1 and 2-2 in Chapter 2 of this dissertation. In terms of the programming itself, a schematic flowchart is shown in Figure 5-8 showing the approach to the CEFM modeling, in which several system parameters including the CGR is calculated [1].

The mixed potential calculation involves contributions from the O₂, H₂, H₂O₂ and the dissolution of the alloy. Hence, the ECP calculation takes all of the cathodic and anodic reactions into consideration. A model created by Macdonald, et al., performs this calculation for 304 stainless steels exposed to high temperatures in pressure water reactors [7]. ECP is limited by the conservation of charge such that at the interface of the far-field potential and the localized potential at the crack mouth amounts to zero.
For calculation of the CGR, the crack environment is divided into internal and an external environments and the crack mouth acts as a border between the two. For the external environment, imposing charge conservation, and assuming Laplace’s equation, \( \nabla^2 E = 0 \), describes the potential (E) distribution near the crack (on the outside of the crack mouth), then the solution, which takes on the form

\[
E(x, y) = \sum_{m=1}^{40} \left[ C_m \cos(\lambda_m x_j) e^{\lambda_m y} + E_s^g \right],
\]

where \( \lambda_m \) is a constant, is solved numerically for the coefficient \( C_m \). The coefficients are used to determine the potential. This coefficient can be expressed as

\[
C_m = \frac{[E_s(0,0)] exp[Bx_j/X_T - x_j]}{\cos(\lambda_m x_j)}.
\]

Further details are described in the paper by Macdonald and Urquidi-Macdonald [1].
Iterations of the executed code occur that first guesses the internal environment ECP and then adjusts it until charge neutrality is reached with the crack tip environment. Within the internal environment, a mechanical treatment of the crack-tip, as described by Ford, et al., described contributions to the overall growth rate according to the slip/dissolution/repassivation model [22-24]. When discovered that Ford’s approach to calculating the crack tip strain rate was empirical in nature, a feature of the CEFM was added to give the option for using Congelton’s or Shoji’s (the approach used for the latest CEFM update) approach who used Gao and Hwang’s formula to calculate the crack tip strain rate [25-27]. Converting the CGR to a crack tip current was then determined by Faraday’s Law, which is

\[
\frac{da}{dt} = \frac{M\bar{I}_0}{2\rho_m\bar{Z}FW\delta},
\]

where \(\rho_m\) is the metal density in (g/cm-3), \(F\) is Faraday’s constant (C/equiv-1), \(a\) is the length of the crack (cm), \(\bar{I}_0\) is the mean current from the crack tip, \(M\) is the composition weighted atomic weight and \(\bar{Z}\) is the composition weighted oxidation state of the metal. The complete descriptions were discussed in the recent CEFM development by S-K Lee, or one of the original papers by Macdonald and Urquidi-Macdonald [1, 11].

The mentioned aspects of the CEFM combine as shown in Figures 5-9 and 5-10.
Figure 5-9: Flowchart of the CEFM process for CGR calculation [1].

Figure 5-10: Flowchart for the internal current calculation [1].
CEFM Findings for AA5083 (lightly sensitized)

S.-K. Lee et al. recently updated the CEFM to predict CGRs for AA5083 [10, 11]. These results await continued calibration from experiments performed on the alloy noting the environmental conditions. Though quite a bit of work has been performed on SCC of AA5083 already, none of the published literature on this subject has specifically accounted for, or taken advantage of measuring the coupling current to give further insight into the SCC process. As a result, some of the electrochemical kinetic data had to be taken from the available literature on pure aluminum. Those values are reported in table 5-3.

