CHARACTERIZATIONS OF ALLOYING CU EFFECT ON
ELECTROCHEMICAL REACTIONS OF Al-CU SOLID SOLUTION ALLOYS

DISSERTATION

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Copper is a major alloying element for high strength aluminum alloys used in the aerospace industry and is known to have a detrimental effect on localized corrosion. Interplay between Cu-bearing intermetallic particles and the matrix containing at least 1.0 wt % solid solution copper is known to induce pit initiation. But Cu additions to aluminum decrease susceptibility to pit initiation provided that Cu is retained in solid solution.

In this study, we show that stimulating alloy dissolution without inducing passive film breakdown significantly ennobles the subsequently measured pitting potential of Al-Cu solid solution alloys. Similar effects are not observed with high purity Al or Al-Zn solid solution alloys. To further investigate the ennobling effect of Cu, metastable pits on high purity Al and Al-Cu solid solution alloys have been examined in detail. Results show that Cu additions decrease the probability of stable pit formation by decreasing metastable pit initiation and growth rates. Surface characterization by scanning transmission electron microscopy and spectral imaging of specially prepared Al-Cu needle-type samples show that Cu is readily enriched at the alloy interface by a range of exposure regimens including those that induce pitting. These results suggest the possibility of local Cu
enrichment at incipient pit sites by metastable pitting, which causes ennoblement of the critical pitting potential.

In the last part of the study, dissolution kinetics of high purity Al, Al-Mg, and Al-Mg-Cu solid solution alloys are investigated by using an artificial pit electrode cell. It has been determined that Cu ennobles dissolution kinetics of artificial pits for Al-Mg-Cu solid solution.
Dedicated to my wife Kyungmin and my daughter Claire
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TABLE OF CONTENTS

ABSTRACT.....................................................................................................................ii
DEDICATION..................................................................................................................iv
ACKNOWLEDGMENTS....................................................................................................v
VITA...............................................................................................................................vii
LIST OF TABLES.........................................................................................................xi
LIST OF FIGURES.......................................................................................................xii

Chapters:
1. INTRODUCTION ........................................................................................................ 1
2. LITERATURE REVIEW ............................................................................................. 7
   2.1 INTRODUCTION ..................................................................................................... 7
   2.2 PITTING CORROSION OF ALUMINUM ALLOYS ................................................ 8
      2.2.1 Pit Chemistry .................................................................................................. 9
      2.2.2 Variables Affecting Pitting Susceptibility ....................................................... 10
      2.2.3 Metastable Pitting Corrosion ....................................................................... 14
      2.2.4 Statistical Analysis of Pitting Corrosion......................................................... 18
   2.3 ALLOYING EFFECTS ON CORROSION OF INTERMETALLIC PARTICLES ....... 24
      2.3.1 Al₂Cu (θ phase)............................................................................................. 26
      2.3.2 Al₂CuMg (S phase)....................................................................................... 27
      2.3.3 Mg(Zn, Cu, Al)₂ (η phase)........................................................................... 30
   2.4 ALLOYING EFFECTS ON CORROSION OF MATRIX PHASE ......................... 31
      2.4.1 Local Acidification Model.............................................................................. 32
      2.4.2 Chemistry Change in Passive Oxide Film..................................................... 35
2.4.3 Change in Dissolution Kinetics ................................................................. 38
2.5 CRITICAL ISSUES ...................................................................................... 40
  2.5.1 Mechanism of Alloying Cu in Solid Solution Aluminum ...................... 40
  2.5.2 Metastable Pitting Behavior of Al-Cu Binary Alloys .............................. 41
  2.5.3 Surface Characterization in the Passive Film of Al-Cu and Al-Mg-Cu Alloys42
2.6 RESEARCH OBJECTIVES ......................................................................... 42
3. A CHARACTERIZATION OF THE INHIBITING EFFECT OF CU ON
METASTABLE PITTING IN DILUTE AL-CU SOLID SOLUTION ALLOYS ........... 59
  3.1 INTRODUCTION ....................................................................................... 59
  3.2 EXPERIMENTAL METHODS ..................................................................... 62
    3.2.1 Pitting potential ($E_{\text{pit}}$) measurements .......................................... 62
    3.2.2 Metastable pitting measurements with Al 99.999 and Al-Cu solid solution
        alloys ....................................................................................................... 63
  3.3 RESULTS ................................................................................................. 64
    3.3.1 $E_{\text{pit}}$ of Al solid solutions ................................................................. 64
    3.3.2 Metastable pitting of Al 99.999 and Al-Cu solid solution alloys .......... 65
    3.3.3 Metastable pit initiation ........................................................................ 68
    3.3.4 Metastable pit growth .......................................................................... 69
    3.3.5 Repassivation ...................................................................................... 69
  3.4 DISCUSSION ........................................................................................... 70
    3.4.1 Effect of Cu on metastable pit initiation .............................................. 70
    3.4.2 Effect of Cu on metastable pit growth ................................................. 72
    3.4.3 Effect of Cu on metastable pit repassivation ..................................... 73
    3.4.4 Evaluation of other effects of Cu on metastable pit repassivation ....... 74
  3.5 CONCLUSIONS ....................................................................................... 76
4. EFFECT OF ALLOYING CU ON ELECTROCHEMICAL REACTIONS OF AL-CU
SOLID SOLUTION ALLOYS—SURFACE CHARACTERIZATION BY XPS AND
TEM ................................................................................................................. 104
  4.1 INTRODUCTION ..................................................................................... 104
  4.2 EXPERIMENTAL METHODS ................................................................. 105
4.2.1 Pitting potential (Epit) measurements after passive dissolution .......... 105
4.2.2 Pitting potential (Epit) measurement by microelectrochemical cell ........ 107
4.2.3 X-ray photoelectron spectroscopy ......................................................... 107
4.2.4 Surface characterization by Scanning Transmission Electron Microscopy (STEM) ................................................................................................................... 108
4.3 RESULTS ..................................................................................................... 109
4.3.1 Statistical measurements on Epit of Al 99.999, Al-2.0Cu and Al-2.0Zn...... 109
4.3.2 Area Effects ............................................................................................ 110
4.3.3 Epit distributions by microelectrochemical cell experiments ................... 111
4.3.4 X-ray photoelectron spectroscopy analysis ........................................... 112
4.3.5 Surface characterization by STEM .......................................................... 114
4.4 DISCUSSION .............................................................................................. 117
4.4.1 The effect of Cu on pitting potential ennoblement .................................. 117
4.4.2 Surface chemistry changes and Epit ennoblement .................................. 119
4.5 CONCLUSIONS ....................................................................................... 121
5. CHARACTERIZATION OF AL-CU AND AL-MG-CU SOLID SOLUTION ALLOY DISSOLUTION KINETICS...................................................................................... 143
5.1 INTRODUCTION ....................................................................................... 143
5.2 EXPERIMENTAL METHODS.................................................................... 145
5.3 RESULTS AND DISCUSSION .................................................................. 147
5.3.1 Al-Cu and Al-Mg-Cu APE pitting and pit growth kinetics ..................... 147
5.3.2 Repassivation of Al-Cu and Al-Mg-Cu APEs ........................................ 150
5.3.3 Cu enrichment by APE dissolution ....................................................... 151
5.3.4 Behavior of APEs during repassivation and cathodic polarization .......... 152
5.3.5 The effect of Cu on dissolution characteristics ....................................... 155
5.4 CONCLUSIONS ....................................................................................... 157
6. CONCLUSIONS AND FUTURE WORK ...................................................... 176
6.1 CONCLUSIONS ....................................................................................... 176
6.2 FUTURE WORK ...................................................................................... 178
Bibliography .................................................................................................. 180
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3. 1: Sample dimensions, electrode areas and heat treatments for materials used</td>
<td>100</td>
</tr>
<tr>
<td>3. 2: Number of available defect sites ($N_0$) and the constant $\tau$ for Al 99.999 and Al-0.2Cu at different applied potentials</td>
<td>101</td>
</tr>
<tr>
<td>4. 1: Samples used for each experiments; pitting potential measurements, microcell, XPS, and STEM analysis</td>
<td>140</td>
</tr>
<tr>
<td>5. 1: Sample dimensions and electrode areas of materials used in the artificial pit electrode cell experiment</td>
<td>174</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2. 1</td>
<td>Typical anodic current transient of metastable pits by potentiostatic measurement on type 302 Stainless Steel [27].</td>
<td>444</td>
</tr>
<tr>
<td>2. 2</td>
<td>Schematic diagram of a repassivating metastable pit [28].</td>
<td>45</td>
</tr>
<tr>
<td>2. 3</td>
<td>Variation of (a) the metastable pit nucleation frequency $\lambda$ and (b) the stable pit nucleation frequency $\Lambda$ with constant applied potential for different stainless steels [102].</td>
<td>46</td>
</tr>
<tr>
<td>2. 4</td>
<td>Frequency of metastable pit nucleation ($\lambda$) for 0.02 % Zn and 0.13 % Zn alloys and pure Al in 0.5 M NaCl at -0.75 V vs. SCE [77].</td>
<td>47</td>
</tr>
<tr>
<td>2. 5</td>
<td>Normal probability plot of $I_{\text{peak}}$ (peak pit current of metastable pit) in 0.5 M NaCl at -0.75 V vs. SCE [77].</td>
<td>48</td>
</tr>
<tr>
<td>2. 6</td>
<td>Normal probability plot of $\Delta t_g$ (pit growth time) in 0.5 M NaCl at -0.75 V vs. SCE [77].</td>
<td>49</td>
</tr>
<tr>
<td>2. 7</td>
<td>Potentiodynamic polarization curves showing the effects of alloying elements on the OCP and $E_{\text{pit}}$ in deaerated 0.1 M KCl [20].</td>
<td>50</td>
</tr>
<tr>
<td>2. 8</td>
<td>Effect of increasing Nb in aluminum on the pitting and repassivation potentials [28].</td>
<td>51</td>
</tr>
<tr>
<td>2. 9</td>
<td>Repassivation potentials of Al-Cu solid solution as a function of Cu content [72].</td>
<td>52</td>
</tr>
<tr>
<td>3. 1</td>
<td>The $E_{\text{pit}}$ distribution of Al 99.999 (2.5×10^{-4} cm²), Al-2.0Cu (1.8×10^{-4} cm²) and Al-2.0Zn (1.3×10^{-4} cm²) determined from potentiodynamic polarization.</td>
<td>78</td>
</tr>
<tr>
<td>3. 2</td>
<td>Anodic polarization curves for Al 99.999, Al-0.2Cu and Al-2.0Cu in deaerated 0.1 M NaCl solution.</td>
<td>79</td>
</tr>
<tr>
<td>3. 3</td>
<td>Current transients of Al 99.999 for 5400 seconds.</td>
<td>80</td>
</tr>
</tbody>
</table>
3. 4: Current transients of Al-2.0Cu for 5400 seconds. .................................................... 81
3. 5: Current versus time records for Al-0.2Cu collected at applied potentials of -0.69, -0.67, and -0.66 V versus SCE ................................................................. 82
3. 6: Current versus time records for Al 99.999 (-0.70 V\text{SCE}), Al-0.2Cu (-0.69 V\text{SCE}) and Al-2.0Cu (-0.69 V\text{SCE}) in deaerated 0.1 M NaCl ............................................. 83
3. 7: Metastable pit initiation frequency (events per 500 sec interval) for Al 99.999 at -0.70, -0.69 and -0.67 V vs. SCE ................................................................. 84
3. 8: Metastable pit initiation frequency (events per 500 sec interval) for Al-0.2Cu at -0.69 and -0.67 V vs. SCE ................................................................. 85
3. 9: Cumulative probability plot of peak pit current, $I_{\text{peak}}$ for Al 99.999 at -0.70, -0.69 and -0.67 V vs. SCE ......................................................... 86
3. 10: Cumulative probability plot of peak pit current, $I_{\text{peak}}$ for Al-0.2Cu at -0.69 and -0.67 V vs. SCE ................................................................. 87
3. 11: Current versus time record of an individual metastable pitting event on Al 99.999. ................................................................................................................................... 88
3. 12: Current versus time record of an individual metastable pitting event on Al-0.2Cu. ................................................................................................................................... 89
3. 13: Frequency of metastable pit initiation for Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE ................................................................. 90
3. 14: Cumulative probability plot of $I_{\text{peak}}$ for Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE ................................................................. 91
3. 15: Cumulative probability plot of $t_{\text{g}}$ for Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE ................................................................. 92
3. 16: Cumulative probability plot of $I_{\text{peak}}/t_{\text{g}}$ for Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE ................................................................. 93
3. 17: Cumulative probability plot of repassivation time for Al 99.999 and Al-0.2Cu. ........................................................................................................ 94
3. 18: Cumulative probability plot of $I_{\text{peak}}/t_{\text{r}}$ for Al 99.999 and $I_{\text{rep1}}/t_{\text{r1}}$ and $I_{\text{rep2}}/t_{\text{r2}}$ for Al-0.2Cu ................................................................. 95
3. 19: Cumulative probability plot of $r_{\text{pit}}$ (radius of metastable pit at $I_{\text{peak}}$) for Al 99.999 and Al-0.2Cu ................................................................. 96
3. 20: Cumulative probability plot of peak pit current density, $i_{\text{peak}}$, at the point of repassivation for Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE................ 97
3. 21: Cumulative probability plot of $I_{\text{peak}}/r_{\text{pit}}$ for metastable pits of Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE.............................................................................. 98
3. 22: Relationship between $(r_{\text{pit}})^2$ and $t_r$ for Al 99.999 at -0.70 V and Al-0.2Cu at -0.69 V vs. SCE (1st and 2nd repassivation)............................................................................ 99

4. 1: Schematic diagram for the pitting potential ($E_{\text{pit}}$) measurement after the passive dissolution............................................................................................................... 123
4. 2: The $E_{\text{pit}}$ distribution of Al 99.999 (2.5×10^{-4} cm²), Al-2.0Cu (1.8×10^{-4} cm²) and Al-2.0Zn (1.3×10^{-4} cm²) without a potentiostatic hold period ($t_{\text{hold}} = 0$ min)............... 124
4. 3: $E_{\text{pit}}$ distributions of Al 99.999 (2.5×10^{-4} cm²) after potentiostatic hold for 0, 50, 100 and 500 min............................................................................................................. 125
4. 4: $E_{\text{pit}}$ distributions of Al-2.0Cu (1.8×10^{-4} cm²) after potentiostatic hold for 0, 50, 100 and 500 min............................................................................................................. 126
4. 5: $E_{\text{pit}}$ distributions of Al-2.0Zn (1.3×10^{-4} cm²) after potentiostatic hold for 0, 100 and 500 min .................................................................................................................. 127
4. 6: $E_{\text{pit}}$ distribution of Al 99.999 depending on exposed area and potentiostatic hold time; i) A = 1.1×10^{-2} cm² from 1200 mm diameter wire and ii) A = 2.5×10^{-4} cm² from 180 mm diameter wire. ................................................................. 128
4. 7: Comparison of $E_{\text{pit}}$ distributions for Al-2.0Cu depending on the potentiostatic hold time; $t_{\text{hold}} = 0$ and 500 min on (a) large area (1.0×10^{-2} cm²) and (b) small area (1.8×10^{-4} cm²).................................................................. 129
4. 8: Potentiodynamic curve and pit image of Al-4.0Cu after cyclic polarizations........ 130
4. 9: Cumulative probability plot of pitting potentials of Al 99.999, Al-0.2Cu, and Al-4.0Cu by microcell experiment............................................................................................................... 131
4. 10: X-ray peak intensities of Cu 2p and Al 2p peaks for Al-2.0Cu after the potentiostatic hold............................................................................................................. 132
4. 11: Oxide film thickness changes of Al 99.999 and Al-2.0Cu before or after the passive dissolution............................................................................................................. 133
4. 12: Scanning transmission image of the tip of an electropolished Al-1.0Cu needle and its companion spectral image. ................................................................................................................. 134
4. 13: Scanning transmission image of the tip of an electropolished Al-2.0Cu needle and its companion spectral image................................................................................................................. 135
4. 14: Current versus time record for an electropolished Al-1.0Cu surface alloy surface during potentiostatic polarization. ................................................................................................................. 136
4. 15: Scanning transmission image of the tip of an electropolished Al-1.0Cu needle after potentiostatic polarization and its companion spectral image. ........................................ 137
4. 16: Scanning transmission image of the tip of Al-2.0Cu needle after polarization scanned from -1.2 to -0.4 V (vs. SCE) and its companion spectral image. ....................... 138
4. 17: Current versus potential of electropolished Al-2.0Cu prior to pit initiation......... 139

5. 1: A schematic drawing of the artificial pit electrode cell................................. 159
5. 2: Cyclic polarization curve of Al-5.0Mg-0.2Cu from its 3rd cycle....................... 160
5. 3: Estimated pit depth using Faraday’s law for Al 99.999 (small), Al-0.1Cu, Al-1.0Cu, and Al-2.0Cu as a function of number of polarization cycles. ........................................ 161
5. 4: Estimated pit depth using Faraday’s law for Al 99.999 (Both of large and small), Al-5.0Mg and Al-5.0Mg-0.2Cu. ................................................................................................................. 162
5. 5: Part of potentiodynamic curves for Al 99.999 (small), Al-0.1Cu, Al-1.0Cu, and Al-2.0Cu after the 10th polarization cycle. ................................................................. 163
5. 6: Pitting potentials of Al 99.999 (small), Al-0.1Cu, Al-1.0Cu and Al-2.0Cu as a function of number of polarization cycles. ................................................................. 164
5. 7: Plot of current density in terms of potential during anodic polarization scanned from –1.4 to 0.4 V (vs. SCE) for Al-5.0Mg-0.2Cu. ................................................................. 165
5. 8: Repassivation behavior of Al 99.999 (small), Al-5.0Mg and Al-Cu alloys. ....... 166
5. 9: Repassivation behavior of Al-5.0Mg and Al-5.0Mg-0.2Cu. .............................. 167
5. 10: Repassivation behavior of Al 99.999 (large) and Al-5.0Mg-0.2Cu. ............... 168
5. 11: Image of artificial pit of Al-5.0Mg-0.2Cu after six polarization cycles. ........ 169
5. 12: (a) Pit morphology of Al-5.0Mg-0.2Cu and EDX spectra for (b) Al K, (c) Cu L and (d) ratio of Cu L to Al K. ........................................................................................ 170
5. 13: Repetitive polarization cycles of Al-5.0Mg-0.2Cu (1st, 2nd, 3rd, 4th, 5th and 6th) and Al-5.0Mg (3rd)................................................................................................................................. 171
5. 14: Cathodic peak current density in terms of polarization cycle number for Al 99.999 and Al-0.1Cu, Al-1.0Cu and Al-2.0Cu. ........................................................................................................ 172
5. 15: Cathodic peak current density in terms of polarization cycle number for Al-5.0Mg and Al-5.0Mg-0.2Cu. .................................................................................................................................................. 173
CHAPTER 1

INTRODUCTION

Copper is one of the most critical alloying elements in aluminum alloys due to its ability to improve strength of aluminum by precipitation hardening. Examples are Al-Cu and Al-Zn-Mg-Cu alloys, which are widely employed in various fields, especially in the aircraft industry, due to their high strength-to-weight ratio. However, Cu also introduces vulnerability to localized corrosion such as pitting, crevice corrosion and intergranular corrosion (IGC). Thus, much research has focused on understanding the mechanism of these localized corrosion process in aluminum alloys in order to prevent or predict failures. It is now known that pitting can initiate at microscopic heterogeneities, such as scratches, inclusions, and intermetallics [1-14]. Precipitate and constituent particles in aluminum alloys contain high concentrations of alloying and impurity elements such as Cu, Zn, Mg, Mn and Fe. Although these particles may lead to improvements in mechanical properties, they exhibit different electrochemical characteristics than the surrounding matrix and locally disrupt the protective oxide film, leading to the
localized corrosion [1]. Consequently, the electrochemical characteristics of various intermetallic compounds have been well documented [3-5, 10, 12, 13, 15-22]. Some studies focused on the interplay between these intermetallic particles and the matrix that contains solid solution copper or zinc to explain the mechanism of localized corrosion of Al alloys [10, 18, 19]. However, it has not been sufficiently clarified why and how these intermetallic particles associate with the inferior corrosion resistance in the alloy matrix.