Table 5-3: Values used in the CEFM for lightly sensitized AA5083-H321 from Ref. [11].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Comment/source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tafel slope for HER</td>
<td>0.117 (V)</td>
<td>[28]</td>
</tr>
<tr>
<td>( i_0 ) for HER</td>
<td>1.5 E - 9 (A/cm(^2))</td>
<td>[28]</td>
</tr>
<tr>
<td>Tafel slope for ORR</td>
<td>0.56 (V)</td>
<td></td>
</tr>
<tr>
<td>( i_0 ) for ORR</td>
<td>3.04 E - 10 (A/cm(^2))</td>
<td>[29]</td>
</tr>
<tr>
<td>Passive current density at steady state</td>
<td>1.69 E - 6 (A/cm(^2))</td>
<td>[29]</td>
</tr>
<tr>
<td>( E_0 ), standard electrochemical potential for aluminum dissolution reaction</td>
<td>-1.66 (V(_{\text{SHE}}))</td>
<td>[30]</td>
</tr>
<tr>
<td>( \epsilon ), strain at fracture of the passive</td>
<td>1.3 E-3</td>
<td>[31]</td>
</tr>
<tr>
<td>( E ), Young’s modulus</td>
<td>70.3 (GPa)</td>
<td>[32]</td>
</tr>
<tr>
<td>( \sigma_c ), critical local stress</td>
<td>1 E - 2 E</td>
<td>[33]</td>
</tr>
<tr>
<td>( G ), shear modulus</td>
<td>26.4 (MPa)</td>
<td>[34]</td>
</tr>
<tr>
<td>Grain-Boundary self-diffusion coefficient</td>
<td>8.75 E - 5 (m(^2)/s)</td>
<td>[34]</td>
</tr>
<tr>
<td>Activation energy for diffusion</td>
<td>84 (KJ/mol)</td>
<td>[34]</td>
</tr>
<tr>
<td>Grain-boundary diffusion width</td>
<td>0.5726 (nm)</td>
<td></td>
</tr>
<tr>
<td>Atomic Volume</td>
<td>6.6167 E -29 (m(^3))</td>
<td>Calculated</td>
</tr>
<tr>
<td>Yield Strength</td>
<td>227.53 (MPa)</td>
<td>[32]</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>26.98 (g/mol)</td>
<td>Property Tables</td>
</tr>
<tr>
<td>Metal density</td>
<td>2.7 (g/cm(^3))</td>
<td>Property Tables</td>
</tr>
</tbody>
</table>
Running the model for the lightly sensitized alloy previously mentioned yielded the results shown in Figure 5-11, as reported by Lee, Lv, and Macdonald [10]. This figure described how the CGR varied with potential using the approach discussed in the previous section. The important aspect of this was that there was a critical potential below which (more negative than) the electrochemical CGR is not affected by potential. Rather, the crack only grew by mechanical creep as described by Wilkinson and Vitek [35]. Experimental results reported by Jones, et al. for the H321 heat treatment were shown to be in good agreement with the model [36].

![Graph showing Crack Growth Rate (CGR) vs. Electrochemical Potential (ECP) for different solution conductivities](image)

Figure 5-11: Results from the CEFM showing how the CGR vs. ECP varies for different solution conductivities Ref. [11]. A few experimental data points reported in the literature for solution treated (ST) and quenched (Q) AA5083 compact tension specimens.

CEFM predictions for the concentrations of the cathodic depolarizers are shown in Figure 5-12. The trend in Figure 5-12a showed that at certain concentrations of \([O_2]\) and \([H_2O_2]\), the ECP increased rapidly. The CGR in the same graph was shown to be independent of the ECP, which likely had to do with the lack of \(O_2\) reduction on the external surfaces. In the second graph Figure 5-12 b, it was demonstrated that the increased \([H_2]\) concentration resulted in suppression
of the CGR and the ECP. In both graphs the presence of the $[\text{H}_2\text{O}_2]$ displaced the ECP in a more positive direction since it is a stronger oxidizing agent (see Lee, or Lee, Lv, and Macdonald for a more detailed explanation) [10, 11].

Figure 5-12: Results of the CEFM showing how the CGR and ECP vary as a function of $[\text{O}_2]$ or $[\text{H}_2\text{O}_2]$ (b.) of $[\text{H}_2\text{O}_2]$ or $[\text{H}_2]$ from Ref. [11].