This study aims to understand corrosion behavior of the matrix containing solid solution copper in Cu-bearing Al alloys. Copper additions to aluminum decrease susceptibility to pit initiation provided that Cu is retained in solid solution. This can be observed as an increase in pitting potential with increasing Cu content in an alloy. To further understand this ennobling effect of Cu, characterization of metastable and stable pitting was conducted. It shows that Cu inhibits pit initiation rates and ennobles pit growth kinetics of Al-Cu solid solution alloys. X-ray photoelectron spectroscopy and scanning transmission electron microscopy were used for surface characterization. Local Cu enrichment associated with the increased pitting and corrosion potentials was observed.

This dissertation consists of six chapters. Chapter 1 is the current chapter giving a brief background and objective of this project. Chapter 2 is a review of the relevant literature. In that chapter, an effort has been made to summarize what major mechanisms for the effects of alloying elements on localized corrosion have been reported.

Chapter 3 describes an inhibiting effect of Cu on metastable pitting in dilute Al-Cu solid solution alloys. Results show that 0.2 wt.% Cu additions decrease the metastable pit initiation rate by more than an order of magnitude and slow the pit growth rate mainly
by decreasing the peak pit current attained. In an Al-2.0 wt.% alloy, metastable pitting events were too rare for rigorous study. Repassivation of metastable pits occurs by a two-stage process in Al-0.2 wt.% Cu alloy. The repassivation rate during the first stage is identical to that of high purity Al and appears to be completely unaffected by Cu in the alloy or in the pit solution. In the second stage, repassivation is slow, but is not believed to affect ultimate pit stability. Overall, Cu additions decrease the probability of stable pit formation by decreasing metastable pit initiation and growth rates.

Chapter 4 presents findings relating pitting potential ennoblement to Cu surface enrichment on dissolving Al-Cu solid solution alloys. Stimulating alloy dissolution without inducing passive film breakdown significantly ennobles the subsequently measured pitting potential in experiments carried out in chloride solutions. The ennobling effect is more difficult to detect in large area electrodes due to pit initiation triggered by defects and inclusions that are more regularly encountered in larger electrodes. Scanning transmission electron microscopy and spectral imaging of specially prepared Al-Cu needle-type samples shows that Cu is readily enriched at the alloy interface by a range of exposure regimens including those that induce pitting. These results suggest the possibility of local Cu enrichment at incipient pit sites by metastable pitting, which causes ennoblement of the critical pitting potential.

Chapter 5 examines the effects of Cu on dissolution kinetics for Al-Cu and Al-Mg-Cu solid solution alloys by using an artificial pit electrode cell. Experimental protocol involved a repetitive cyclic polarization between −1.8 and 0.4 V (vs. SCE). The cyclic polarization was intended to form Cu enriched layers at pit walls after each cathodic polarization and measure pitting potential during the subsequent anodic
polarization. Cu additions ennobled dissolution kinetics of Al-Cu and Al-Mg-Cu solid solution alloy artificial pits. Pitting and repassivation potentials of Al-Cu(-Mg) solid solutions were generally higher than those of pure Al at each different pit depth. Surface characterization by SEM/EDS after cathodic polarization scanned from 0.4 to $-1.8$ V (vs. SCE) showed evidence of Cu enrichment on the bottom of Al-Mg-Cu solid solution artificial pit.

Chapter 6 summarizes key findings and makes conclusions regarding the effect of alloying Cu on the localized corrosion of Al-Cu solid solutions. Future work has been suggested to obtain further understanding on various aspects of this project.
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CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Aluminum alloys have been utilized in various areas because of desirable mechanical properties and good resistance to most types of corrosion. The corrosion properties originate from the passive oxide film on aluminum surface. However, under certain conditions, localized corrosion such as pitting, crevice, or intergranular corrosion can occur at surface heterogeneities in the oxide film such as the interface between intermetallic particles and matrix phase. The role of alloying elements on localized attack is important to understand in order to prevent and control localized corrosion in aluminum alloys. The purpose of this chapter is to provide a critical review of previous studies on pitting corrosion of aluminum alloys. The review is focused on proposed mechanisms for the alloying effect on corrosion behavior of different materials, and several key techniques that have helped to elucidate the mechanism. First, classic features of pitting corrosion in aluminum alloys will be summarized. Then, the role of intermetallic particles on localized corrosion of aluminum alloys will be reviewed in
detail along with corrosion of the surrounding matrix phase. While much has been carried out for important intermetallic particles in aluminum alloys [1, 3, 5, 8, 10, 11, 13, 22, 23, 35, 47, 56, 74, 83, 90, 97], comparatively little work has focused on the surrounding solid solution matrix phase. Since pitting is affected by the interaction between intermetallic particles and the surrounding alloy matrix, emphasis should also be placed on the corrosion behavior of the matrix.

Statistical and stochastic analysis for metastable pitting will also be reviewed in detail, particularly as they apply to metastable pitting. It has been suggested that metastable and stable pits are identical except that stable pits continue to grow whereas metastable pits repassivate [28]. From metastable pitting studies, many aspects of stable pitting can be revealed.

### 2.2 PITTING CORROSION OF ALUMINUM ALLOYS

Pitting corrosion is a common form of localized corrosion in aluminum alloys. It is characterized by stable and metastable pitting [28, 29]. Every stable pit first initiates and grows as a metastable pit. When the critical condition for pit stabilization is achieved, the initiated pit stabilizes. However, when it fails to sustain conditions for growth, it dies and is classified as “metastable”. Metastable pitting itself is characterized by three stages during its life; initiation, growth, and repassivation [19, 28, 29, 52, 70, 78, 79]. The lifetime of metastable pit is typically short; on the order of seconds. In potentiodynamic experiments, metastable pits appear at potentials lower than the critical pitting potential at which stable pit forms.
2.2.1 Pit Chemistry

A protective oxide films develops spontaneously on aluminum alloy surfaces in natural environments and provides corrosion resistance by reducing the corrosion rate. The thin (approximately, 2 ~ 4 nm) protective oxide film consists of largely amorphous alumina [21]. Once the oxide film is in an aqueous solution, hydrolysis of the alumina produces hydrated oxides, Al₂O₃·H₂O on the aluminum surface [33]. The Pourbaix diagram (i.e., potential vs. pH diagram) for aluminum reflects the thermodynamic stability of the Al₂O₃·H₂O film at 25 °C [68]. Aluminum is passive and protected by a stable Al₂O₃·H₂O film in the pH range of 4 ~ 8.5. In this passive range, however, aluminum and its alloys are susceptible to pitting [29]. Pitting on aluminum involves two partial electrochemical reactions (i.e., anodic and cathodic reactions). The local anodic reaction leads to the decrease in pH by hydrolysis:

\[
Al \rightarrow Al^{3+} + 3e^- \quad \text{Eqn. 2.1}
\]

\[
Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad \text{Eqn. 2.2}
\]

The local cathodic reactions are hydrogen evolution and oxygen reduction reaction. The hydrogen evolution consumes protons and the oxygen reduction reaction produces OH⁻ anions. Hence, there is an increase in pH at local cathodic sites.

In acidic environment:
\[2H^+ + 2e^- \rightarrow H_2\]  
\[O_2 + 4H^+ + 4e^- \rightarrow 2H_2O\]

Eqn. 2.3

Eqn. 2.4

In neutral/alkaline environment:
\[2H_2O + 2e^- \rightarrow H_2 + 2OH^-\]

Eqn. 2.5

\[O_2 + 2H_2O + 4e^- \rightarrow 4OH^-\]

Eqn. 2.6

In order to initiate pitting, aggressive anions are necessary. Chloride anions can migrate from the bulk electrolyte to the inside pit in order to satisfy charge neutrality.

2.2.2 Variables Affecting Pitting Susceptibility

Characteristic potentials or currents are used to evaluate susceptibility to pitting. It should be noted that these characteristic potentials tend to be sensitive to experimental conditions, such as surface roughness [9], crystallographic orientation [19, 51, 103, 104], potential scan rate [49, 88, 89, 98], Cl\(^-\) concentration [69, 89, 98], and exposed surface area of the metal or alloy [4, 8, 98]. In a cyclic potentiodynamic polarization experiment, the pitting potential (\(E_{\text{pit}}\)), repassivation potential (\(E_{\text{rep}}\)), open-circuit potential (\(E_{\text{oc}}\)), and passive current density (\(i_{\text{pass}}\)) can be obtained. During anodic polarization, a stable pit forms at \(E_{\text{pit}}\) where current density increases by several orders of magnitude. The increasing current density can be stopped and decreased by lowering the applied potential. The growing pit will repassivate at \(E_{\text{rep}}\) where the current density falls back to \(i_{\text{pass}}\). It is generally considered that a material susceptibility scales with the magnitude of the difference in \(E_{\text{pit}} - E_{\text{rep}}, E_{\text{pit}} - E_{\text{oc}}\) or \(E_{\text{rep}} - E_{\text{oc}}\).
The pitting potential of aluminum or stainless steels has been reported to increase with scan rate \([49, 88, 89, 98]\). Shibata and Takeyama reported that pitting potential of stainless steels varies with the square root of the scan rate \([88]\). It has been observed in pure aluminum that the pitting potential varies as the log of the scan rate \([98]\).

In terms of exposed area, Boehni and Suter measured the pitting potential of stainless steel using microelectrochemical techniques, where the exposed surface area was as small as \(300 \mu m^2\) \([8]\). The pitting potential increased from 300 mV (vs. SCE) for a 1000 \(\mu m\) diameter microelectrode to 1100 mV (vs. SCE) for a 50 \(\mu m\) diameter microelectrode. They stated that the increased \(E_{pit}\) was due to the smaller area, which have a lower probability of containing a critical flaw that would initiate pitting. In stainless steels, microstructural flaws such as MnS inclusions have been observed to act as preferential nucleation sites for pit initiation \([8, 102]\). Pitting potentials in high purity aluminum where intermetallic particles are not common have also shown an area dependence \([98]\). In the case of high purity aluminum, pit initiation has been attributed to geometric surface flaws in the oxide film \([9]\). Wall and Martinez measured the area effect on pitting potential of high purity aluminum using a statistical approach \([98]\). They collected pitting potentials from pure aluminum wires with areas ranging from \(10^{-7}\) to \(10^{-3}\) cm\(^2\). They reported that pitting potential of pure aluminum is proportional to log \((1/\text{area})\). Their explanation was that this happens because the number of defect sites scales with electrode area. They also introduced a concept of heterogeneous versus homogeneous pit initiation and used following equation to describe their ideas \([98]\):
where $E_{\text{pit}}$ is pitting potential, $\gamma$ is constant ($V^{-1}$), $\nu$ is scan rate ($Vs^{-1}$), $A$ is area, $\beta$ is constant ($s^{-1}\mu m^{-2}$) and $E_{\text{crit}}$ is a critical potential, below which the initiation rate is zero. $E_{\text{crit}}$ is the minimum observable $E_{\text{pit}}$. Several constants from the statistical studies of Shibata and Takeyama [88, 89] and Baroux [4] were used for their validation of area dependence on homogeneous or heterogeneous pit initiation. In their definitions, heterogeneous pit initiation occurs preferentially at unique sites that are vulnerable to initiation whereas homogeneous pit initiation occurs in the absence of discernible specific sites, and each unit area has equal probability of pit initiation. It was experimentally observed that smaller area ($\sim 10^{-4} \text{ cm}^2$) follows homogeneous pit initiation whereas larger area ($\sim 10^{-3} \text{ cm}^2$) meets criteria for heterogeneous pit nucleation.

The pitting potential has been reported to depend on crystallographic orientation. Yasuda et al. reported the dependence of pitting potential on plane as follows; $E_{\text{pit}} (111) < E_{\text{pit}} (110) < E_{\text{pit}} (100)$ [103]. Recently, however, Yu and Natishan found somewhat different results showing that $E_{\text{pit}} (111) < E_{\text{pit}} (100) < E_{\text{pit}} (110)$ for pure aluminum single crystals [104]. They continued their investigation by studying metastable pitting activities for each orientation [19]. The number of metastable pits per unit area, which were counted from metastable current spikes, characterized the metastable pitting activity. They found that the (111) crystal plane showed the highest number of metastable pits at a given potential [19]. The (100) crystal plane exhibited the second highest metastable pitting activity, while the least activity came from the (110) crystal plane. They explained
that the crystal plane with a higher planar atomic density would be more likely to produce a higher aluminum ion concentration at the site of metastable pits. Although they did not point it out in their studies [19, 104], it is notable that there is a positive relationship between metastable pitting activity and susceptibility to stable pitting.

There are also reports that have revealed the relationship between characteristic potentials and Cl$^-$ concentration. Pitting potential and repassivation potential are found to be inversely proportional to the logarithm of Cl$^-$ concentration for passive metals such as aluminum [69] and others [48, 51]. Chloride concentration also affects metastable pitting activity, which will be reviewed in detail in the next section. Chlorides are known to be one of the aggressive anions causing localized breakdown of the protective oxides [7, 25, 29, 105]. Although Kruger [46], Strehblow [91] and others [29] have proposed several mechanisms for Cl$^-$ ion interactions with the protective passive oxides in affecting the localized corrosion, nothing is conclusive for understanding the role of Cl$^-$ in initiating pitting. Nonetheless, the proposed mechanisms can be generally categorized into the following classes:

i) Ion migration/penetration of the oxide

ii) Adsorption/ion displacement leading to oxide thinning

iii) Breakdown and repair of oxides

The ion migration/penetration model is based on penetration of aggressive anions through passive film to cause pit initiation [38]. This concept is supported by the results that show an induction time for pit initiation and chloride ion incorporation [45, 53]. The
adsorption model is based on displacement of adsorbed $O_2$ replaced by chloride and consequently the adsorbed ions lead to a thinning of the passive film and pit initiation [7, 48, 94, 95]. Some evidence has shown that the combination of penetration and adsorption play a role in the localized attack. X-ray photoelectron spectroscopy (XPS) analysis by Yu and Natishan revealed that chlorides were present not only as an adsorbed species at the surface of the aluminum oxide but also as an incorporated species within the passive film at potentials below the pitting potential [105]. They found that the adsorbed $Cl^-$ migrated from the solution/aluminum oxide interface into the passive film prior to a stable pit initiation. $Cl^-$ migration has been reported to occur once a critical anodic potential is reached [105].

The breakdown model explains that pit initiates due to mechanical film rupture at local sites [79].

### 2.2.3 Metastable Pitting Corrosion

In many studies it has been noted that initiated pits may rapidly repassivate [27, 37, 80, 102]. Among these, Frankel et al. termed the phenomenon “metastable pitting” [27] which has unified other terminologies such as unstable pitting [80], current transients in the repassivation region [37], or micro pits [102].

There are three distinct electrochemical tests employed to investigate metastable pitting. One is the galvanostatic experiment that measures potential transients under an applied anodic current. Secondly, open-circuit potential (OCP) transients can be measured at a given current. Last is the potentiostatic experiment that collects current transients under constant applied potential. This method is widely used in the field of
electrochemical noise analysis. The applied potential can be raised step by step and consequently, more current transients can be observed. An example of current transient for metastable pitting is shown in Figure 2.1 [27]. Anodic current starts to increase and this represents the initiation of the pit. The current increase continues for a few seconds, indicating the growth of metastable pit. Then the current drops back to its baseline current, representing the repassivation. When stability of a metastable pit is achieved, the pit current remains high and increasing. The chance of achieving pit stability increases with increasing applied potential. Typically, metastable pits do not create significant damage on a surface. The diameter of metastable pit is on the order of only a few micrometers [18, 66].

Critical factors determining the repassivation of metastable pits have not yet been clarified completely. One theory given by Frankel et al. [27, 28] based on the work in stainless steels is that pits repassivate when the protective pit cover ruptures resulting in dilution of the aggressive pit environment (Figure 2.2). The rupture event may be triggered by hydrogen evolution inside the pit.

Stable pitting and metastable pitting are closely related. Many efforts have been made to study metastable pitting to gain better understanding of stable pitting [51, 69, 77, 89, 102]. In these studies, the various parameters that characterize pitting such as peak pit current (I\text{pit} or I\text{peak}), growth time (\Delta t_g), repassivation time (\Delta t_r), or peak pit current density (i_{peak}) have been measured and characterized to explain the behavior of metastable pitting. Among them, Pride and Scully studied metastable pitting of pure aluminum and reported criteria for pit stability. [69]. They conducted a metastable pitting experiment for high purity Al foil in deaerated 10^{-3} M NaCl at a constant applied
potential of −0.5 V (vs. SCE). They defined the peak pit current, \( I_{\text{pit}} \) as the maximum pit current minus the baseline current [69]. In addition, the growth time of metastable pit, \( \Delta t_g \) (the time between initiation and the peak pit current) and the repassivation time of metastable pit, \( \Delta t_r \) (the duration between the peak pit current and the return to the baseline current) could be observed as a function of a constant applied potential. Peak pit current density, \( i_{\text{peak}} \), was calculated by dividing peak pit current by pit size. The size of metastable pit can be estimated from the charge passed during the growth time (\( \Delta t_g \)). Pride and Scully assumed that metastable pit on their high purity Al electrode was hemispherical and calculated radius of metastable pit using a Faraday relationship:

\[
\gamma_{\text{pit}} = \left( \frac{3AW}{2\pi F \rho} \right)^{\frac{1}{3}} \left( \int_{i_i}^{i_{\text{max}}} (i_{\text{app}} - i_{\text{ox}}) \, dt \right)^{\frac{1}{3}}
\]

Eqn. 2.8

where \( r_{\text{pit}} \) is the pit radius, \( AW \) is the atomic weight of pure Al (26.98 g/mol), \( z \) is the valence (3 equiv/mol), \( F \) is the Faraday's constant (96,487 C/equiv), \( \rho \) is the density (2.7 g/cm\(^3\)), \( i_{\text{app}} \) is the anodic current, \( i_{\text{ox}} \) is the passive current, \( i_i \) is the initiation time, and \( i_{\text{max}} \) is the time at which \( i_{\text{peak}} \) is reached [69]. They also measured the pit size by Scanning Electron Microscopy (SEM) and optical microscopy. From the comparison, they showed that actual metastable pit radius measured by optical microscopy is slightly larger than the calculated radius. It proved that the assumption of hemispherical pit and estimation by using a Faraday relationship is reasonable to evaluate metastable pit size on pure Al.

Pride and Scully used the calculated value of \( r_{\text{pit}} \) to define a condition for pit stabilization of pure Al, which is \( I_{\text{pit}} / r_{\text{pit}} > 10^{-2} \) A/cm. They plotted the data to find a
relationship between peak pit current, $I_{\text{pit}}$, and pit radius at peak pit current, $r_{\text{pit}}$. Their criterion for pit stability (*i.e.*, $I_{\text{pit}} / r_{\text{pit}} > 10^{-2}$ A/cm) states that transition from metastable to stable pitting occurs when the value of $I_{\text{pit}} / r_{\text{pit}}$ exceeds $10^{-2}$ A/cm. Similar values of the $I_{\text{pit}} / r_{\text{pit}}$ criterion had been reported by others. Williams *et al.* reported the same criterion to evaluate pit stabilization for stainless steels [101, 102]. Their criterion for pit stabilization was that $I_{\text{pit}} / r_{\text{pit}}$ should be more than $4.0 \times 10^{-2}$ A/cm for a metastable pit to stabilize. Other research on single crystal beryllium [51] also found that the value of $I_{\text{pit}} / r_{\text{pit}}$ should exceed $4.8 \times 10^{-2}$ A/cm for beryllium pit stabilization, which is slightly larger than those for pure Al [69] and stainless steels [101, 102].

The growth time of a metastable pit, $\Delta t_g$, is a key indicator for comparison of metastable to stable pits. Metastable pits start to repassivate after $\Delta t_g$, while stable pits that have grown for the same time ($\Delta t_g$) do not. The criterion for the growth of stable pits ($I_{\text{pit}} / r_{\text{pit}} \geq 10^{-2}$ A/cm) proves that currents of stable pits rise at a faster rate than those of metastable pits for the same initial time period, $\Delta t_g$. This assessment shows that there exists a pit growth relationship for each pit suggested by $I \sim (\Delta t_g)^a$ where $a_{\text{stable}} > a_{\text{metastable}}$. Pride *et al.* found that $a_{\text{metastable}}$ ranged from 0.03 to 0.4 with increasing the applied potential, whereas $a_{\text{stable}}$ was approximately 0.5 [69]. Hunkeler and Bohni showed that the stable pit growth in pure Al followed the $I \sim t^{1/2}$ relationship [40]. For stainless steels, Newman and Williams found the metastable pit growth relationships between $I \sim t^{1/2}$ and $I \sim t^2$ [24, 101, 102]. As the applied potential increased, the relationship of $I \sim t^{1/2}$ for metastable pit growth changed into $I \sim t^2$. 

17
There are many documents regarding metastable pitting occurring on aluminum [19, 40, 52, 69, 77], single crystal beryllium [51], titanium [17, 44] and stainless steels [8, 16, 24, 27, 37, 65, 66, 81, 88, 102]. Different materials exhibit different forms of transients. Typical metastable current transients in stainless steels consist of an initial rise that roughly corresponds to the relationship of \( I \sim t^2 \) followed by a subsequent sharp decay (Figure 2.1) [27]. Other investigations have reported the same type of the transients for stainless steels [65, 81]. Metastable current transients on a single-crystal beryllium exhibit a sharp increase in anodic current followed by sharp decay that is proportional to \( t^{-2} \). However, Cheng and Luo reported different type of current decay on type A516-70 carbon steel [18]. They divided the repassivation process into two steps. As repassivation starts the current quickly drops to an intermediate value and it slowly decays to background current. The slow current decay was proportional to \( t^{-0.5} \). They suspected that the existence of new deposit or corrosion product is possible and these caused the exponential decay [18].

2.2.4 Statistical Analysis of Pitting Corrosion

Pitting corrosion is characterized by large scatter in the experimental data. Pitting potentials, times of initiation, pit growth rates, and locations of attack in the passive film all show much dispersion. This nature of pitting requires a statistical analysis for a complete evaluation.

Shibata and Takeyama conducted statistical analysis for stainless steels [89]. They showed the distribution of \( E_{\text{pit}} \) of type 304 SS as a function of potential scan rate [89].
The distribution is plotted in a probability versus pitting potential [89]. The probability for pitting was defined as:

\[ P(E) = \frac{n}{1 + N} \]

Eqn. 2.9

where \( N \) is the total number of specimens examined, and \( n \) is the number of specimens that experienced pitting at a potential of \( E \) or lower. The median fraction, which comes at \( P(E) = 50\% \), is a representative point for a given experimental condition. Analysis of the pit initiation rate (\( \lambda \)) showed that it was proportional to the applied potential [89]. The pit initiation rate, which is the frequency of pit initiation per unit time, is given by:

\[ \lambda(t) = -\frac{d \ln P(t)}{dt} \]

Eqn. 2.10

where \( P(t) \) here is different from \( P(E) \). \( P(t) \) is the proportion of "non-pitted" specimens at time \( t \) and can be considered as a survival probability [89]. The survival probability \( P(t) \) is the proportion of non-pitted specimens:

\[ P(t) = 1 - P(E) = 1 - \frac{n}{1 + N} \]

Eqn. 2.11

The survival probability versus induction time as a function of applied potential can be plotted once the distribution of induction time is obtained at each applied potential
Survival probability decreased with the increase in applied potential at a fixed induction time, which indicates that more specimens were pitted as the potential was increased. The pit initiation rate, $\lambda(t)$, which is determined from the negative slope of $P(t)$ increased with the applied potential. The pitting susceptibility of pure Cu has also been statistically investigated using the pit initiation rate [71]. Qafsaoui and Mankowski calculated the pit initiation rate, $\lambda(t)$, deduced from the pit induction time distributions for pure Cu at several potentials between 100 and 550 mV (vs. SCE) in chloride-containing borate buffered solutions [71]. It was found that $\lambda(t)$ increases linearly with the applied potential as well as chloride concentration.

Williams and coworkers exploited and applied the ensemble statistic approaches set by Shibata into a metastable pitting study [99, 100, 102]. It was possible to extend Shibata's approaches for stable pitting to metastable pitting since metastable pits occur before stable pits, and shows the same stages (i.e., initiation, pit growth, and repassivation) as stable pits. Moreover, a great number of individual metastable pits can be generated, so statistical approaches are easily applied. Williams et al. characterized the transition from passivity to metastable pitting and finally stable pitting for stainless steels by developing the following equation [102]:

$$\Lambda = \lambda \exp(-\mu \tau_c)$$  \hspace{1cm} \text{Eqn. 2.12}

where $\lambda$ (cm$^{-2}$ s$^{-1}$) characterizes the time-independent homogeneous initiation rate of metastable pits. Each metastable pit has probability $\mu$ (cm$^{-2}$ s$^{-1}$) of repassivation, unless it goes beyond a critical age $\tau_c$ (s), at which it becomes stable. $\Lambda$ (s$^{-1}$) is the initiation
frequency of the stable pits. Here it should be noted that Williams' notation is different from that of Shibata who denoted $\lambda$ as the initiation frequency of stable pits [89]. The initiation frequency of metastable pits, $\lambda$ (cm$^{-2}$s$^{-1}$), can be derived from counting current peaks that exceed an arbitrary value and reported as around $+0.5$ $\mu$A from the base current line [100, 102]. The critical age, $\tau_c$ (s), was derived by analysis of the induction time distribution [100]. The repassivation probability of metastable pits, $\mu$ (cm$^{-2}$s$^{-1}$), was indirectly obtained from the slope of the induction time distribution [100]. Finally, the initiation frequency of stable pit, $\Lambda$ (s$^{-1}$), and its potential dependence was obtained by counting in an anodic scan rate, $\nu$ (Vs$^{-1}$), the number of pitted specimens of which current exceeded an arbitrary limit (10 $\mu$A in their work) [100, 102]. This was expressed in the following equation:

$$\Lambda = -\nu \frac{d \ln[P_r(E)]}{dE} \quad \text{where} \quad P_r(E) = \frac{n(E)}{N+1}$$

Eqn. 2.13

In this equation, the survival probability of potential $P_r(E)$ is equivalent to $P(t)$ in equation 2.11 where $n(E)$ is the number of the non-pitted specimens at potential $E$. To sum up, equation 2.12 that expresses the relationships between metastable and stable pitting implies the following idea:

Probability of formation of a stable pit = (Probability of initiation of a metastable pit) $\times$

(Transition probability from metastable to stable pit)
This concept was validated by the result that the rates of both $\Lambda$ and $\lambda$ exhibited similar dependence on potential, although their magnitudes were different (Figure 2.3) [102]. The concept also implies the significant notion that statistical characterization of stable pits can be achieved by statistical characterization for metastable pits, which are more easily and numerously obtained than stable pits. Based on the findings that there exists correlation between $\Lambda$ and $\lambda$, Williams et al. argued that the initiation frequency of metastable pit, $\lambda$, can be used to assess corrosion susceptibility without causing significant damage to the material. However, they also pointed out that $\lambda$ should not be a deterministic value to compare corrosion susceptibility of different materials [102]. Different sites of possible corrosion might be activated at different potentials for different materials [102]. In essence, $\exp(-\mu \tau_c)$ varies with material contributing to corrosion behavior in a way not characterized by $\lambda$ alone [102].

Sato and Newman showed evidence that alloying Zn into Al has more influence on the "transition probability from metastable to stable pit" (i.e., $\exp(-\mu \tau_c)$) than on "the probability of nucleation of a metastable pit" (i.e., $\lambda$) [77]. In deaerated 0.5 M NaCl, they investigated the effect of alloying Zn (0.02 and 0.13 wt %) in a solid solution Al on the behavior of metastable and stable pitting. In an analysis of metastable current transients, similar trends in $\lambda$ for 0.02 and 0.13 % Zn alloys and for pure Al as a function of time were observed (Figure 2.4). The result suggests that the frequency of metastable current spikes ($\lambda$) does not depend so much on the Zn content. Two characteristic quantities, $I_{\text{peak}}$ and $\Delta t_g$, were used to prove metastable pit propagation dependence on Zn content. As described earlier, $I_{\text{peak}}$ represents the peak current of a metastable pitting event and $\Delta t_g$ is
the metastable pit growth time (the time between initiation and the I_{peak}). It was found that the presence of 0.13 % Zn increased the I_{peak} to about five times as high as pure Al (Figure 2.5) [77]. The normal probability plots of Δt_{g} versus Zn content showed that by alloying 0.13 % Zn, the Δt_{g} was increased to about twice that of pure Al (Figure 2.6) [77]. These results unambiguously indicated that alloying Zn increased metastable pit growth kinetics by making metastable pits grow faster and for a longer time [77]. Although Sato and Newman did not mention the concept of Williams et al. (Equation (10)), it was shown that the alloying Zn in the Al matrix alters "the transition probability from metastable to stable pit" rather than modifying "the initiation frequency of metastable pit." Their conclusion is that Zn can act as an activator for Al by increasing the Al dissolution rate and enhancing the rate of metastable pit propagation [77]. Sato and Newman proposed that it is not necessary to hypothesize any other mechanism of Zn, such as chemistry change in the passive film by alloying element. This model was proposed by Moshier and coworkers studying on supersaturated Al-Mo, -Cr, -Va, and -Zr [20, 58, 59]. More details about the model of Moshier et al. will be introduced shortly. Muller and Galvele also reported that alloyed Zn in Al at very low levels activates the dissolution kinetics [60]. They showed that alloying of Al with Zn decreased the pitting potential as much as 200 mV [60].
2.3 ALLOYING EFFECTS ON CORROSION OF INTERMETALLIC PARTICLES

Pitting occurs when there is a local breakdown of protective oxide film on the metal surface followed by rapid dissolution of the underlying metal. Thus, research has focused on the properties of oxide film on aluminum alloys [7, 26, 34, 63, 90, 107]. However, studies of the oxide film alone cannot sufficiently characterize pitting susceptibility for aluminum alloys, because microstructural heterogeneity is the key factor in controlling the corrosion resistance for commercial alloys. This microstructural heterogeneity enhances a material's mechanical properties but weakens the corrosion resistance. The heterogeneity includes precipitates as well as constituent particles (i.e., second phase intermetallic particles). The size of these intermetallic particles ranges from 0.01 to 10 µm in diameter [14].

Pitting has been observed at intermetallic particles, in the surrounding Al matrix, or at the periphery of intermetallics adjacent to the matrix [43, 106]. One of the possible theories for the mechanism of pitting corrosion in aluminum alloys associated with intermetallic particles and surrounding Al matrix is the micro galvanic coupling theory. The theory attributes the localized breakdown to electrochemical potential difference between the particles and the matrix [11, 21, 29]. This electrode potential difference would initiate and accelerate the development of pitting in the more active phase. Micro galvanic coupling is governed by [72]:

i. Electrochemical properties of the matrix and the intermetallic particles,

ii. Cathode to anode ratio on the surface,
iii. Composition of the matrix and intermetallic particles,

iv. Composition of the electrolyte in contact with the particles.

To better understand localized corrosion due to galvanic coupling, many studies have examined the electrochemical behavior of several important intermetallic particles. The results have generally revealed that the $\theta$ (Al$_2$Cu) phase is noble with respect to its surrounding matrix [84, 92], and S (Al$_2$CuMg) as well as $\eta$ (Mg(Zn, Cu, Al)$_2$) phase are active with respect to the matrix [11, 15, 23, 54, 74, 75]. The local alkalinization model has been proposed to explain the interplay between intermetallic particles and matrix phase in Cu-bearing aluminum alloys. Vukmirovic et al. explained that dealloyed S phase serves as cathode active to oxygen reduction and matrix phase undergoes Al dealloying causing Cu enrichment [22, 23, 97]. Leclere and Newman simulated the alkalinization induced pitting by immersing Al-Cu solid solution alloys in high alkaline solutions [50]. They suggested that nano Cu particles are attributed to alkalinization and induced corrosion by acting as local cathode [50]. Their rationale is that local alkalinity will be generated by Cu particles, which will then dissolve Cu-bearing intermetallic particles and surrounding matrix phase. Nonetheless, there still is an unclear understanding of the micro galvanic coupling because, surprisingly, there is insufficient characterization of the electrochemical behavior of the alloy matrix phase.

This rest of section will cover a brief review of corrosion behavior of individual intermetallics. Then, in the following section, the review continues with the effects of alloying elements in solid solution with aluminum on corrosion behavior. This area has not been systematically investigated, although there are several in-depth documents. The
The most significant and well-known fact is that alloying Cu in a solid solution Al matrix increases pitting and corrosion potential, which is described as an ennobling effect [21].

2.3.1 Al2Cu (θ phase)

The strength of copper-containing Al alloys can be improved by precipitation hardening due to formation of Al2Cu (θ phase) intermetallic particles. Formation of the θ phase can be achieved by an age-hardening process, which produces a very fine dispersion of precipitate particles. Formation of a θ phase occurs via intermediate phases such as θ'' and θ' precipitates from Guinier-Preston (GP) zones by decomposition of supersaturated solid solution [30, 67]. GP zones can form if the aging temperature is held below the GP zone solvus curve in the Al-Cu phase diagram.

Many electrochemical experiments have reported that the θ phase is noble with respect to the Al matrix [31, 55, 70, 84]. For example, Scully et al. measured the open-circuit potential (OCP) for the bulk Al2Cu phase and pure Al in deaerated Cl− containing solutions of pH ranging from 2 to 10 [84]. The OCP results showed that the θ phase has a more positive potential than that of pure Al by as much as 750 mV depending on solution pH [84]. As a result the electrochemically ennobled θ phase supports a local cathodic reaction that consumes hydrogen ions. This results in high pH at the particle and the matrix boundary. The alkaline environment then dissolves the matrix. Localized corrosion was studied on sputtered Al-Cu alloy thin film containing the θ phase in an aged condition [82]. Most of the pits in the alloy were observed at grain boundaries where the θ phase precipitated [82]. Results showed that the θ phase enhanced the
cathodic reaction, resulting in an increase in the pit density and in the pit growth rate [82].

In the 1970s, Galvele and co-workers found that the $\theta$ phase is noble to both the Al matrix (Al-4 wt % Cu) and the Cu-depleted zone (Al-0.2 wt % Cu) [31]. Pitting resistance of Al with small amount of Cu retained in solid solution is higher than that of pure Al [61]. However, once the $\theta$ phase formed, the pitting resistance of the Al-Cu alloy was lower than pure Al [61]. Galvele et al. explained that the $\theta$ phase is detrimental to pitting resistance because its creation will produce a Cu-depleted zone near the phase, which has a lower pitting potential.

It should be noted that the Al$_2$Cu particle demonstrates appreciable anodic as well as cathodic kinetics relative to pure Al. Scully et al. observed an oxygen evolution reaction on the $\theta$ phase under anodic polarization [84]. It was argued that presence of metallic copper generates conductive oxide film on the $\theta$ phase, which supports oxygen evolution. The OCP of the $\theta$ phase measured was equal to or higher than the pitting potential of pure Al [84]. Electrochemical quartz crystal microbalance (EQCM) studies have been used to measure the cathodic corrosion rate of thin-film analogs of Al$_2$Cu phase [3]. It was shown that cathodic corrosion reaction is supported by Al$_2$Cu phase and the reaction can be inhibited by chromate.

2.3.2 Al$_2$CuMg (S phase)

Aluminum alloys with copper as the principal alloying element, such as AA2024-T3 (Al-4.4Cu-1.5Mg-0.6Mn), retain Cu in solid solution and in several second phase particles. Most of the particles are (Al, Cu)$_6$Mn, Al$_7$Cu$_2$Fe, and Al$_2$CuMg (S phase) in the AA2xxx series alloy [11]. Among these particles, the S phase is the most important one
in determining corrosion resistance, because the particles represent 60% of the total second phase particles ranging from 0.5 to 10 µm in diameter and cover ~ 3.0% of the total surface of AA2024-T3 [11].

There have been extensive studies on the electrochemical behavior of the S phase and its electrochemical behavior [10-13, 15, 22, 23, 96, 97]. The most significant feature of corrosion associated with the S phase compound has been found to be a redistribution and enrichment of copper. The redistributed and enriched copper on an Al-Cu-Mg alloy surface can cause deleterious effects on corrosion resistance by stimulating cathodic reactions (i.e., oxygen and hydrogen reduction reactions) and thereby increasing the corrosion rate. The open-circuit potential of the bulk S phase was measured to be active with respect to the alloy matrix [13]. This result predicts that dissolution will occur on the S phase rather than in the alloy matrix. A contradictory result was presented showing that pitting was observed in the matrix adjacent to the S phase, which indicates that the matrix was actually active to the S phase when pitting occurred [41]. Buchheit et al. showed evidence of S phase dealloying that answers at least partially why and how this complicated phenomenon was observed [11, 13, 15]. They proposed that the redistribution and enrichment of the copper by dealloying of the S phase is mostly responsible for poor corrosion resistance in Al-Cu-Mg alloys [11, 15]. The Al2CuMg particle is initially active with respect to the matrix so that the preferential dissolution of Al and Mg leaves behind Al2CuMg particles as a Cu-enriched remnant that is noble to the matrix.

Supporting evidence for the above mechanism has been reported. Electron optical analysis demonstrated that the hydrous corrosion product layer contains small metallic
Cu clusters (10 ~ 100 nm in diameter) [11], and real pit morphology for AA2024-T3 in a neutral 5.0 % salt-spray test showed deposits of metallic Cu [15]. A rotating ring-disk collection experiment (RRDCE) supports the facts that the non-faradic liberation as well as the following oxidation of Cu clusters can occur during the dealloying of S phase [15]. In this RDCE, Cu ions due to oxidation of Cu were formed by dissolution of the bulk S phase in 0.5 M NaCl, even though the dissolution occurred at potentials negative to the reversible potential of Cu.

Vukmirovic and co-workers also presented similar results supporting the copper enrichment and redistribution mechanism [97]. Scanning electron microscopy (SEM) revealed that the Cu-rich remnant after the dealloying of the S phase formed a porous sponge structure with very high surface area [97]. It is known that the re-distributable Cu can be released from the S phase particles and also from the matrix. The surface coverage fraction of the S phase in 2024-T3 is approximately 3.0 % [11], and there is believed to be ~ 0.2 to 0.5 wt % Cu in the alloy matrix [57]. It is not clear, however, which source releases more Cu for its redistribution. Vukmirovic et al. concluded that matrix dealloying and S phase dealloying equally contribute to the Cu redistribution during corrosion of AA2024-T4 in 0.5 M NaCl [97]. They also showed that the matrix dealloying mechanism leads to a change in pH around the S phase and its surrounding matrix. This mechanism describes how, as the reduction of oxygen (i.e., $2H_2O + O_2 + 4e^- = 4(OH)^-$) occurs on the dealloyed S phase, the pH of the local cathode increases to about 9.0 ~ 9.5 [2, 64], which results in an increase in the pH around the adjacent matrix. The alkaline environment is severe enough to dissolve aluminum selectively via the soluble $Al(OH)_4^-$ anion. This matrix dealloying can liberate Cu from
the matrix phase into Cu particles that will act as local cathodic sites, which enhances further matrix dealloying.

Another study using a rotating ring-disk collection experiment (RRDCE) was conducted to determine which mechanism (i.e., matrix dealloying or Cu-containing phase dealloying) plays the key role in releasing copper [6]. Al-Cu binary alloys were prepared by solution heat treatment (SHT) followed by artificial aging process. It was assumed that the collected amount of Cu would scale with the Cu content in the matrix if the matrix dealloying were the dominant mechanism. If the $\theta$ phase dealloying were prevailing, then the released Cu would be proportional to the volume fraction of the $\theta$ phase particles. In brief, they found that copper redistribution from $\theta$ phase dealloying is dominant on a short time scale, whereas the contribution of copper from matrix alloying prevails after a long immersion time.