To reinforce the points made in the previous figures from the CEFM, the influence of conductivity, the $[\text{O}_2]$ and the $[\text{H}_2]$ on CGR were reported and shown in Figures 5-13 a and b. In Figure 5-13, increasing conductivity resulted in less sensitivity to $[\text{O}_2]$ as CGR increases occurred at higher concentrations. At higher conductivities, the throwing power of the current increased and the result was a higher sensitivity that came with the increased availability of $[\text{O}_2]$ and CGR increases at lower concentrations.
Figure 5-13: Results of the CEFM showing how the CGR vs. ECP for different solution conductivities from Ref. [11].
Conclusions

In this chapter, the general approach to the CEFM was presented and some background was given. The application of the CEFM to AA5083 was accomplished by Lee, et al., and a few of the results were presented here [10, 11]. This approach remained true to the model’s roots in determinism and considered the case of the lightly sensitized alloy. However, because of the newness of applying the CEFM to SCC of AA5083, which involves considerations of varying DOS level amongst other material and environmental considerations, more experimentation and information was needed.

Because the CEFM involved collaborations from various researchers, a complete expansion of the model was beyond the scope of this dissertation. The recent literature published on the topic as it relates to the effect of DOS on the crack growth rate and the electrochemical information now available has been highlighted. Hence, the foundation for expansion has been made.
References


15. Searles, J.L., *The Electrochemical Characteristics of Al3Mg2 and Stress Corrosion Cracking Behavior of AA5083 (Al-4.5Mg-1.0Mn)*, MS Ohio State University, 2000.


Chapter 6

Discussion and Future Work

The work in this dissertation focuses on the experimental validation of the deterministic modeling approach that predicts SCC in AA5083. The experimental results are also needed for future customization of the CEFM. As a result, the recent application of the CEFM to AA5083 reported by S.-K. Lee and colleagues, which only covers one sensitization condition (lightly sensitized, which translates to a DOS≈6.3 mg/cm²), can be expanded [1, 2]. In the previous chapter, the recent studies found in the literature that have taken on the task of determining how the DOS affects the amount of β coverage on the grain boundaries for different orientations were explored. This information will be used to update the electrochemical inputs to the future CEFM code. In this chapter, the overall results of this study are discussed as a means to continue the CEFM expansion process. A brief discussion of the findings in this dissertation is presented first. Once the CEFM predictions are combined with the experimental work presented in this dissertation for heavily sensitized and as-received AA5083, a foundation will be laid for moving forward with the CEFM calibration as there are mechanical and electrochemical aspects that must be changed. The orientation anisotropy and the crack-tip chemistry changes for more sensitized specimens. The approach of considering the influence of the external environment and thus, the coupling current, is what will distinguish the current research from other models.
Discussion

The research presented in Chapter 2 of this dissertation first justifies the use of the SVP for detection of the coupling current from μm to mm-size localized galvanic corrosion events. The initial set of experiments was designed to mimic the behavior of alloys with intermetallic compounds (IMC). Initially, SVP maps captured anodic currents flowing from the anodic bulk aluminum to the Cu-wire implants which were in physical contact with each other. Eventually, the much smaller pitting events are imaged in the SVP maps as the cathodic regions on the maps decrease with time. An insulating spacer was added to the fabricated galvanic couple to spatially separate the anode and cathode. The result of this study once the anodic Al was connected externally via the potentiostat was a ring of depressed current density. While these experiments helped to establish the proper SVP settings for measuring these coupling currents, they also gave understanding to the behavior of the local corrosion events around IMCs. The plan for future experiments is to further examine the interaction of the Al matrix with the β phase by creating similar galvanic couples.

This dissertation also presents successful mapping of the coupling currents that occur during SCC of AA5083 in diluted saltwater for the first time. Upon the foundational fracture mechanics studies, the expected fracture toughness values are established for a few different environmental conditions. These conditions include the testing of as-received and sensitized specimens in air and in the diluted saltwater (0.06 M solution that was used to match the conditions of our featured SVP study). In the analysis of the typical fracture mechanics study, $K_{ISCC}$ is identified for sensitized specimens by looking for the continual decrease of unload/reload slopes. Fractography of the sample through light and scanning electron microscopy reveals non-straightened crack fronts of an electrochemical nature that accelerates more quickly in the center of the specimen at low K values and may even experience a reversal of that trend at higher K.
values based on the shading present of corrosion product on the fracture surface. More analysis is necessary, but we can conclude that for this TL orientation, which is not the most susceptible to IGSCC, that the crack growth mechanism changes a few times based on whether H ingress, anodic dissolution of β via intergranular corrosion, or mechanical creep is the main contributor to crack growth. In fact, what is referred to as zone C in figure 3-12 may need more divisions to show this observation.