2.3.3 Mg(Zn, Cu, Al)$_2$ ($\eta$ phase)

Electrochemical studies have shown that the $\eta$ phase is active with respect to the alloy matrix. The OCP of $\eta$ phase was measured at about $-1100$ mV (vs. SCE) in 1.0 M NaCl solution [54]. Sedriks et al. reported an OCP of $-1035$ mV (vs. SCE), which is not significantly different [85]. It is known that the $\eta$ phase has considerable solid solubility for Cu and Al. Ramgopal et al. studied the electrochemical behavior of the $\eta$ phase as a function of Cu and Al concentration in an attempt to understand IGC in AA7xxx series [74]. They prepared the $\eta$ phase as a form of thin film using a flash evaporation technique. Cyclic polarization experiments in deaerated 0.5 M NaCl were conducted for
three different compositions: MgZn$_2$, Mg(Zn, Cu)$_2$, and Mg(Zn, Al)$_2$. Their results showed that the OCP of MgZn$_2$ was $-1400$ mV (vs. SCE) in deaerated 0.5 M NaCl and was increased by as much as 250 and 300 mV when 17 and 27 atom % Cu were added, respectively [74]. The mechanism of why and how a small addition of Cu increased the OCP is not well known. The addition of Cu also raised the breakdown potential of MgZn$_2$ thin film. In contrast, the addition of Al did not alter the OCP and pitting potential of MgZn$_2$ notably. The cyclic polarization curve showed that there was a reduction of Zn during the reverse potential scans. This happened because the anodic forward scan dissolved Zn at the breakdown potential, and the dissolved Zn ion plated back during the cathodic reverse scan.

2.4 ALLOYING EFFECTS ON CORROSION OF MATRIX PHASE

The matrix in Al alloys can be considered to be a solid solution, having different concentrations of alloying elements from intermetallic particles. This has an effect on electrochemical properties. Hollingsworth and Hunsicker reported solution potentials of Al-X binary alloys (X; Cu, Si, Mg, and Zn) in an electrolyte of 53 g/L NaCl and 3 g/L H$_2$O$_2$ [39]. Though the authors did not mention it, the reported potential (i.e., solution potential) was equivalent to corrosion potential ($E_{\text{corr}}$) as well as pitting potential ($E_{\text{pit}}$) due to the high oxidizing environment by hydrogen peroxide. The solution potential shifted to more positive values as more elements such as Cu or Si were added in Al. The added Zn caused a reverse effect, which decreased the solution potential. There have been many noteworthy studies to explain the effect of alloying additions in Al solid
solutions [20, 28, 58-62, 73, 77, 78, 87]. Possible mechanisms for the protection induced by alloying element in solid solution of aluminum were identified from these literatures. The samples were solid solution phases of Al-X binary alloys (X; Cr, Mo, Ta, Zr, V, W, Nb, Zn and Mg) [20, 28, 58, 59, 62, 73, 76-78, 86, 87, 93]. Alloying noble elements like Mo, Cr, W, Nb or Cu increase the pitting potential, where alloying active elements like Ga, Hg, Mg or Zn decrease the pitting potential. In a broad view, two different explanations have been proposed; 1) chemistry change in the passive film by enrichment of alloying element and 2) change in dissolution kinetics. In a system of Al-Cu solid solutions, the exact mechanism by which operates is still not clear. It is expected that Cu might be enriched because frequently all the electrochemical reaction occurs well below the reversible potential of Cu. The enriched Cu might cause modification in oxide film chemistry as well as dissolution kinetics. Understanding the applicable mechanism will help to understand the interplay between intermetallics and the surrounding matrix. The details about these studies on the effect of alloying additions are reviewed in the following.

2.4.1 Local Acidification Model

Muller and Galvele were the first to report that Cu dissolved in solid solution increase the resistance to pitting corrosion in sodium chloride electrolytes [60, 61]. They measured pitting potentials of Al-Cu, Al-Zn and Al-Mg solid solutions in 1.0 M NaCl. The pitting potential was increased as much as 200 mV for an addition up to 4.0 wt % and decreased as much as 100 mV by 2.0 wt % Zn. Nevertheless, it should be noted that this improvement as a function of dissolved Cu content is only effective when the Cu
content is below the solid solubility limit. Once the amount of Cu exceeds this limit, Cu will unavoidably lead to a formation of second phase particle such as Al₂Cu in the host matrix as a result of aging process.

Muller and Galvele suggested a mechanism of local acidification on metal-electrolyte interface to explain the increased pitting potential by Cu and decreased pitting potential by Zn [32]. According to their model, the pitting potential is determined by following equation [32, 60]:

\[
E_{\text{pit}} = E_{\text{corr}}^* + \eta + \varphi + E_{\text{inh}}
\]

Eqn. 2.14

where \( E_{\text{pit}} \) is pitting potential, \( E_{\text{corr}}^* \) is corrosion potential of the metal in the pit-like solution, \( \eta \) is the overpotential needed to achieve a net anodic current through the pit, \( \varphi \) is the potential gradient inside the pit and \( E_{\text{inh}} \) is the contribution to the pitting potential due to inhibitors present in the electrolyte like \( \text{OH}^- \) ions. Muller and Galvele explained that a certain degree of local acidification is required to observe pitting potential and \( E_{\text{corr}}^* \) and \( \eta \) which determine \( E_{\text{pit}} \) are interplayed with local acidification. The localized acidification is determined by hydrolysis of Al cations:

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

Eqn. 2.15

\[
\text{Al}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Al}^{\text{OH})_3^- + 3H^+}
\]

Eqn. 2.16
Protons can be consumed by hydrogen evolution reaction—one of local cathodic reactions in pit inside—as expressed by:

\[ 2H^+ + 2e^- \rightarrow H_2 \]

Eqn. 2.17

They continued to explain that the localized acidification cannot be maintained at potentials around \( E_{corr}^* \) since the rate of hydrolysis of dissolved metal aluminum is equal to that of hydrogen evolution reaction. So the only way to produce protons that will lead to the localized acidification is to apply positive overpotential (\( \eta \)). This is the typical reason that pitting occurs at potentials equal to, or higher than, corrosion potential. They reported that the \( E_{corr}^* \) is increased when Cu is alloyed because the overpotential for hydrogen evolution on copper is lower than that on aluminum [60]. And this increased \( E_{corr}^* \) contributes the increase in pitting potential. The localized acidification model that Muller and Galvele have proposed could have been given more credit if evidence of local Cu enrichment was provided. They suspected the existence of Cu enrichment in pit inside after preferential dissolution of Al but they did not present it. What Muller and Galvele neglected in the model is that a greater overpotential (\( \eta \)) is essential to get enough acidification to increase pitting potential in Al-Cu alloys. It is considered that a relatively low acidic environment might be formed on Cu enriched layer in pit inside based on the observation that rate of hydrogen evolution consuming protons on passivated pure Cu is higher than that on passivated pure Al. Consequently, the only way to compensate the loss of protons on Cu enriched layers is to apply more positive overpotential (\( \eta \)) to
supply enough dissolved Al ions for its hydrolysis reaction. However, it is noted that this notion assumes that hydrogen evolution rate is still faster on non-passivated Cu than on non-passivated Al.

### 2.4.2 Chemistry Change in Passive Oxide Film

Increased resistance to localized corrosion in Al solid solutions has been attributed to the enhanced passivity due to the increased relative amount of oxidized alloying element compared to oxidized Al in the passive film. Moshier, Davis and coworkers proposed that the enrichment of oxidized alloying element caused by the preferential Al oxidation in passive films on supersaturated Al-transition metal solid solutions (Al-Mo, -Cr, -Ta, and –Zr) was responsible for increased pitting resistance [20, 58, 59]. In potentiodynamic polarization measurements, it was found that the pitting potential was increased in 0.1 M KCl as a function of concentration of the alloying elements [59]. Furthermore, investigation on the passive film by XPS revealed that Mo was present in the form of molybdate ($MoO_4^{2-}$) which was speculated to impede the ingress of chloride anions resulting in an increase in pitting resistance [59]. Similarly, oxidized forms of the solid solution elements (*i.e.* $MoO_4^{2-}$, CrOOH, Ta$_2$O$_5$ or ZrO$_2$) in the passive film were proposed to inhibit the adsorption of chloride ions, and increase resistance to pit initiation. For Al-Cr, XPS analysis revealed that the passive film was enriched with CrOOH that acted as a barrier for Cl$^-$ and for oxygen movement. The Cr exhibited two oxidation states, Cr$^{3+}$ and Cr$^{6+}$, depending on its concentration in the substrate. For low Cr content, Cr$^{3+}$ ion was observed below the pitting potential, while the Cr$^{6+}$ state was dominant above the pitting potential. But in the case of high Cr content,
the prevalent form was Cr\textsuperscript{6+} in concentrations that increased with increasing anodic
overpotential. The soluble CrO\textsubscript{3} oxide from Cr\textsuperscript{6+} was non-protective [59]. Compared to
the passive film on Al-Mo, a thinner oxide film was observed on Al-Cr. It is not well
understood why the passive film on Al-Cr was much thinner than that on Al-Mo.

For Al-Ta alloys, Davis et al. showed that the pitting potential was much higher
than that of pure Al [20]. Enrichment of Ta\textsubscript{2}O\textsubscript{5} in the passive film was detected after
immersion and polarization in KCl and Na\textsubscript{2}SO\textsubscript{4} solutions. It was suggested that the
preferential oxidation of Al leads to the enrichment of oxidized Ta and the subsequent
formation of Ta\textsubscript{2}O\textsubscript{5} at the metal/film interface, which acts as a barrier layer to the
migration of Cl\textsuperscript{−} and oxygen [20]. It was proposed that the pitting took place due to the
local breakdown of the Ta\textsubscript{2}O\textsubscript{5} film; however, no evidence was given to support this
hypothesis [20]. Their research continued on Al-Zr alloy, and they found similar results
to Al-Mo, Al-Cr and Al-Ta, which was ZrO\textsubscript{2} enrichment in the passive film on Al-Zr
alloy [20]. The potentiodynamic polarization curve in deaerated 0.1 M KCl illustrated the
OCP and the pitting potential for Al-Zr as well as Al-Ta, Al-Mo, Al-Cr, Al-Si and Al-Cu
alloy (Figure 2.7) [20]. The passive region from OCP up to the pitting potential in Al-Zr
was comparatively smaller by as much as \sim 150 mV compared to Al-Ta. It was suggested
that the enriched Zr is less effective in inhibiting the migration of Cl\textsuperscript{−} and oxygen because
the ZrO\textsubscript{2} film on Al-Zr alloys is thicker and, hence, less protective [20]. Al-Ta and Al-Zr
alloys have only one oxidized form of solute, which are Ta\textsubscript{2}O\textsubscript{5} and ZrO\textsubscript{2}, respectively. On
the other hand, Al-Mo and Al-Cr generated up to three different oxidized states.

As discussed above, solid solution alloying may change the chemistry of the
passive film in such a way as to enrich the solute elements (i.e., Mo, Cr, Ta, and Zr) after
the dissolution of the more reactive Al. The oxidized solute (i.e., $MoO_4^{2-}$, CrOOH, $Ta_2O_5$ and $ZrO_2$) will inhibit the adsorption of $Cl^-$, which is responsible for the increased resistance against pitting. Natishan et al. proposed another inhibiting mechanism for chloride anion adsorption [62]. They explained that the inhibition of $Cl^-$ adsorption could be attributed to the pH of zero charge of an oxide ($pH_{pzc}$). The $pH_{pzc}$ is defined as the pH at which the surface of the oxide has a net zero charge [62]. It was argued that the alloying lowers the $pH_{pzc}$ increasing the range of conditions when the passive film has a net negative charge. This negative net charge on the oxide surface will attract cations, and therefore prevent the adsorption of chloride anions.

The solute enrichment mechanism seems to be valid for Al-X binary alloys (X; Mo, Cr, Ta and Zr). However, Shaw et al. showed contradicting results from Al-W thin film [86, 87]. A considerable increase in the pitting potential was presented by alloying W in solid solution aluminum, in spite of the finding that W was depleted and not enriched in the passive film on Al-W alloys [87]. They argued that the passivity enhancement of Al-W might originate from a structural modification that removes the atomistic defect structure by alloying W. It was suggested that Reflection-extended x-ray absorption fine structure spectroscopy (reflEXAFS) might be able to measure the structure property of the passive oxide film on metal. Studies on the passive films of aluminum alloys turn out to be insufficient to rationalize the effects of every alloying element. In certain cases like Cr and Ta, there is an enrichment of alloying elements in the passive film. However, the enrichment is not significant for Al-Mo alloy. Moreover, even depletion of the solute is observed with an increase in pitting resistance for Al-W
alloys. Direct evidence elucidating the relationship between the increase in pitting potential and the chemistry change in the passive film has not been clearly established.

Inturi and Smialowska suggested a different point of view based on the solubility of the oxides of the alloying elements in active pitting. They proposed that the solute elements play a more important role in the active pit surface than in the passive film. It was argued that the increase in pitting potential has to do with a decrease in the solubility of the oxides of the alloying elements. In the presence of alloying elements whose oxides are stable, a lower pH is needed to hydrolyze these oxides, which would therefore require a higher potential. Thin films by addition of W, Mo and Nb into pure Al were tested, and their results indicated the relationship between oxides solubility and pitting potential [42]. The challenge of this view is that the thermodynamic solubilities they used are different from the experimental solubilities. The solubility they referred to was under the condition of pH 0, which was normally too acidic for pit environments in aluminum alloys.

2.4.3 Change in Dissolution Kinetics

Frankel and Newman suggested that the major effect of alloying elements in solid solution Al is to alter the pit dissolution kinetics rather than to change chemistry in the passive film [28, 77]. Frankel et al. studied pitting behavior on several sputter-deposited thin films of aluminum alloys [28]. The added elements were Mo, Cr, Mn, W, V and Nb in the form of thin film (100 ~ 200 nm). The electrolyte tested was 0.1 M NaCl. Analysis of repassivation, pitting potential, and pit current density revealed that the main role of solute enrichment was to change the pit growth. The repassivation potential in bulk material varies with experimental parameters, such as the scan rate and the potential at
which the applied potential is reversed in cathodic direction. However, in thin film, repassivation potential is reproducible and meaningful in that pits in thin films grew in 2-dimensional fashion due to the limited depth for growth, and repassivated when the critical pit environment for pit stability was not satisfied [28]. Pits could not initiate until the pitting potential and the initiated pit stopped growing at the repassivation potential. Pits could not grow below the repassivation potential. According to this notion, the finding that repassivation potentials of Al-Nb alloys were higher than pitting potential of pure Al is consistent with the pit growth interpretation of pitting resistance (Figure 2.8) [28]. The results showed that repassivation potential was ~ 100 mV lower than the pitting potential, and this difference did not depend on alloying concentration variation (Figure 2.8) [28]. Therefore, it was clear that the contribution of passive film to the increased pitting resistance was smaller than the pit growth consideration. According to their explanation, there are two sets of conditions for the pit to repassivate. One is the tendency for the material to repassivate related to the critical pit current density and the critical pH in the pit. The other is the ability of the pit to maintain a critical environment at a controlled potential, which is related to the dissolution kinetics [28]. In order to keep stable pits growing in a strongly passivating material, the critical pH must be low enough. Since cation hydrolysis controls the pH in the pit, a higher cation concentration and a consequent higher critical pit current density are required to drop pH in the pit. A material that readily repassivates must show a higher critical pit current density in order to maintain the growth of stable pits. The results showed that the current density below which pits repassivate was constant as a function of Nb or Cr content [28]. They
attributed this to a decrease in the ability of the dissolving metal to maintain the critical pit environment as a result of ennobled dissolution kinetics [28].

Ras and Pistorius showed that dissolution kinetics was not a critical factor to the increased pitting potential by vanadium additions in 18 % chromate ferritic stainless steels [76]. They measured metastable pit growth of the stainless steels and also conducted artificial pit electrode experiments to find out any change in dissolution kinetics by vanadium additions. It was concluded that there exists no single dominant effect by alloying vanadium. Unlike molybdenum additions in stainless steels, vanadium did not decrease dissolution rates. Instead, they studied the effect of vanadium on metastable pits and concluded that the reduced initiation frequency of metastable pit was more or less attributable to the increased pitting resistance by alloying vanadium [76].

There was research on Al-Cu solid solutions in terms of Cu effect on dissolution kinetics [73]. Cu was reported to ennoble the dissolution kinetics by showing that repassivation potentials were raised by Cu contents in Al-Cu solid solution alloy (Figure 2.9). The study also found out that Zn increases the dissolution kinetics in Al-Zn solid solution whereas Mg has little effect on the dissolution kinetics of Al-Mg solid solution.

2.5 CRITICAL ISSUES

2.5.1 Mechanism of Alloying Cu in Solid Solution Aluminum

It is well known that the galvanic coupling between the intermetallics and the surrounding matrix plays a key role in reducing corrosion resistance in commercial aluminum alloys. Based on the literature review on the corrosion behavior of
intermetallics and alloy matrix in Al alloys, it is obvious that most of the systematic efforts have been focused on several key intermetallic phases but not much on the matrix phase. The Cu enrichment and redistribution mechanism has been suggested and demonstrated to be effective in explaining the corrosion behavior of S and θ phase particles. However, no plausible mechanism for the ennobling effect of Cu in solid solution Al has been presented. Although two different views on the effect of alloying elements have been proposed (i.e., chemistry change in passive oxide film and change in dissolution kinetics), it still remains in question which of the two models is dominant, or whether the combination of the models is prevalent, or if there is another mechanism for the ennobling effect of alloying Cu in Al solid solution.

2.5.2 Metastable Pitting Behavior of Al-Cu Binary Alloys

Sato and Newman investigated the metastable pitting behavior of Al-Zn binary alloys and concluded that the change in dissolution kinetics is mostly responsible for the activating effect of Zn in solid solution Al [77]. Frankel and co-workers suggested that alloying noble elements such as Nb, Mo, Ta, Cr, V and W in pure Al should ennable the dissolution kinetics rather than alter chemistry in the passive oxide film [28]. However, there has been no investigation on the metastable pitting of Al-Cu solid solution alloys systemically. This study should help to determine whether the change in dissolution kinetics also has the greatest influence on the ennobling effect of Cu in solid solution Al.
2.5.3 Surface Characterization in the Passive Film of Al-Cu and Al-Mg-Cu Alloys

Moshier and coworkers proposed the other mechanism stating that the chemistry change in the passive film is responsible for the effect of alloying elements in pure Al [20, 58, 59]. Although there have been many reports about the increase in pitting potential \( (E_{\text{pit}}) \) of Al-Cu binary alloys compared to pure Al, no extensive surface characterization in the passive film has ever been investigated. By using various surface characterization tools such as XPS, TEM and SEM/EDS, a better understanding of the chemistry in the passive film of Al-Cu binary alloys should help to find out the mechanism of the ennobling effect of Cu.

2.6 Research Objectives

In an attempt to understand alloying Cu effects on Al-Cu solid solution alloys, we carried out a two-part study aimed at characterizing the events leading up to the stabilization of pitting. The first part involves a detailed electrochemical characterization of individual and ensemble metastable pitting events. The methods of Sato and Newman [77] have not been used to characterize pitting and individual metastable pitting data such as \( I_{\text{peak}}, \Delta t_g, \) and \( \Delta t_r \) in Al-Cu solid solutions with variable Cu content. The second part involves a thorough characterization of the evolution of oxide film chemistry during potentiostatic polarization in the passive regime and as metastable pitting evolves. The surface characterization will employ XPS, TEM and EDS in combination with SEM to examine the chemistry in the passive oxide film and whether an enrichment of Cu after the dissolution of Al-Cu solid solutions occurs. By combining the information obtained
from these two approaches, it is intended to develop a comprehensive and consistent model accounting for the effect of solid solution alloying elements on the pitting behavior of Al alloys. On a practical basis, combined characterizations from intermetallics and matrix corrosion should contribute in understanding why the localized corrosion morphologies and stress corrosion cracking (SCC) behaviors are so different between the 2xxx and 7xxx series aluminum alloys.
Figure 2.1: Typical anodic current transient of metastable pits by potentiostatic measurement on type 302 Stainless Steel [27].

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Figure 2.2: Schematic diagram of a repassivating metastable pit [27].

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Figure 2.3: Variation of (a) the metastable pit nucleation frequency $\lambda$ and (b) the stable pit nucleation frequency $\Lambda$ with constant applied potential for different stainless steels [102].

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Figure 2.4: Frequency of metastable pit nucleation ($\lambda$) for 0.02 % Zn and 0.13 % Zn alloys and pure Al in 0.5 M NaCl at $-0.75$ V vs. SCE [77].

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Figure 2. 5: Normal probability plot of $I_{\text{peak}}$ (peak pit current of metastable pit) in 0.5 M NaCl at $-0.75$ V vs. SCE [77].

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Figure 2. 6: Normal probability plot of $\Delta t_g$ (pit growth time) in 0.5 M NaCl at $-0.75$ V vs. SCE [77].

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Figure 2. 7: Potentiodynamic polarization curves showing the effects of alloying elements on the OCP and $E_{\text{pit}}$ in deaerated 0.1 M KCl [93].

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Figure 2. 8: Effect of increasing Nb in aluminum on the pitting and repassivation potentials [28].

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Figure 2.9: Repassivation potentials of Al-Cu solid solution as a function of Cu content [73].

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CHAPTER 3

A CHARACTERIZATION OF THE INHIBITING EFFECT OF CU ON
METASTABLE PITTING IN DILUTE AL-CU SOLID SOLUTION ALLOYS

3.1 INTRODUCTION

Copper is a potent precipitation-strengthening agent in aluminum. Cu additions up
to about 5.0 wt % lead to alloys with very high strength and good toughness when
subjected to natural or artificial aging. It is generally understood that gains in mechanical
properties that derive from Cu alloying and aging also result in a decrease in corrosion
resistance due to the formation of Cu-rich intermetallic particles. These particles tend to
localize electrochemical activity on the alloy surface and induce pitting and intergranular
forms of corrosion [1-14].

An effect of Cu alloying additions not as widely appreciated is inhibition of localized
corrosion in its initial stages. This effect is observed almost exclusively in Al-Cu solid
solutions. For example, in an early study of this subject, Muller and Galvele examined
the effect of Cu content on pitting potentials of Al-Cu solid solution in alloys in sodium
chloride solutions [15, 16]. An increase in the pitting potential of 200 mV was observed
in 1.0 M NaCl solution as the solid solution Cu content increased from 0.0 to 5.0 wt. %. It was further noted that if these solid solutions were aged to induce the formation of θ phase precipitates, Al₂Cu, the pitting potential of the alloy was decreased to a level commensurate with the pitting potential of Cu-depleted zones around precipitates. While the origins of the reduction in pitting potential upon artificial aging may be debated, this loss in corrosion resistance by Cu-rich particles is the more familiar effect of Cu alloying on the corrosion of Al alloys [3, 4, 8, 9].

Increased resistance to localized corrosion in other Al solid solutions has been attributed to the enhanced passivity due to enrichment of the oxidized alloying element in the passive film. Moshier, Davis and coworkers proposed that the enrichment of oxidized alloying elements in passive films on supersaturated Al-transition metal solid solutions (Al-Mo, -Cr, -Ta, and –Zr) was responsible for increased pitting resistance [17-19]. In potentiodynamic polarization measurements, it was found that the pitting potential increased in 0.1 M KCl with increasing concentration of the element in the alloy [18]. Investigation on the passive film by x-ray photoelectron spectroscopy (XPS) revealed that the Mo was present in the form of molybdate (MoO₄⁻²), which was proposed to impede the ingress of chloride anions leading to an increase in pitting resistance. Similarly, oxidized forms of the solid solution elements (i.e. MoO₄⁻², CrOOH, Ta₂O₅ or ZrO₂) in the passive film were proposed to inhibit the adsorption of chloride ions, and increase resistance to pit initiation.

Shaw et al. showed somewhat contradictory results from Al-W supersaturated solid solutions [20]. In potentiodynamic polarization measurements, the pitting potential was found to increase with increasing W content in the alloy. Interestingly, surface
analysis showed that W (in oxidized form) was depleted in the passive film compared to the underlying alloy substrate. It was argued that the passivity enhancement of Al-W originated from a structural modification of the film by W due to removal or modification of the atomistic defect structure.

Others have proposed that the increased localized corrosion resistance of solid solution alloying elements is predominantly determined by the effects on local dissolution kinetics [21-24]. Frankel *et al.* studied pitting behavior of a range of several sputter-deposited supersaturated Al alloy thin films (100 to 200 nm Al-Mo, -Cr, -Mn, -W, -V and -Nb) in 0.1 M NaCl [21]. Ennoblement of repassivation potentials, pitting potentials, and pit dissolution kinetics by these alloying element additions was thought to decrease the ability to maintain a critical environment for pit growth rather than to increase the ability of pits to repassivate. Sato and Newman conducted a comparative study of metastable pitting of very dilute Al-Zn solid solutions and pure Al to understand the activating effect of Zn in an Al [22, 23]. Results showed that the metastable pit initiation rate was independent of Zn concentration in the alloy. However, metastable pit growth kinetics was increased leading to overall decrease in pitting potential for such alloys.

In this study, we have used experimental approaches similar to those of Sato and Newman to characterize the effect of Cu on the metastable of pitting of Al-Cu solid solutions [22, 23]. Specifically, we have examined the effect of solid solution Cu on the frequency of metastable pit initiation, pit current density ($i_{\text{peak}}$), pit growth rate ($I_{\text{peak}}/t_g$), pit growth time ($t_g$), peak pit current ($I_{\text{peak}}$), pit repassivation time ($t_r$) and pit repassivation rate ($I_{\text{peak}}/t_r$). An analysis based on these results indicates an important
contribution to the inhibiting effect of Cu in Al-Cu solid solutions is associated with a
decrease in the nucleation rate of metastable pits and a decrease in the metastable pit
propagation rate. Both effects are expected to contribute to decrease the probability of pit
stabilization and result in an increase in the observed pitting potential.

3.2 EXPERIMENTAL METHODS

3.2.1 Pitting potential ($E_{\text{pit}}$) measurements

Measurements were carried out using 180 µm or 500 µm diameter 99.999 % pure
aluminum wires from Puratronic, Alfa® Aesar® (hereafter Al 99.999), 150 µm diameter
Al-2.0 wt.% Cu (hereafter Al-2.0Cu), and 130 µm diameter Al-2.0 wt.% Zn (hereafter
Al-2.0Zn) wire. Al-2.0Cu and Al-2.0Zn wires were specially prepared by Ames
Laboratories, Ames, IA. The Al 99.999 wires were used in the as-received condition
while the Al-2.0Cu and Al-2.0Zn were solution heat-treated for one hour at 535 °C and
480 °C, respectively, followed by a quenching in cold water to retain Cu and Zn in solid
solution. Dimensions of the wires and their solution heat treatments are summarized in
Table 3.1. Electrode arrays were constructed by potting 25 wire samples in epoxy in a 5 x
5 element array. In order to reduce crevice corrosion, a low viscosity epoxy (EPO-THIN
by Buehler®) was used to pot the wire arrays. Arrays were then polished gradually and
carefully up to 1200 grit SiC paper. In order to minimize precipitation in the Al-Cu solid
solution alloys, samples were stored under refrigerator at 0 to −20 °C except when they
were being potted, polished or electrochemically tested. The total time from solution
treating and quenching to the completion of electrochemical testing did not exceed five
days for any array used in this study to further limit precipitation and to enhance repeatability among replicate measurements.

Pitting potential measurements were made in aerated 0.1 M NaCl solutions on electrode arrays using a Model 900 Multichannel Microelectrode Analyzer (MMA) (Scribner Associates). The MMA controlled a three-electrode measurement comprising single counter and reference electrodes and the 25-segment working electrode. The current in each segment in the working electrode was recorded individually. A scan rate of 0.5 mVs$^{-1}$ was used for all measurements. Data analysis was carried out using MMA Live software installed in a personal computer.

3.2.2 Metastable pitting measurements with Al 99.999 and Al-Cu solid solution alloys

Al 99.999, Al-2.0Cu and Al-0.2 wt.% Cu (hereafter Al-0.2Cu) were prepared to analyze metastable pitting transients during potentiostatic polarization in argon-deaerated 0.1 M NaCl solution. Al-0.2Cu was prepared by induction melting. The compositions of Al-2.0Cu and Al-0.2Cu plates were confirmed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) on small samples completely dissolved in a fixed volume of acid solution. Samples that were 1.0 cm in thickness were cold rolled to a final thickness of 0.5 cm. Samples were then mounted in epoxy and finished with 1200 grit SiC paper polishing in ethyl alcohol. The procedure of exposing the sample area was similar to methods described by Lillard [25]. To reduce crevice corrosion, 3M Electroplating tape® with a hole cut by a punch was pressed down onto the sample surface. Apiezon black wax was applied along the interface of metal and the tape. The
final exposed area was between 0.08 and 0.10 cm² (Table 3.1). Between successive experiments, these samples were solutionized and quenched into cold water to minimize precipitation in the alloys. Samples were carefully examined for the evidence of crevice corrosion after experiments. Results were discarded if crevice corrosion was suspected. In order to obtain a fully deaerated electrolyte, the 0.1 M sodium chloride was sparged for at least 8 hours before all the tests. These experiments were carried out using a PC4™ potentiostat (Gamry Instruments, Inc.) operated at a data collection frequency of 10 Hz. The samples were allowed to stabilize in solution under free corrosion conditions for one hour prior to polarization. Upon polarization, current transients were recorded for 5,400 seconds for Al 99.999 and Al-0.2Cu and 3,400 seconds for Al-2.0Cu. For all of the experiments described above, a saturated calomel electrode reference electrode and platinum sheet counter electrode (12 cm²) were used. All potentials are referred to against the saturated calomel electrode potential (+0.241 V vs. standard hydrogen electrode).

3.3 RESULTS
3.3.1 E_{pit} of Al solid solutions

Copper additions to aluminum increase the pitting potential (E_{pit}) provided that Cu is retained in solid solution. Figure 3.1 shows cumulative distribution plots of E_{pit} for Al 99.999 (area of 2.5 x 10^{-4} cm²), Al-2.0Cu (area of 1.8 x 10^{-4} cm²) and Al-2.0Zn (area of 1.3 x 10^{-4} cm²) determined from potentiodynamic polarization, which illustrate the nature and magnitude of the ennobling effect of Cu on E_{pit}. The E_{pit} distribution of Al-2.0Cu ranged from −0.6 to −0.4 V and was shifted towards more positive potentials
compared to Al 99.999. Al-2.0Zn showed the most negative $E_{\text{pit}}$ distribution, but was just slightly more negative than that of Al 99.999.

### 3.3.2 Metastable pitting of Al 99.999 and Al-Cu solid solution alloys

Figure 3.2 shows anodic polarization curves for Al 99.999, Al-0.2Cu and Al-2.0Cu solid solution alloys in deaerated 0.1 M NaCl. In these plots $E_{\text{corr}}$ and $E_{\text{pit}}$ increase as Cu content increases. The addition of 2.0 wt.% Cu measurably reduces the passive current density and apparently eliminates all episodes of metastable pitting prior to the onset of stable pitting.

To characterize the dependence of metastable pitting on Cu content, samples were potentiostatically polarized at various potentials in the passive region several tens of millivolts below the median $E_{\text{pit}}$ values determined from replicate polarization curve measurements. Figure 3.3 shows metastable pitting in the current versus time records for Al 99.999 collected at potentials between $-0.70$ and $-0.67$ V. In each case, discrete short spikes from pitting events are superimposed on a slowly decaying background current. There is no obvious difference in the frequency of metastable pit initiation at the three potentials, but the peak heights decrease sharply as the applied potential is reduced from $-0.67$ to $-0.70$ V.

The current versus time records for Al-2.0Cu collected over a potential range immediately below its pitting potential (from $-0.59$ to $-0.69$ V) showed remarkably different behavior (Figure 3.4). At $-0.59$ V, which is at the foot of the $E_{\text{pit}}$ cumulative distribution curve in Figure 3.1, the sample formed a stable pit within 10 seconds. At lower potentials, a gradual decay in the measured current was observed, but all current
transients associated with metastable pitting events were absent or below detection limits. The absence of metastable pitting at −0.67 or −0.69 V is not surprising given the polarization curve for Al-2.0Cu shown in Figure 3.2. However, over the whole potential range examined, current-time records either showed no metastable pitting, or pitted in a stable manner without evidence of prior metastable pitting.

Figure 3.5 shows current versus time records for Al-0.2Cu electrodes potentiostatically polarized in the potential range below its pitting potential (−0.66 to −0.69 V). The electrode polarized at −0.66 V pitted stably in about 300 seconds. The other records show current transients superimposed on a decaying background current. The effect of Cu on metastable pitting is most apparent in a comparison of the current versus time records shown in Figure 3.6. This figure shows current versus time records for Al 99.999 at −0.70 V and Al-0.2Cu and Al-2.0Cu at −0.69 V. Even though Al 99.999 was polarized at a slightly lower potential, the magnitude of the current and the intensity and frequency of metastable pitting as indicated by the current spikes were much greater than either Cu-bearing alloy. The Al-2.0Cu sample showed essentially no metastable pitting. In all three alloys the apparent background current density decreases with increasing exposure time unlike other results, which showed a decrease and a gradual increase in current [22, 23, 26]. This increase in the apparent background has been attributed to acidification of the interfacial electrolyte [22, 23].

Quantitative analysis of the current versus time records for Al 99.999 and Al-0.2Cu shows that small additions of Cu significantly lower the metastable pit initiation rate. Figures 3.7 and 3.8 show initiation rates for Al 99.999 and Al-0.2Cu at potentials ranging from −0.67 to −0.70 V. In both alloys, rates decrease with increasing exposure
time. They decrease sharply for Al-0.2Cu and somewhat less sharply for Al 99.999. The initiation rate for Al-0.2Cu is about an order of magnitude lower than for Al 99.999 and drops to less than 10 events per 500 sec at both potentials for which records are shown.

The current versus time records also show that the peak current developed by metastable pits is reduced by the addition of 0.2 wt.% Cu. Figures 3.9 and 3.10 show cumulative distribution plots of the peak pit current, $I_{\text{peak}}$, developed by metastable pits in Al 99.999 and Al-0.2Cu. $I_{\text{peak}}$ was taken as the difference between the maximum current measured in a transient and the apparent background current. For Al 99.999, the median $I_{\text{peak}}$ increases from about 40 to 200 nA as the potential increases from $-0.70$ V to $-0.67$ V. By comparison, there is no increase in the median $I_{\text{peak}}$ of about 30 nA for Al-0.2Cu as applied potential increases from $-0.69$ and $-0.67$ V. For Al-0.2Cu, the magnitude of the largest metastable pitting events at $-0.67$ V is greater than those at $-0.69$ V, but they are more than an order of magnitude smaller than the largest events in Al 99.999.

Metastable pit growth and repassivation rates for Al 99.999 at $-0.70$ V, and Al-0.2Cu at $-0.69$ V were calculated using methods described by Sato and Newman [27]. The current versus time records in this comparison were collected at different potentials, but these represent the best comparison that could be made from these experiments in view of constraints imposed by the desire to avoid the onset of stable pitting within the 5400 second record interval and the need to clearly resolve current transients from one another.

Figures 3.11 and 3.12 show the current versus time trace of single metastable pitting transients for Al 99.999 and Al-0.2Cu, and provide graphical definitions of the key characteristics of these transients. Slightly different parameter definitions were needed for each alloy as noted below. For Al 99.999, $I_{\text{peak}}$ is a peak pit current ($\sim 40$ nA)
above the background current, $I_{BG} \sim 60$ nA. $I_{apex}$ is the sum of $I_{peak}$ and $I_{BG} \sim 100$ nA, $t_g$ is pit growth time, and $t_r$ is pit repassivation time. For Al-0.2Cu, $I_{peak}$ and $I_{apex}$ are defined as they were for Al 99.999. Repassivation of Al-0.2Cu occurred in two distinct steps. From the point where the current fell sharply, repassivation began. At longer times the current decreased at a slower rate. Both steps in the repassivation process were characterized by a time increment ($t_{r1} + t_{r2} = t_r$), and a total current drop ($I_{rep1} + I_{rep2} = I_{apex} - I_{BG2}$). The first stage of repassivation was differentiated from the second stage by drawing a straight line starting at $I_{apex}$ through the next several data points. The demarcation between stage one and two was taken to be the point where the fit and the measured current data diverged.

Apparent pit radii, $r_{pit}$, were estimated using the total charge passed, plus 15 % to account for oxidation current consumed by hydrogen reduction in pits on the electrode [28], and Faraday’s law. In these estimates, it was assumed that pits were hemispherically shaped, 3 equivalents of charge were passed per mole of alloy oxidized, the molar mass of the alloy was 27 g/mol, and the density (both alloys) was 2.7 g/cm³.

3.3.3 Metastable pit initiation

Figure 3.13 shows the frequency of metastable pit initiation for Al 99.999 and Al-0.2Cu as a function of exposure time during potentiostatic polarization at $-0.70$ and $-0.69$ V vs. SCE, respectively, in 0.1 M NaCl. The initiation rate is reported as the number of rising current spikes above the background current per 500 seconds time interval. Both Al 99.999 and Al-0.2Cu showed decreasing metastable pit initiation rates with increasing exposure time suggesting consumption of a finite number of initiation
sites on the sample surface. Despite the fact that Al-0.2Cu was polarized to a slightly higher potential than Al 99.999, a lower passive background current was exhibited and the pit initiation rate was smaller by about one order of magnitude. The pit initiation frequency for Al-2.0Cu was essentially zero and was not plotted.

3.3.4 Metastable pit growth

Figure 3.14 and Figure 3.15 show cumulative distribution plots of peak pit current, \( I_{\text{peak}} \), and pit growth time, \( t_g \), respectively. These parameters characterize metastable pit growth. In Figure 3.14 the median of the distribution of \( I_{\text{peak}} \) for Al 99.999 is 1.3 times higher than that of Al-0.2Cu. Some of the metastable events for Al 99.999 exhibit peak pit current values of more than 100 nA, while peak pit currents for Al-0.2Cu tend to be somewhat smaller and less dispersed. For Al-0.2Cu, the largest \( I_{\text{peak}} \) was 60 nA and the smallest \( I_{\text{peak}} \) was 15 nA.

Cumulative distributions for pit growth time (\( t_g \)) are shown in Figure 3.15. These are nearly same for Al 99.999 and Al-0.2Cu ranging between 0.1 and 1.2 sec. Metastable pit growth rate (\( I_{\text{peak}}/t_g \)) was determined from the peak pit current and the growth time are shown in Figure 3.16. The growth rate of Al 99.999 is 1.3 times higher than that of Al-0.2Cu at the median of the distribution reflecting mainly the difference in \( I_{\text{peak}} \) between the two alloys.

3.3.5 Repassivation

An initial comparison of individual metastable pit transients suggests that repassivation of pits in Al 99.999 (Figure 3.11) is considerably more prompt than Al-
Repassivation of Al-0.2Cu consistently displayed a distinctive two-stage behavior. The first stage ($t_{r1}$) was prompt, with current dropping sharply from $I_{apex}$. The second stage ($t_{r2}$) was characterized by an episode of much slower current decay. Figure 3.17, a cumulative distribution plot comparing the prompt repassivation duration for Al-0.2Cu ($t_{r1}$) to the total repassivation duration in Al 99.999 ($t_r$), suggests that Cu in solid solution enhances prompt repassivation. However, the corresponding repassivation rates ($I_{peak}/t_r$, or $I_{rep1}/t_{r1}$) are virtually identical suggesting that pit repassivation in both materials occurs by similar mechanisms (Figure 3.18). Stage-two repassivation kinetics in Al-0.2Cu are much slower, but are not believed to affect overall pit stability because the pit loses its critical characteristics during the stage-one repassivation.