This featured study of the dissertation is the joint mechanical and local electrochemical analysis performed with the unique fracture mechanics setup (where the sample lays on its side) and the SVP. Establishing the nature of the current exiting the crack and notch was made possible by setting up a Mg alloy wire into the sample to act as a fiducial marker similar to those experiments discussed in Chapter 2. Hence, notches in these specimens begin as anodic and that anodic current decays with time. As the crack grows, it develops enhanced activity more than the notch. Furthermore, anodic and cathodic zones were observed on the SVP maps near stress corrosion cracks which are further evidence of the existence of CCs. Analysis of the CC vs. load curve for the unsensitized AA5083 in diluted saltwater shows a single global peak near the $K_{ISCC}$. This seems to suggest a single crack growth mechanism is occurring. In fully sensitized specimens, multiple local peaks occur after the $K_{ISCC}$, which may result from several different crack growth mechanisms.

Ultimately, the most important finding is the ability to spatially resolve and track crack growth electrochemically. Future experiments need to examine multiple samples at the conditions used for this study. However, each experiment is time consuming yielding more quality rather than quantity. The qualitative study reveals quantitative results, but the focus in the follow-up experiments is gathering more data from single samples than before. The following steps accomplish this goal:
1. Incorporate an unload/reload procedure from Chapter 3 in the SVP fracture mechanics setup.
2. Add systematic load plateaus and SVP maps before and after the $K_{\text{ISC}}$ to complete the CGR curve.
3. Institute acoustic emissions during the loading.

In the following sections, steps that can be taken for investigating the mitigation of SCC of sensitized AA5083 based on the ability to spatially resolve the CC resulting from the linkage of the crack’s internal and external environments are presented.

**Coatings and Anodizing: Options for SCC Mitigation?**

A possibility for future experiments involves testing different coatings for the AA5083. A lot of interest has been growing in the application different thin film, hydrophobic coatings for corrosion resistance [3-8]. Another approach that has been used in protection from general corrosion of Al alloys is anodizing [9-13]. There is a considerable opportunity to explore these techniques for SCC mitigation as well. By changing some of the input values of the CEFM (e.g., the standard exchange current density [SCED] multiplier) to investigate the presence of a coating or a dielectric film on the alloy’s surface and theory can be compared to experiments [1, 2]. The results of the effect of inhibition of the cathodic reactions calculated by the model from reference [1, 2] are shown in Figure 6-1.
Figure 6-1: a.) ECP vs. [O2] as predicted by the CEFM for AA5083-H321 using various SECD multipliers showing strong inhibition of ORR when the SECD decreases and strong catalysis when the SECD increases b.) CGR behavior vs. [O2] for different SECD values from Ref. [2].
When the SECD for ORR >1, the model reflects the conditions for catalysis of the overall reaction. When the SECD<1, inhibition is reflected in the trends. The results show that there is a critical \([O_2]\) below which, the crack growth rate (CGR) is not affected by inhibition or catalysis. The reason for a null effect of the CGR as a function of \([O_2]\) in this region is that the creep/mechanical CGR dominates the electrochemical CGR. Furthermore, the CGR and ECP are independent of the catalysis conditions, according to the CEFM predictions [1,2]

**Calibration of the CEFM**

The work published on the CEFM by S-K Lee, et al. included calibrations for AA5083 [1, 2]. However, further research still needs to be conducted due to the lack of available electrochemical data at the time of the research. For example, some of the properties for pure-Al were inserted for the AA5083 code since the AA5083 values were not found in the literature. Furthermore, some mechanical and electrochemical properties vary as a function of DOS and sample orientation. In Chapter 6, some studies were identified that clarify the coverage of \(\beta\) on the grain boundaries as a function of DOS and sensitization time. Future experiments should be implemented by adjusting the material and electrochemical inputs in the CEMF.