Using apparent pit radii (Figure 3.19), the peak pit current densities were calculated and compared for Al-0.2Cu and Al 99.999 in Figure 3.20. Peak pit current densities are identical for both alloys supporting the notion that repassivation proceeds in a manner that is nominally identical in both materials.

3.4 DISCUSSION

3.4.1 Effect of Cu on metastable pit initiation

Data collected in this study show that Cu in solid solution exerts an inhibiting effect on stable pit initiation by inhibiting the initiation of metastable pits. This translates into an increase in pitting potential because the probability of forming stable pits is decreased [29]. In these measurements, the occurrence of metastable pitting was confined to a narrow potential range below the stable pitting potential whose breadth decreased with increasing Cu content. Addition of 0.2 wt.% Cu to Al decreased the metastable pit
initiation rate and addition of 2.0 wt.% Cu eliminated detectable metastable pitting in these experiments altogether (Figure 3.6). In the potentiodynamic polarization curves this effect is manifested as an increase in $E_{\text{pit}}$, and a sharpening of the polarization curve at $E_{\text{pit}}$. In Figure 3.2 for Al 99.999, the transition from passivity to stable pitting is gradual as metastable pitting intensifies prior to pit stabilization. In Al-2.0Cu the transition between passivity and pitting is quite sharp suggesting initiation and stabilization of essentially a single site on the electrode surface.

According to Pistorius and Burstein [30, 31], the number of pit initiation events per unit area ($N$) decreases exponentially with exposure time and is proportional to the number of available defect sites ($N_0$) on an alloy surface:

$$N = N_0 \exp\left(-\frac{t}{\tau}\right)$$  \hspace{1cm} \text{Eqn. 3.1}

where, $t$ is exposure time and $\tau$ is a constant with units of s$^{-1}$. A comparison of the metastable pit initiation rates between Al 99.999 and Al-0.2Cu in Figures 3.7 and 3.8 suggests that Cu additions decrease the number of available sites for pit initiation, $N_0$. Table 3.2 shows the details about this. For instance, the number of available defect sites, $N_0$, for Al 99.999 was the smallest as 181.5 at $-0.69$ V$_{\text{SCE}}$ whereas that for Al-0.2Cu was the largest was 44.4 at $-0.67$ V$_{\text{SCE}}$.

How decreased rates of metastable pit initiation lead to reduced chances for stable pitting is explained in the work of Williams and co-workers [29, 32, 33] According to this treatment, the relationship between stable and metastable pit initiation rates is:
\[ \Lambda = \lambda \exp(-\mu \tau_c) \]  
Eqn. 3.2

where \( \Lambda \) is a frequency of stable pit initiation (sec\(^{-1}\)), \( \lambda \) is a frequency of metastable pit initiation (sec\(^{-1}\)), \( \tau_c \) is a critical age determining a transition from metastable to stable pit (sec), and \( \mu \) is a probability of metastable pit repassivation (sec\(^{-1}\)). Equation 3.2 shows that the effect of Cu on reducing the frequency of metastable pit initiation (\( \lambda \)) directly decreases the frequency and probability of stable pit initiation thereby leading to increased values of \( E_{\text{pit}} \).

### 3.4.2 Effect of Cu on metastable pit growth

Under the conditions established in these experiments, the main effect of Cu on metastable pit growth is associated with a reduction in \( I_{\text{peak}} \), which is directly compared for Al 99.999 and Al-0.2Cu in Figure 3.14, and is presented for a broader range of potentials in Figures 3.9 and 3.10. Because the growth time of metastable pits in the two alloys is similar (Figure 3.15), the growth rate of metastable pits in Al-0.2Cu is somewhat slower (Figure 3.16). Assuming that pits grow subject to ohmic control, the decreased growth rate in Al-0.2Cu is due either to an ennoblement of the pit bottom potential, blocking of current path in the pit due to pit geometry or product formation, or some combination of both. The effect of Cu on ennoblement in reducing dissolution kinetics of artificial crevices has been explicitly considered by others [15, 24], and the effect is significant. Neither the effect of Cu on the evolution of pit morphology at these length
scales nor the nature of product formation in metastable pits is well known at the present time.

### 3.4.3 Effect of Cu on metastable pit repassivation

The pits examined in the current versus time records for Al 99.999 at −0.70 V and Al-0.2Cu at −0.69 V fell below accepted pit stability criteria indicating that repassivation was inevitable, which was the intent of these experiments. Based on the work of Williams et al., stable pit growth is expected from pits for which $I_{\text{peak}}/r_{\text{pit}}$ exceeds $4 \times 10^{-2}$ A/cm$^2$ [34]. According to Galvele, stable pits occur when the product of the pit depth time the pit current density, $x \cdot i$, exceeds $10^{-2}$ A/cm [35]. Figure 3.21 shows a cumulative distribution of $I_{\text{peak}}/r_{\text{pit}}$ values for metastable pits in Al 99.999 and Al-0.2Cu. $I_{\text{peak}}/r_{\text{pit}}$ for Al-0.2Cu is shifted to lower values compared to 99.999Al, but the range of all values is less than $10^{-3}$ A/cm. Selected calculations of the quantity $x \cdot i$ are much less than $10^{-2}$ A/cm consistent with the Galvele criterion.

The similarity in the peak pit current densities and the repassivation rates between the two alloys suggests that the factors limiting pit life are the same in both cases. This would also suggest that alloyed Cu plays no role, either directly or indirectly through modification of the environment in early stage pit repassivation. The claim of similarity in repassivation rates is contingent on a two-stage repassivation process for Al-0.2Cu. A similar type of repassivation process has been observed by Cheng and Luo on carbon steel [36]. In that case, it was suspected that there was a freshly deposited layer on the pit wall that caused the slow decay after a fast primary repassivation process. Redeposition of a porous Cu-enriched layer on the pit wall by precipitation or reduction remains a
possibility in these experiments, even at very low pit potentials, in view of non-Faradaic pathways for Cu release from corroding Al alloys [10, 37]. Under the conditions used in the present experiments, this extended second stage of repassivation does not lead to an increased probability of pit stabilization because it does not alter the ultimate fate of the pit once the first stage of repassivation is complete. An important attribute of repassivated pit sites in this regard is that they do not appear to support subsequent pit initiation as suggested by the decrease in pit initiation rate with increasing exposure time (e.g., Figure 3.8).

3.4.4 Evaluation of other effects of Cu on metastable pit repassivation

Muller and Galvele observed a 200 mV increase in the pitting potential for Al-Cu solid solutions up to 5.0 wt.% Cu in a study of the effect of alloy composition on pitting in Al solid solutions in 1.0 M NaCl solutions [16, 35]. According to a model proposed on the basis of these results, a pit must maintain certain acidity to sustain its growth. In the case of Al-Cu alloys, Cu was speculated to be enriched in pits as Al preferentially dissolved. Cu-enriched pit walls led to ennoblement by discharging hydrogen at enhanced rates compared to pure Al leading to an increase in the potential needed to sustain a critical environment. In other words, Cu enriched walls led to an increased pitting potential. While this is a rational interpretation that is generally consistent with the effect of Cu on hydrogen reduction kinetics, the hydrogen reduction kinetics on bare Al may not be much different than those on Cu in pit-like solutions. Evidence for Cu surface enrichment was not an objective of the present study and the results that have been
developed neither confirm or refute the mechanistic arguments made by Muller and Galvele.

Ramgopal and Frankel developed a more direct interpretation of the inhibiting effect of Cu in Al-Cu solid solutions based on measurement of the anodic polarization response of artificial crevices using a decreasing potential scanning approach [24]. Their results showed that Cu ennobles Al dissolution kinetics by increasing the exchange current density and the Tafel slope of the dissolution partial reaction. This increases the repassivation potential and reduces dissolution kinetics producing the observed inhibiting effect. An effect of Cu enrichment at pit walls on local pH was not invoked in their interpretation. In the present study, metastable pit growth kinetics inferred from current transients is slightly reduced by addition of 0.2 wt.% Cu to Al, but first stage repassivation kinetics is not affected at all.

On the basis of their analysis of pitting in Al-Zn solid solutions, Sato and Newman pointed out that complete repassivation of a localized corrosion site is controlled by dilution of the critical local environment by diffusion of Al ions from the pit without an effect attributable to Zn or Zn ions [22]. Experimentally, the duration of the repassivation transient, \( t_r \), should be related to the diffusivity of Al ions and the pit radius according to:

\[
t_r = \frac{r_{\text{pit}}^2}{D_{\text{eff}}} \quad \text{Eqn. 2.3}
\]
where $r_{pit}$ is the radius of a hemispherical pit at $I_{peak}$ determined from the Faraday’s law estimation described earlier, and $D_{eff}$ is the effective diffusivity of Al ions in the pit. Figure 22 shows a plot of $r_{pit}^2$ versus $t_r$ for Al and $t_{r1}$ and $t_{r2}$ for Al-0.2Cu. The figure shows that the prompt repassivation behavior of metastable pits in Al-0.2Cu is identical to that of pits in Al 99.999. The effective diffusivity of $3.8 \times 10^{-9}$ cm$^2$/s agrees well with the value of $4 \times 10^{-9}$ cm$^2$/s reported by Sato and Newman for Al-0.13Zn [38] and conforms to the notion of Al ion diffusion-controlled repassivation independent of alloying element.

An effective diffusivity of $7.5 \times 10^{-11}$ cm$^2$/s is estimated when the stage-two repassivation is considered. Sluggish mass transport in this case may reflect an effect from a product layer involving Cu accumulated in the pit or at the pit wall.

### 3.5 CONCLUSIONS

1. A multi-electrode approach was used to collect statistically large populations of pitting potential measurements on Al 99.999, Al-0.2Cu, Al-2.0Cu, and Al-2.0Zn solid solution alloys ($area \cong 10^{-4}$ cm$^2$). Results confirmed that Cu dissolved in solid solution ennobles pitting compared to Al 99.999, while Zn activates it.

2. A study of individual metastable pit transients showed that Cu in solid solution depresses the metastable pit initiation rate. In 0.1 M NaCl solution, the initiation rate is decreased by an order of magnitude by the addition of 0.2 wt.% Cu and is essentially eliminated by addition of 2.0 wt.% Cu.
3. It was also found that Cu inhibits the dissolution kinetics of metastable pits by reducing the peak current ($I_{\text{peak}}$). Considering probabilistic frameworks describing formation of stable pits from metastable ones, the decrease in the metastable pit initiation and growth rates lower the probability of formation of stable pits resulting in the observed increases the pitting potential due to alloying Al with Cu.

4. Cu additions do affect the repassivation behavior of metastable pit in Al, resulting in a distinctive two-stage repassivation process. Two-stage repassivation consists of a rapid initial repassivation event and a much slower second stage of repassivation. A comparison of first stage repassivation kinetics in Al-0.2Cu with those of Al 99.999 shows that rates are essentially identical.
Figure 3.1: The $E_{\text{pit}}$ distribution of Al 99.999 ($2.5 \times 10^{-4}$ cm$^2$), Al-2.0Cu ($1.8 \times 10^{-4}$ cm$^2$) and Al-2.0Zn ($1.3 \times 10^{-4}$ cm$^2$) determined from potentiodynamic polarization.
Figure 3. 2: Anodic polarization curves for Al 99.999, Al-0.2Cu and Al-2.0Cu in deaerated 0.1 M NaCl solution.
Figure 3.3: Current transients of Al 99.999 for 5400 seconds.
Figure 3.4: Current transients of Al-2.0Cu for 5400 seconds.
Figure 3. 5: Current versus time records for Al-0.2Cu collected at applied potentials of −0.69, −0.67, and −0.66 V versus SCE.
Figure 3. 6: Current versus time records for Al 99.999 (−0.70 $V_{SCE}$), Al-0.2Cu (−0.69$V_{SCE}$) and Al-2.0Cu (−0.69 $V_{SCE}$) in deaerated 0.1 M NaCl.
Figure 3. 7: Metastable pit initiation frequency (events per 500 sec interval) for Al 99.999 at −0.70, −0.69 and −0.67 V vs. SCE.
Figure 3.8: Metastable pit initiation frequency (events per 500 sec interval) for Al-0.2Cu at −0.69 and −0.67 V vs. SCE.
Figure 3. 9: Cumulative probability plot of peak pit current, $I_{\text{peak}}$ for Al 99.999 at $-0.70$, $-0.69$ and $-0.67$ V vs. SCE.
Figure 3. 10: Cumulative probability plot of peak pit current, $I_{\text{peak}}$ for Al-0.2Cu at $-0.69$ and $-0.67$ V vs. SCE.
Figure 3.11: Current versus time record of an individual metastable pitting event on Al 99.999.
Figure 3. 12: Current versus time record of an individual metastable pitting event on Al-0.2Cu.
Figure 3. 13: Frequency of metastable pit initiation for Al 99.999 at −0.70 V and Al-0.2Cu at −0.69 V vs. SCE.
Figure 3. 14: Cumulative probability plots of $I_{\text{peak}}$ for Al 99.999 at $-0.70 \text{ V}$ and Al-0.2Cu at $-0.69 \text{ V}$ vs. SCE.
Figure 3.15: Cumulative probability plots of $t_g$ for Al 99.999 at $-0.70$ V and Al-0.2Cu at $-0.69$ V vs. SCE.
Figure 3. 16: Cumulative probability plots of $I_{\text{peak}}/t_g$ for Al 99.999 at $-0.70$ V and Al-0.2Cu at $-0.69$ V vs. SCE.
Figure 3. 17: Cumulative probability plot of repassivation time for Al 99.999 and Al-0.2Cu.
Figure 3. 18: Cumulative probability plots of $I_{\text{peak}}/t_r$ for Al 99.999 and $I_{\text{rep1}}/t_{r1}$ and $I_{\text{rep2}}/t_{r2}$ for Al-0.2Cu.
Figure 3. 19: Cumulative probability plots of $r_{pit}$ (radius of metastable pit at $I_{peak}$) for Al 99.999 and Al-0.2Cu.
Figure 3.20: Cumulative probability plots of peak pit current density, $i_{\text{peak}}$, at the point of repassivation for Al 99.999 at $-0.70$ V and Al-0.2Cu at $-0.69$ V vs. SCE.
Figure 3. 21: Cumulative probability plots of $I_{\text{peak}}/r_{\text{pit}}$ for metastable pits of Al 99.999 at $-0.70$ V and Al-0.2Cu at $-0.69$ V vs. SCE.
Figure 3. 22: Relationship between $(r_{pit})^2$ and $t_r$ for Al 99.999 at $-0.70$ V and Al-0.2Cu at $-0.69$ V vs. SCE (1$^{st}$ and 2$^{nd}$ repassivation).

Al 99.999 and Al-0.2Cu (1$^{st}$ repassivation), $3.8 \times 10^{-9}$ cm$^2$/s

Al-0.2Cu (2$^{nd}$ repassivation), $7.5 \times 10^{-11}$ cm$^2$/s
Table 3.1: Sample dimensions, electrode areas and heat treatments for materials used.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Wire (MMA)</th>
<th>Plate (Metastable Pitting)</th>
<th>Solution Heat Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diameter (µm)</td>
<td>Area (cm²)</td>
<td>Area (cm²)</td>
</tr>
<tr>
<td>Al 99.999</td>
<td>180</td>
<td>2.5×10⁻⁴</td>
<td>0.08 ~ 0.10</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>2.0×10⁻³</td>
<td></td>
</tr>
<tr>
<td>Al-0.2Cu</td>
<td>—</td>
<td>—</td>
<td>0.08 ~ 0.10</td>
</tr>
<tr>
<td>Al-2.0Cu</td>
<td>150</td>
<td>1.8×10⁻⁴</td>
<td>0.08 ~ 0.10</td>
</tr>
<tr>
<td>Al-2.0Zn</td>
<td>130</td>
<td>1.3×10⁻⁴</td>
<td>—</td>
</tr>
</tbody>
</table>
Table 3.2: Number of available defect sites ($N_0$) and the constant $\tau$ for Al 99.999 and Al-0.2Cu at different applied potentials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Applied Potential (vs. SCE)</th>
<th>$N_0$</th>
<th>$\tau$</th>
<th>Accuracy (%)</th>
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REFERENCES


CHAPTER 4

EFFECT OF ALLOYING CU ON ELECTROCHEMICAL REACTIONS OF AL-CU SOLID SOLUTION ALLOYS — SURFACE CHARACTERIZATION BY XPS AND TEM

4.1 INTRODUCTION

Al-Cu binary alloys are less susceptible to pit initiation than pure aluminum provided that the alloyed Cu is retained in solid solution. This effect is evident in experiments showing that pitting potential, $E_{\text{pit}}$, increases with Cu content in Al-Cu solid solution alloys [11, 18-20]. The corrosion potential, $E_{\text{corr}}$ is also reported to increase with alloy Cu content and degree of Cu surface enrichment [10]. Among these studies, Muller and Galvele proposed an explanation for the ennobling effect [18, 19]. They argue that Cu is enriched on the surface of incipient pits resulting in faster hydrogen reduction kinetics than on pure Al surfaces. This consequently ennobles the dissolution kinetics by depolarization of the hydrogen reduction reaction, which results in an increased pitting potential. The phenomenon of Cu surface enrichment has been demonstrated for aged Cu-containing aluminum alloys and has been attributed to the fact that alloy dissolution
occurs well below the reversible potential for Cu [4, 6-8, 17, 24-26]. In some reports, it has been speculated that that passivating effects are a result of a Cu-enriched surface layer [21]. Although the effect of solid solution Cu content on the pitting potential in Al-Cu solid solutions is relatively well established, whether Cu surface enrichment occurs or plays a role in promoting resistance to pitting is not established with as much certainty.

In an attempt to explore the effects of alloyed Cu on interfacial structure and chemistry and their relation to the ennoblement of $E_{\text{pit}}$ in Al-Cu solid solutions, a two-part study was undertaken. In the first part, many replicate pitting potential measurements were collected for Al 99.999, Al-Cu, and Al-Zn solid solutions to characterize the extent of the ennobling effect of Cu on the pitting potential. The second part involved the surface characterization of Al-Cu solid solution alloys after exposure to aggressive chloride solutions by x-ray photoelectron spectroscopy, scanning transmission electron microscopy and spectral imaging of specially prepared needle-type samples in an effort to discover structural, chemical or morphological effects associated with alloyed Cu that might contribute to the observed increase in $E_{\text{pit}}$.

4.2 EXPERIMENTAL METHODS

4.2.1 Pitting potential ($E_{\text{pit}}$) measurements after passive dissolution

Electrochemical measurements were carried out using a segmented working electrode approach involving electrode arrays. Arrays were constructed from wire stock that was 180 $\mu$m or 500 $\mu$m in diameter for 99.999 % pure Al (Puratronic, Alfa® Aesar®, hereafter Al 99.999), 150 $\mu$m diameter for Al-2.0wt%Cu (hereafter Al-2.0Cu), and 130 $\mu$m diameter for Al-2.0wt%Zn (hereafter Al-2.0Zn). Al-2.0Cu and Al-2.0Zn wires were
specially prepared for this study by Ames Laboratories, Ames, IA. The Al 99.999 wires were used in the as-received condition while the Al-2.0Cu and Al-2.0Zn were solution heat-treated for one hour at 535 °C followed by a quenching in cold water to retain Cu and Zn in solid solution. Dimensions of the wires and their solution heat treatments are summarized in Table 4.1. Electrode arrays were constructed by potting 25 wire samples in epoxy in a regular 5 x 5 arrangement. In order to reduce crevice corrosion, a low viscosity epoxy (EPO-THIN by Buehler®) was used for potting. Arrays were then polished gradually and carefully up to 1200 grit SiC paper. In order to minimize precipitation in the Al-Cu solid solution alloys, samples were stored in a refrigerator at about –20 °C except when they were being potted or electrochemically tested. The total time from solution treating and quenching to the completion of electrochemical testing did not exceed five days for any array used in this study to further limit precipitation and to enhance repeatability among replicate measurements.