**Refined Experimental Path**

Based on the results of this research, a refined experimental path should be defined to verify the current predictions made for lightly sensitized AA5083 with the CEFM and to possibly explore the mechanisms that change with DOS levels. The first adjustment in the set of experiments that should follow this work is to use a sample where the load is applied (if the sample is loaded in tension) in the short transverse of the AA5083 slab. The sample orientation
SL or ST has proven to be the most susceptible to sudden failure when undergoing IGSCC or IGC [14-16]. Because of the changed specimen dimensions, a new or adjusted fracture mechanics test machine that also allows for simultaneous mechanical and electrochemical data collection will also be required (as the thickness dimension of the specimens in those orientation are limited).

Acoustic emissions information that was collected for some of the work mentioned in this dissertation has yet to be processed. Acoustic emissions refers to the release of sound waves from small microscopic-sized events, such as cracking originating from defects in a sample with an applied stress, that could go undetected unless the sample fails [17, 18]. An example of the acoustic emission signal obtained during a fracture process is shown in Figure 6-2.

![Figure 6-2: Two examples of AE information that is obtained from the a.) crack growth and propagation and the b.) failure of steel cables obtained from Ref. [18]](image-url)
There are also other features of the AE signal (other than those shown in Figure 6-2), such as Peak Definition Time, Hit Definition Time, and Hit Length can be used to better interpret or filter the incoming signal. Piezoelectric sensors may be used to detect these micro-events. This tool will help bring clarity to the question of the micro-fracture dimension and mechanism in AA5083 and other future alloys. Once again, the hope for this body of work is to continue to encourage an approach (through experimental validation of the CEFM model) to SCC mitigation that invokes determinism via the natural laws and considers more heavily the effects of the external environment on SCC.

The work in this dissertation has given validity to the existence of measureable coupling currents by designing a fracture mechanics setup for obtaining simultaneous mechanical and localized corrosion behavior. The coupling current has also accounted for the positioning of the crack as a function of time and stress intensity with reasonable accuracy. Hence, because of the spatial resolution of the SVP, findings from the experiments and modeling have had important implications for the environmentally assisted cracking and fracture mechanics community, which are:

1. SCC can be monitored *in-situ* based on the presence of the CC.
2. A new fracture mechanics configuration involving horizontal machine orientation and samples lying on their side was introduced.
3. Coupling of the crack internal and the external environments was verified experimentally with spatial resolution, which can lead to new mitigation strategies.

Such advancements from the original coupling current experiments were made possible by considering backbones of the CEFM, which are the natural law of charge conservation and the differential aeration hypothesis.
References


Krystaufeux Williams studies corrosion science and engineering under his adviser, Dr. Digby Macdonald. He also serves as a Student Career Experience Program (SCEP) employee at the Center for Corrosion Science and Engineering at the Naval Research Laboratory in Washington, DC. There he performs his research on the environmental effects of corrosion including stress corrosion cracking and corrosion fatigue of different alloys. He obtained dual bachelor degrees from Lincoln and Drexel Universities in physics and mechanical engineering, respectively, as a participant in Lincoln’s Advanced Science and Engineering Reinforcement (LASER) program. Krystaufeux earned a master’s degree in physics from Delaware State University and a master’s degree from the Pennsylvania State University in materials science and engineering.

Krystaufeux has served as a member of the National Society of Black Engineers, the National Society of Black Physicist, and the American Society of Mechanical Engineers, SPIE (the international society for optics photonics). Currently, he is a member of the Materials Research Society, National Society of Corrosion Engineers, and the Electrochemical Society. In 2012, he received the outstanding student poster award from the Aluminum Week Conference in Chicago, IL. for his work on “Mechanistic Determination of SCC in Aluminum Alloys,” and continues to give invited talks on the topic based on his findings.