Measurements were made in aerated 0.1 M NaCl solutions on electrode arrays using a Model 900 Multichannel Microelectrode Analyzer™ (MMA) (Scribner Associates). The MMA controlled a three-electrode measurement comprising a single counter and reference electrode and 25-segment working electrode. The current in each segment in the working electrode was recorded individually. A scan rate of 0.5 mVs⁻¹ was used for all measurements. Data analysis was carried out using MMA Live™ software installed in a personal computer. The experimental protocol involved potentiodynamic polarization into the passive region from corrosion potential (Ecorr); a potentiostatic hold for 0, 50, 100, or 500 minutes; then continued potentiodynamic polarization until all elements on the array exhibited a pitting potential (Epit). The purpose
of the potentiostatic hold was to examine any effect of passive dissolution on oxide film chemistry and subsequent protectiveness. The hold potential applied was half-way between the $E_{\text{corr}}$ and $E_{\text{pit}}$ measured in previous experiments with bulk electrodes. $E_{\text{hold}}$ was $-0.70 \ V_{\text{SCE}}$ for Al 99.999, $-0.75 \ V_{\text{SCE}}$ for Al-2.0Cu and $-0.97 \ V_{\text{SCE}}$ for Al-2.0Zn. Several replicate arrays were measured for each alloy at each hold time ($t_{\text{hold}}$) so that the number of individual $E_{\text{pit}}$ measurements ranged from 50 to 75 for each unique condition. Figure 4.1 schematically illustrates how this experiment was carried out.

To investigate area effects on pitting potential ($E_{\text{pit}}$), a standard electrochemical cell was used. The sample used was Al-2.0Cu plate with an exposed area of $10^{-2} \ \text{cm}^2$. The experimental procedures were identical to those of the MMA experiments except that i) a PC4™ potentiostat (Gamry Instruments, Inc.) was used to control the experiment, ii) the exposed area was larger ($10^{-2} \ \text{cm}^2$), and iii) a fewer number of measurements were carried out.

4.2.2 Pitting potential ($E_{\text{pit}}$) measurement by microelectrochemical cell

Certain experiments were carried out using a microcell technique [3] to create small exposed areas approaching that of wire electrodes used in array-based experiments ($10^{-4} \ \text{cm}^2$). The materials used in these experiments were taken from Al 99.999, Al-2.0Cu and Al-4.0Cu sheet stock.

4.2.3 X-ray photoelectron spectroscopy

Surface analysis by X-ray photoelectron spectroscopy (XPS) was conducted on Al 99.999 and Al-2.0Cu samples after immersion in 0.1 M NaCl solution and potentiostatic
polarization in their respective passive regimes (500 min at −0.75 V_{SCE} for Al 99.999 and 500 min at −0.70 V_{SCE} for Al-2.0Cu). Spectra were collected by a Kratos AXIS His 165 Ultra spectrometer using a monochromated Al Kα source (1486.6 eV, 10 mA and 13 kV). The Carbon 1s peak at 284.5 eV was used for referencing the collected spectra, which were analyzed using Kratos VISION2 software. In preparation for surface analysis, samples were polished using methods described for the MMA experiments, and masked to expose an area of about 10⁻² cm². After the passive dissolution treatment, samples were dried and loaded into XPS via ambient air transfer.

4.2.4 Surface characterization by Scanning Transmission Electron Microscopy (STEM)

STEM and spectral imaging were carried out on specially prepared needle samples suitable for corrosion exposures to examine Cu surface enrichment after corrosion exposures. Al 99.999, Al-1.0Cu and Al-2.0Cu samples were electrochemically polished and prepared as very thin wires for analysis. The wire samples were electropolished at 18 V in a methanol plus 5.0 % perchloric acid solution at −30 °C for several seconds. The samples were removed, stirred and rinsed in DI water for at least 60 seconds after polishing. After the electrochemical polishing, samples were analyzed by STEM. For corrosion experiments, the electrochemically-polished samples were loaded onto a vertically oriented adjustable micromanipulator and carefully lowered into 0.1 M NaCl solution surface until the end of wire tip just touched the solution surface. The point when the end of wire tip exposed in the solution was easily determined by monitoring the electrochemical response of the sample using a Gamry PC4™ potentiostat.
X-ray spectral images were acquired using a Tecnai F205 scanning transmission electron microscope operated at 20 kV equipped with an energy-dispersive X-ray (EDX) detector. The spectral image was collected with a resolution of 100 × 100 pixels in a frame size of 500 × 500 nm at a data collection rate of 2 pixels per second. The spectral image data-analysis approach used in this study was based on a new automated, unbiased, multivariate statistical analysis [13-15]. A unique feature of this automated analysis is that it requires no assumptions on the presence or absence of any elemental constituent, and it shows quantitative agreement between raw and processed data [15].

4.3 RESULTS

4.3.1 Statistical measurements on \( E_{\text{pit}} \) of Al 99.999, Al-2.0Cu and Al-2.0Zn

Figure 4.2 shows cumulative distribution plots of the \( E_{\text{pit}} \) for Al 99.999 (2.5 \( \times \) 10\(^{-4}\) cm\(^2\)), Al-2.0Cu (1.8 \( \times \) 10\(^{-4}\) cm\(^2\)) and Al-2.0Zn (1.3 \( \times \) 10\(^{-4}\) cm\(^2\)) determined from potentiodynamic polarization in which samples were not subject to a potentiostatic hold in the passive region. The \( E_{\text{pit}} \) distribution of Al-2.0Cu ranged from –0.6 to –0.4 V\(_{\text{SCE}}\) and was distinctly shifted towards more positive potentials compared to Al 99.999. Al-2.0Zn showed the most negative \( E_{\text{pit}} \) distribution, but was just slightly more negative than that of Al 99.999.

Figure 4.3, 4.4 and 4.5 show \( E_{\text{pit}} \) distributions for Al 99.999, Al-2.0Cu and Al-2.0Zn as a function of the potentiostatic hold time, \( t_{\text{hold}} \). \( E_{\text{pit}} \) distributions of all three materials shifted in the positive direction with increasing \( t_{\text{hold}} \), but the extent of the shift depended strongly on alloy composition. For Al 99.999, the \( E_{\text{pit}} \) distribution after \( t_{\text{hold}} = 50\) min overlapped with that of \( t_{\text{hold}} = 0\) min. A slight increase in the \( E_{\text{pit}} \) distribution was
observed when $t_{\text{hold}}$ was either 100 or 500 min. At the median of the distribution, $E_{\text{pit}}$ increased from about $-0.65$ V to about $-0.60$ V as $t_{\text{hold}}$ increased from 0 to 500 minutes. The $E_{\text{pit}}$ distribution for Al-2.0Cu also increased with $t_{\text{hold}}$ and a substantial increase occurred for $t_{\text{hold}} = 500$ minutes (Figure 4.4). At the median of the distribution, $E_{\text{pit}}$ for $t_{\text{hold}} = 0$ min was $-0.55$ V$_{\text{SCE}}$, but increased to $0.05$ V$_{\text{SCE}}$ for $t_{\text{hold}} = 500$ min. A significant dispersion in the $E_{\text{pit}}$ distribution also developed with increasing $t_{\text{hold}}$. For $t_{\text{hold}} = 500$ min., the measured $E_{\text{pit}}$ values spanned nearly 0.6 V$_{\text{SCE}}$.

The pitting potential for Al-2.0Zn also increased after potentiostatic polarization in the passive region as shown in Figure 4.5; though not as dramatically as was observed for Al-2.0Cu. For $t_{\text{hold}} = 100$ min., the $E_{\text{pit}}$ distribution was shifted positively by about 0.2 V compared to that of $t_{\text{hold}} = 0$ min. Increasing the hold time to 500 minutes did not shift the $E_{\text{pit}}$ distribution for Al-2.0Zn appreciably beyond that observed for $t_{\text{hold}} = 100$ min.

### 4.3.2 Area Effects

Generally, as electrode area is decreased, the measured pitting potential increases, all other factors being equal [28]. The probability of the electrode containing a particularly weak site that initiates pitting at low potentials decreases as the exposed area decreases. In some of these experiments, this effect exerts more influence on the pitting potential than compositional effects associated with Cu alloying additions.

The nature of the area effect on measured pitting potential is illustrated by the $E_{\text{pit}}$ data for Al 99.999 in 0.1 M NaCl in Figure 4.6. In these experiments, wire electrode arrays were fabricated using wires with exposed areas of 0.00025 or 0.011 cm$^2$. Whether subject to no potentiostatic holding or a prior 500-minute potentiostatic hold, the median
of the pitting potential distribution for the smaller electrodes was shifted in the positive
direction by 50 to 80 mV.

Figure 4.7 is comparable to Figure 4.6 and shows the effect of electrode area on
the ennoblement of $E_{\text{pit}}$ for Al-2.0Cu in 0.1 M NaCl. For an electrode area of 0.00018
cm$^2$, a 500-minute potentiostatic polarization increases the $E_{\text{pit}}$ distribution by nearly 0.5
V compared to the case where no prior potentiostatic hold is applied. In contrast, when
the electrode area is increased to 0.01 cm$^2$ the ennobling effect associated with the prior
potentiostatic hold is not observed. This suggests that whatever the ennobling effect is, it
is not capable of protecting the most potent defects that can exist on the surface.

4.3.3 $E_{\text{pit}}$ distributions by microelectrochemical cell experiments

The observed ennoblement in the pitting potential of Al-Cu solid solutions is not
unique to MMA-based experiments involving prior potentiostatic polarization in the
passive region. Figure 4.8 shows the polarization response of Al-2.0Cu that was first
subject to cyclic polarization between $-1.3$ and $-0.45$ V (four cycles at 5 mVsec$^{-1}$) in
aerated 0.01 M NaCl solution. In the figure, polarization response of Al-2.0Cu with no
prior cyclic polarization is also shown. No pitting was induced during cycling, but
surface modification and defect healing like that occurring in the potentiostatic
experiments was expected. This measurement was made on sheet stock material using an
electrochemical microcell that exposed an area of 0.00018 cm$^2$. The curve shows a broad
passive region in which the current steadily increases followed by a sharp breakdown
potential that was not preceded by any observable metastable pitting. This sharp break is
taken as evidence of breakdown of essentially one defect site on the surface.
Figure 4.9 shows cumulative distributions of $E_{\text{pit}}$ values for Al 99.999, Al-0.2Cu and Al-2.0Cu measured using the microcell approach for surfaces that were and were not subject to prior cyclic polarization. The $E_{\text{pit}}$ for Al 99.999 was not increased by prior cyclic polarization and completely overlapped with the $E_{\text{pit}}$ values from polarization curves collected in a conventional manner (i.e., Al 99.999). Ramp-up denotes the conventional polarization whereas CP indicates the prior cyclic polarization. The $E_{\text{pit}}$ distribution is increased by about 0.2 V at the median for Al-0.2Cu (i.e., 0.2Cu ramp-up and 0.2Cu CP) and by about 0.05 V at the median for Al-4.0Cu (i.e., 0.4Cu ramp-up and 0.4Cu CP). The dispersion in the $E_{\text{pit}}$ distribution increases noticeably as the Cu content of the alloy increases suggesting that Cu content leads to a defect-healing but also may introduce particularly effective pit-initiating defects.

### 4.3.4 X-ray photoelectron spectroscopy analysis

X-ray photoelectron spectroscopy was carried out on Al 99.999 and Al-2.0Cu samples subject to potentiostatic polarization in their respective passive regions using protocols described above to determine if observed ennoblement of the pitting potential was associated with a change in passive film chemistry or thickness. Interestingly, any changes in passive film chemistry were below the detection limits in these XPS experiments and passive films on both substrates were observed to thicken at virtually identical rates.

Figure 4.10 shows a map of the integrated intensity from the Cu 2p spectral region collected from the surface of an Al-2.0Cu surface after potentiostatic polarization in aerated 0.1 M NaCl for 500 minutes at $-0.70 \ V_{\text{SCE}}$. The image is noisy without clear
evidence of local or global Cu enrichment. Detailed spectra from the Cu 2p and Al 2p regions were collected from 4 separate locations from the surface as noted in the Cu map image of Figure 4.10. There is no evidence of Cu at the outermost layers of the surface film.

To determine if the presence of Cu in the alloy affected the thickness of the passive film that formed during potentiostatic polarization, a film thickness calculation was carried out. In these experiments, metallographically polished Al 99.999 and Al-2.0Cu samples were potentiostatically polarized at $-0.75 \, \text{V}_{\text{SCE}}$ in an aerated 0.1 M NaCl solution for 500 min. Alexander et al. have shown an equation to calculate oxide film thickness at the surface of aluminum by using XPS [19]:

$$d_{\text{xps}} = \lambda_0 \sin \theta \ln\left(\frac{N_m \lambda_m I_O}{N_o \lambda_o I_m} + 1\right) \quad \text{Eqn. 4.1}$$

Estimation of surface oxide thickness, $d_{\text{xps}}$, was made from the Al 2p oxide to metal peak ratio ($I_o / I_m$). In this expression, the ratio of volume densities of aluminum atoms in metal to those in the oxide, $N_m/N_o$, was 1.6, calculated from the densities for Al = 2.7 g/cm$^3$ and anodic alumina = 3.1 g/cm$^3$. Effective attenuation lengths were taken to be $\lambda_o = 2.9$ nm for the oxide and $\lambda_m = 2.4$ nm for the metal and were calculated from inelastic mean free path values tabulated in the NIST standard database [20]. The take-off angle ($\theta$) was 90°. Prior to use in the oxide film thickness calculation, background correction in the Al 2p spectral region was performed using a Tougaard background-fitting algorithm resident in Kratos VISION2 software.
In these experiments, Al 99.999 thickened from 3.15 to 5.49 nm, and Al-2.0Cu thickened from 2.73 to 4.74 nm (Figure 4.11). While the passive film thicknesses are slightly different between the two samples, both increased thicknesses by 1.74 times due to potentiostatic polarization. Because of the small difference in film thickness and the identical film thickening rates demonstrated by the two materials, it is difficult to attribute the increase in pitting potential in the case of Al-2.0Cu after potentiostatic polarization to either a global change in passive film chemistry due to Cu surface enrichment, or an increased passive film thickness.

4.3.5 Surface characterization by STEM

In contrast to XPS results, STEM and spectral imaging show clear evidence of Cu surface enrichment by Al-Cu alloy dissolution. This is due to the differences in exposures used, and to differences in the spatial resolution of the techniques. Moreover, results show that dissolution under a range of different conditions leads to enrichment of Cu at Al-Cu alloy surfaces suggesting that this behavior is a characteristic of dilute alloy dissolution.

Preparation of needle samples for STEM requires electrochemical polishing of wire stock in a methanol plus 5.0 % perchloric acid solution. This treatment leads to unavoidable Cu surface enrichment whose extent appears to depend on the Cu content of the stock wire material. Figure 4.12 shows a scanning transmission image of the tip of an electropolished Al-1.0Cu needle and its companion spectral image. The EDS spectra associated with the red and green pixels in the image are also provided. Based on raw peak intensity, the Cu to Al ratio in the green regions is about ten times greater than that
in the red regions. The spectral image shows a green region at the limb of the needle indicating Cu enrichment. It is likely that the whole surface of the sample is similarly enriched, but is detected only at the apparent sample limb where the interfacial region can be a large fraction of the x-ray generation volume. On the sample face, there is a significant contribution to the EDS spectrum from the underlying Al-rich sample, which masks any Cu enrichment in the comparatively small volume of the sample surface layer.

Cu surface enrichment of Al-2.0Cu by electropolishing in perchloric acid-methanol solutions results in the formation of Cu-rich clusters at the sample surface (Figure 4.13). Cu enrichment is evident in the concentrated green pixellation along the limb of the needle at locations where nodular features in the STEM image are present. As in the previous spectral image green pixellation is indicative of compositions that are comparatively Cu-rich compared to regions of red on the basis of a the raw Al to Cu EDS peak height ratio. The Cu enrichment associated with Cu clusters is more readily apparent where clusters lie along the limb of the needle than on the needle face presumably because they comprise a larger fraction of the x-ray generation volume when they are in that location. Cu-rich clusters have been observed directly in corroding Al$_2$CuMg particles present in 2024-T3 alloys exposed to dilute chloride solutions under free corrosion conditions [5]. Their presence has also been inferred from XPS data of corroded Al$_2$Cu thin film deposits [26]. Figure 4.13 suggests that dissolution of comparatively dilute Al-Cu alloys can also lead to the formation of Cu clusters with possible consequences for so-called non-Faradaic dissolution of Cu and subsequent deposition corrosion [2].
Localized corrosion also leads to Cu surface enrichment. Figure 4.14 shows a current versus time record for an electropolished Al-1.0Cu alloy surface during potentiostatic polarization at \(-0.700 \text{ V}_{\text{SCE}}\) in aerated 0.1 M NaCl solution. This particular sample developed an overall net cathodic current during the course of the experiment, but transients associated with metastable pitting on the sample surface are evident on a gradually increasing cathodic current background. A particularly large transient is detected at 4500 second, after which the net cathodic current is reduced suggesting an increased anodic partial current. Indeed, imaging the sample after exposure revealed the presence of a pit near the tip of the needle sample. Because stable pitting usually destroyed the small needle samples in other experiments unless interrupted quickly, this particular site is believed to be an example of a metastable pit. A spectral image collected from the base of the pit (Figure 4.15) shows clear evidence Cu surface enrichment, suggesting that metastable pitting (albeit under conditions of slight cathodic polarization) can result in localized Cu surface enrichment.

It is generally known that cathodic polarization and attendant cathodic corrosion will enrich an Al-Cu surface with Cu. Figure 4.16 shows how Cu is distributed through the corrosion product that forms during cathodic corrosion. A voluminous corrosion product layer enriched in Cu near the metal-product interface is observed. This product layer, believed to have formed during cathodic polarization, is far less compact than that formed under electrolytic etching or anodic polarization experiments. This product was produced by potentiodynamic polarization in a scan initiated at \(-1.2 \text{ V}_{\text{SCE}}\), ramped through the cathodic region in the positive direction through the corrosion potential in to the anodic region until pitting was detected at about \(-0.4 \text{ V}_{\text{SCE}}\) (Figure 4.17). The pitting
potential measured did not indicate any significant ennoblement as shown in Figures 4.2 and 4.4.

4.4 DISCUSSION

4.4.1 The effect of Cu on pitting potential ennoblement

The results of the electrochemical experiments illustrate the ennobling effect of Cu additions on the pitting of Al. The ennobling effect is strong in experiments using very small electrodes, but is weak or absent in experiments with larger area electrodes. Results also show that ennoblement is enhanced by potentiostatic polarization in the passive regime.

The effect of electrode area on the extent of ennoblement observed in pitting potential measurements can be understood in the context of arguments presented by Wall and Martinez, who distinguish homogeneous and heterogeneous forms of pit initiation [23]. According to their arguments, heterogeneous pit initiation refers to pitting at specific sites that possess a high probability of pitting. In our case, these sites include intermetallic particles, oxide inclusions and grain boundaries. Homogeneous pit initiation refers to initiation in the absence of obvious initiation sites. An important aspect of homogeneous pit initiation is that each unit area of the surface has equal probability of pitting.

In experiments with small areas \((10^{-4} \text{ cm}^2)\) Al 99.999 electrodes, replicate measurements of the pitting potential were dispersed only by about 20 mV around the mean value (Figure 4.3). In the context of the Wall-Martinez definitions, these
measurements characterize a homogeneous pit initiation process. Essentially, the use of small area, high-purity electrodes minimizes the possibility for heterogeneous pit initiation because vulnerable defects tend to be excluded. Interestingly, for small area electrodes of Al 99.999 potentiostatic polarization in the passive region did not increase the mean pitting potential nor did it increase its dispersion significantly. This suggests that this particular polarization regimen did not fundamentally alter the probability of pitting, nor did it introduce defects that might lead to heterogeneous pit initiation.

Adding Cu or Zn to Al changes the probability of stable pitting as suggested by the change in the mean value of the pitting potential, and leads to the introduction of heterogeneous pit initiation sites as suggested by the increase in the dispersion in replicate pitting potential measurements. Both of these phenomena are evident in the data shown in Figure 4.2. A 2.0 wt.% addition of Cu to Al increases the mean pitting potential compared to Al 99.999, while 2.0 wt.% Zn decreases it. In Chapter 3, the increase in $E_{\text{pit}}$ for dilute Al-Cu solid solutions has been attributed to a decrease in the metastable pit initiation and growth rates associated with Cu alloying additions. The decrease in $E_{\text{pit}}$ for dilute Al-Zn alloys has been attributed to increased metastable pit growth kinetics [22, 23]. The dispersion in the $E_{\text{pit}}$ data sets for the three materials is shown in Figure 4.2. Additions of Cu and Zn increase the $E_{\text{pit}}$ dispersion by about ten times compared to Al 99.999. This suggests that increased alloying brings a component of heterogeneity to the pit initiation process. This may arise due to the formation of Cu-rich precipitates in the case of Al-Cu alloys and, in the case of both alloys, due to the possibility of particle formation involving strongly insoluble impurity elements that accompany the main Zn or Cu alloying additions.
Potentiostatic polarization of Al-Cu solid solutions leads to ennoblement of $E_{\text{pit}}$ to an extent that is not demonstrated by Al 99.999 or Al-Zn solid solutions. The ennoblement is characterized by an increase in the mean $E_{\text{pit}}$ and an increase in the dispersion of replicate $E_{\text{pit}}$ measurements (Figure 4.4). One interpretation of these results is that Al-Cu alloys possess an ability to heal incipient defects (both those that affect homogeneous and heterogeneous pit initiation) when the dissolution rate is increased slightly due to modest potentiostatic or cyclic polarization. This healing effect may be associated with Cu surface enrichment as is discussed in more detail below.

In experiments with larger area Al-Cu alloy electrodes, $E_{\text{pit}}$ ennoblement by prior polarization is reduced or is absent (Figure 4.6 and 4.7). One interpretation is that the likelihood of a significant pit-initiating defect increases as electrode area increases. While evidence for $E_{\text{pit}}$ ennoblement can be found in carefully prepared Al-4.0Cu solid solutions, it is not reasonable to expect ennoblement in electrochemical determinations of $E_{\text{pit}}$ in large area electrodes prepared from commercial alloys such as 2024-T3 (Al-4.5Cu-1.5Mg), which contain a very high number density of intermetallic particles that affect pit initiation. Attempts in our labs to observe $E_{\text{pit}}$ ennoblement of 2024-T3 have been unsuccessful unless very small electrode areas are used [16]. In the case of commercial alloys, healing of defect sites by alloyed Cu and its attendant effects on initiation and propagation of localized corrosion remain an intriguing and unexplored issue.

4.4.2 Surface chemistry changes and $E_{\text{pit}}$ ennoblement

The literature contains many reports of Cu surface enrichment by corrosion of Cu-bearing Al alloys [3, 14-16, 27-29], usually under far more aggressive exposure
conditions than were used in this study. Many of these reports involve the phenomenon of deposition corrosion [12], which arises from the dissolution and redeposition of Cu on a corroding Al alloy surface [2]. No enrichment was detected by XPS analysis of Al-2.0Cu surfaces that had been subject to potentiostatic polarization in the passive region despite the fact that identical treatments resulted in significant $E_{\text{pit}}$ ennoblement. Slight thickening of the passive film was induced by polarization, but the presence or absence of Cu in the alloy did not affect the film-thickening rate compared to high purity Al. One possibility for the apparent absence of Cu in XPS characterization is that Cu enrichment was localized to defects in the passive film and the total extent of enrichment was below XPS detection limits—a problem that has been identified by others in similar characterization experiments [26, 27].

STEM and spectral imaging experiments, which were carried out under more aggressive exposure conditions showed clear evidence of Cu surface enrichment. The results from these experiments do not apply directly to the electrochemical experiments or surface characterization by XPS because all samples were necessarily subject to electropolishing, which resulted in some degree of Cu surface enrichment. Nonetheless, they do illustrate important aspects of how alloy dissolution affects interfacial chemistry of Al-Cu alloys.

First and foremost, these results show that Cu surface enrichment due to alloy dissolution is a characteristic behavior of Al-Cu alloys. Surfaces were found to be enriched after dissolution under acidic oxidizing conditions, and after cathodic polarization (alkaline conditions). The voluminous corrosion product formed on cathodically polarized samples did contain elevated levels of Cu, but did not appear to
promote ennoblement of $E_{\text{pit}}$. Compact Cu-enriched layers that tended to form under acidic conditions were associated with an ennoblement of $E_{\text{pit}}$. The existence of Cu-rich nodules on corroded Al-Cu alloys surfaces indicates Cu mobility via surface diffusion or by dissolution and replating.

Mainly because of their continuity and uniformity, it is speculated that continuous, compact Cu enriched layers observed on needle surfaces and in pits on needles do not form by dissolution and replating of Cu as appears to be the case in deposition corrosion. Rather, they appear to be the result of selective dissolution of the Al component of the alloy. In this sense, their mechanism of formation bears a close resemblance to classical dealloying with the notable exception that the enriched component is the minority component in the alloy system [1, 9].

Perhaps the most interesting finding from the perspective of localized corrosion is the presence of Cu in the base of pits. This finding suggests that localized corrosion may lead to the localized Cu surface enrichment. A localized compositional change suggested by this observation may account for why strong $E_{\text{pit}}$ ennoblement can be detected without significant changes in interfacial Cu concentration.

4.5 CONCLUSIONS

1. Cu additions to Al alloys will increase $E_{\text{pit}}$ measured electrochemically provided that the Cu is retained in solid solution and the density of heterogeneous pit initiation sites is low.
2. Electrochemically stimulated dissolution ennobles the subsequently measured pitting potential for Al-Cu alloys provided that the dissolution does not lead to localized corrosion in the first place. The ennobling effect is diminished or absent in large area electrodes containing heterogeneous defects that are not healed by during stimulated dissolution.

3. STEM shows that Cu surface enrichment by dissolution under conditions of aggressive, uniform electrochemical dissolution, cathodic polarization (alkaline cathodic corrosion) and pitting.

4. In STEM, localized corrosion leads to ennoblement of $E_{\text{pit}}$. 
FIGURES

Figure 4. 1: Schematic diagram for the pitting potential ($E_{\text{pit}}$) measurement after the passive dissolution.

- Hold time ($t_{\text{hold}}$) = 50, 100 or 500 min
- Potential (V vs. SCE) vs. Time
- $0.5 \text{mV/s}$
- $E_{\text{pit}}$, $E_{\text{hold}}$, $E_{\text{corr}}$
Figure 4.2: The $E_{\text{pit}}$ distribution of Al 99.999 ($2.5 \times 10^{-4}$ cm$^2$), Al-2.0Cu ($1.8 \times 10^{-4}$ cm$^2$) and Al-2.0Zn ($1.3 \times 10^{-4}$ cm$^2$) without a potentiostatic hold period ($t_{\text{hold}} = 0$ min).
Figure 4.3: $E_{\text{pit}}$ distributions of Al 99.999 ($2.5 \times 10^{-4}$ cm$^2$) after potentiostatic hold for 0, 50, 100 and 500 min.
Figure 4.4: $E_{pit}$ distributions of Al-2.0Cu ($1.8 \times 10^{-4}$ cm$^2$) after potentiostatic hold for 0, 50, 100 and 500 min.
Figure 4.5: $E_{\text{pit}}$ distributions of Al-2.0Zn ($1.3 \times 10^{-4}$ cm$^2$) after potentiostatic hold for 0, 100 and 500 min.
Figure 4.6: $E_{pit}$ distribution of Al 99.999 depending on exposed area and potentiostatic hold time; i) $A = 1.1 \times 10^{-2} \text{ cm}^2$ from 1200 mm diameter wire and ii) $A = 2.5 \times 10^{-4} \text{ cm}^2$ from 180 mm diameter wire.
Figure 4.7: Comparison of $E_{\text{pit}}$ distributions for Al-2.0Cu depending on the potentiostatic hold time; $t_{\text{hold}} = 0$ and 500 min on (a) large area ($1.0 \times 10^{-2}$ cm$^2$) and (b) small area ($1.8 \times 10^{-4}$ cm$^2$).
Figure 4.8: Potentiodynamic curve and pit image of Al-4.0Cu after cyclic polarizations.
Figure 4. 9: Cumulative probability plots of pitting potentials of Al 99.999, Al-0.2Cu, and Al-4.0Cu by microcell experiment.
Figure 4.10: X-ray peak intensities of Cu 2p and Al 2p peaks for Al-2.0Cu after the potentiostatic hold.
Figure 4.11: Oxide film thickness changes of Al 99.999 and Al-2.0Cu before or after the passive dissolution.
Figure 4.12: Scanning transmission image of the tip of an electropolished Al-1.0Cu needle and its companion spectral image.
Figure 4.13: Scanning transmission image of the tip of an electropolished Al-2.0Cu needle and its companion spectral image.
Figure 4. 14: Current versus time record for an electropolished Al-1.0Cu surface alloy surface during potentiostatic polarization.
Figure 4.15: Scanning transmission image of the tip of an electropolished Al-1.0Cu needle after potentiostatic polarization and its companion spectral image.
Figure 4. 16: Scanning transmission image of the tip of Al-2.0Cu needle after polarization scanned from $-1.2$ to $-0.4$ V (vs. SCE) and its companion spectral image.
Figure 4. 17: Current versus potential of electropolished Al-2.0Cu prior to pit initiation.
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Table 4.1: Samples used for each experiments; pitting potential measurements, microcell, XPS, and STEM analysis.
REFERENCES


5.1 INTRODUCTION

Al-Cu binary alloys are less susceptible to pit initiation than pure aluminum when Cu is retained in solid solution. In chapter 2 and 3 and results by others [1, 2], this phenomenon is manifested in electrochemical measurements showing that pitting potential ($E_{\text{pit}}$) increases as solid solution Cu content increases. Effects of other solid solution alloying element additions such as Zn and Mg have also been studied [2-5]. Zn additions decrease the pitting potential while Mg additions have no discernable effect [2, 4]. Solid solution alloying additions have also been shown to affect metastable pitting [3, 6]. Cu additions decrease the frequency of metastable pit initiation as well as metastable pit growth kinetics [6]. Zn additions, on the other hand, increase dissolution kinetics but not alter initiation frequency [3].

Artificial pit electrode (APE) approaches have been used to study various aspects of stable pit growth. These electrodes consist of a wire made for the metal or alloy of
interest potted in an inert, non-conductive mounting. The pit is formed at flat face where the wire exits the mount. By dissolving the wire back into the mount an artificial pit is formed. Advantages of this approach are that important geometric aspects of pits are replicated, activation of the entire electrode surface is possible and the same occluded environment chemistries that form in real pits can be developed. The simple configuration facilitates characterization by electrochemical, optical and other methods.

In terms of electrochemical characterization, rigorous evaluation of pit dissolution kinetics is made possible because the active pit area can be accurately estimated, and remains essentially constant during the course of the experiment. Examples of how APEs have been used to understand pitting include the work of Tester and Isaacs who developed a mass transport-controlled model for pitting in nickel and stainless steel by measuring current versus time at potentials above $E_{\text{pit}}$ [7]. Akiyama and Frankel studied aluminum dissolution kinetics in 0.1 M NaCl solution using a closely related artificial crevice technique to show that dissolution kinetics were initially subject to ohmic control, but then became mass transfer-controlled as the crevice deepened [8]. A related artificial crevice method was used to study to characterize dissolution kinetics for dilute Al-Cu, Al-Zn and Al-Mg solid solutions [5]. It was observed that Cu ennobles dissolution kinetics as Cu content increases.

In the present study, we have attempted to characterize the effect of Cu on the dissolution behavior of several simple solid solution Al alloys. Al-Cu, Al-Mg, and Al-Mg-Cu solid solution alloy artificial pit electrodes were fabricated and tested in 0.1 M NaCl. Experimental protocol involved a repetitive cyclic polarization between $-1.8$ and $0.4$ V. After one or two cycles, electrode surface was recessed forming the geometry of
artificial pit. This repetitive cyclic polarization is a somewhat atypical though not unprecedented approach for use with APEs [9]. The advantage of this approach is that it allows periodic measurement of pitting and repassivation potentials after episodes of prior APE dissolution and enables measurement of cathodic kinetics on passivated pit surfaces whose chemistry may have been altered by Cu enrichment. Each of these electrochemical diagnoses helps illuminate the effect of Cu on pit dissolution kinetics.

5.2 EXPERIMENTAL METHODS

High purity aluminum wires were purchased from AlfaAesar®, Johnson Matthey Company. Al-Cu wires were prepared by Ames Laboratories, Ames, IA. Most samples for this study had a cross-sectional area of about 10⁻⁴ cm² except Al-5.0Mg-0.2Cu and one of the two Al 99.999 wires. Table 5.1 provides details on composition and geometry for the materials used in this study. The high purity aluminum wires were used in the as-received condition. Al-Cu wires were solution heat-treated at 535 °C for 1 h and water quenched to retain Cu in solid solution. For Al-Mg and Al-Mg-Cu wires, solution heat treatment was carried out at 480 °C for 1h followed by quenching.

The artificial pit electrodes used in this study were fabricated based on details available in the literature [5, 7-11]. The wire stock material was mounted in epoxy resin and polished flat to create the ‘lead-in-pencil’ APE. For electrochemical experiments, the flat polished surface of the mounted electrode faced upward. Figure 5.1 shows a schematic of the APE arrangement used in this study. A platinum sheet counter electrode and a saturated calomel electrode (SCE) were used in all experiments. Experiments were carried out in a 250 ml cell using 0.1 M NaCl solutions prepared from reagent grade salt...
and 18 MΩ-cm deionized water. Electrodes were subject to cyclic polarization between −1.8 V to 0.4 V at a sweep rate of 0.5 mVs⁻¹ for as many as 17 cycles. The potential and current data were recorded using a Gamry PC4™/FAS1 potentiostat. This experimental protocol enabled measurement of the repassivation potential and pitting potential after an episode of pit dissolution. It also enabled a characterization of pit growth kinetics in the presence of a deliberately Cu-enriched surface under pit environmental conditions. Additionally, while the cathodic branch of the polarization curve measured in these experiments does not have a direct relation to pit dissolution behavior, sample-to-sample comparisons of cathodic behavior showed important differences in behavior that were related to the presence of Cu in the electrode material and its accumulation at the pit surface during polarization experiments.

After the cyclic polarization experiments, scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) were used to characterize pit surface morphology and composition. Epoxy resin was injected into the artificial pit hole that remained after electrode dissolution in order to prevent any possible mechanical damage on the pit surface during sectioning. Once the injected resin cured, the electrode was cut vertically and polished until the surface of artificial pit wall was exposed in cross section. The polishing was carried out gradually to a 1 µm finish with diamond paste in ethanol. The sample was coated by gold in a sputter chamber. SEM/EDX characterization was performed using an FEI Sirion SEM with field emission gun operating at 12 kV.
5.3 RESULTS AND DISCUSSION

5.3.1 Al-Cu and Al-Mg-Cu APE pitting and pit growth kinetics

Figure 5.2 shows an APE polarization curve from the 3rd cycle applied to Al-5.0Mg-0.2Cu, which illustrates the nature of electrochemical response observed. The three main items of interest in these curves are the pitting potential \( E_{\text{pit}} \) on the forward scan, an episode of pit growth from the pitting potential to the repassivation potential \( E_{\text{rep}} \), and the cathodic branch of the polarization curve.

Figure 5.3 shows the estimated pit depth as a function of polarization cycles between for Al 99.999, Al-0.1Cu, Al-1.0Cu, and Al-2.0Cu APEs with areas of about \( 2.0 \times 10^{-4} \) cm\(^2\). Pit depths were estimated using Faraday’s law and the charge passed during the period of pit growth, \( i.e., \) from the pitting potential to the repassivation potential. The charge associated with dissolution, \( Q_{\text{net}} \), was estimated to be:

\[
Q_{\text{net}} = Q_{\text{ano}} - |Q_{\text{cath}}| = 0.85Q_{\text{ano}} \quad \text{Eqn. 5.1}
\]

In this expression, \( Q_{\text{ano}} \) is local anodic charge and \( Q_{\text{cath}} \) is the cathodic charge supported on the dissolving APE surface, which was assumed to be 15% of the total anodic charge passed over the interval in question. Oxygen reduction was assumed not to be a significant contributor to cathodic charge. The form of Faraday’s law used relate charge to mass dissolved was:

\[
Q_{\text{ano}} = \frac{Q_{\text{net}}}{0.85} = \frac{I_{\text{net}} \times \text{time}}{0.85} = \frac{n \pi r^2 dp F}{M} \quad \text{Eqn. 5.2}
\]
where r is radius of wire, ρ is density of Al (2.7 g/cm³), n is equivalents number (3 equiv/mol), F is Faraday’s constant (96,487 C/equiv), and M is atomic mass of Al (27 g/mol). From Equation 5.2, the estimated pit depth (d) was calculated as:

\[ d = \frac{I_{\text{net}} \times \text{time} \times M}{0.85 \pi r^2 \rho n F} \]  

Eqn. 5.3

The same values of ρ, n and M were used for Al-0.1Cu, Al-1.0Cu, Al-2.0Cu, Al-5.0Mg, and Al-5.0Mg-0.2Cu electrodes (discussed below). The final estimated pit depths corresponded well with direct measurements of pit depths determined by sectioning APEs at the conclusion of the experiments.

For each of the materials in Figure 5.3, pit depth increments generally diminish with each successive cycle. The rate at which growth increments diminish increases with increasing alloy Cu content so that at the conclusion of the experiment the deepest pit is Al 99.999 and the shallowest is Al-2.0Cu. The inhibiting effect demonstrated in these experiments is significant in the case of Al-2.0Cu where a 25 % reduction in pit depth is observed and negligible in the case of Al-0.1Cu.

In Figure 5.4, the estimated pit depth is compared for Al 99.999 and Al-5.0Mg electrodes (2.0 × 10⁻³ cm²), along with Al 99.999 and Al-5.0Mg-0.2Cu (2.3 × 10⁻⁴ cm²). Due to differences in available wire stock and the fact that artificial pit growth rates are strongly dependent on electrode diameter, a direct comparison of Al-5.0Mg and Al-5.0Mg-0.2Cu was not possible. In the comparison presented, pure Al and Al-5.0Mg
dissolution kinetics are virtually identical at first, but after some amount of prior dissolution, Al-5.0Mg kinetics diminished slightly. Dissolution kinetics for Al-5.0Mg-0.2Cu are slower than those of pure Al across the whole comparison. From these data, we conclude that a large addition of Mg to Al slightly reduces dissolution kinetics. Considering the data from Figures 5.3 and 5.4, we conclude that Cu additions on the order of a few tenths of a weight percent produce a small, but in these experiments, discernible reduction in pit dissolution kinetics.

During potential cycling, the surface of the APE was expected to enrich with Cu at potentials below the reversible potential for Cu. We speculate that this enrichment leads to an ennoblement in the pitting potential measured during subsequent activation in the polarization cycle in a manner similar to what has been observed in other studies [12]. Figure 5.5 shows the polarization response in the vicinity of the APE pitting potential after the tenth polarization cycle for Al 99.999, Al-0.1Cu, Al-1.0Cu, and Al-2.0Cu. In this example, which is representative of the data set, the pitting potential does in fact increase as alloy Cu content increases. In Figure 5.6, APE pitting potentials are shown for these alloys after each polarization cycle. The measured $E_{\text{pit}}$ values fluctuate from cycle to cycle, but for Al-2.0Cu there is a distinct increasing trend in $E_{\text{pit}}$. There may be increasing trends for Al-0.1Cu and Al-1.0Cu, but these are more difficult to separate from the $E_{\text{pit}}$ data for Al 99.999. In this regard, the trend in $E_{\text{pit}}$ with alloy composition is similar to that observed for pit growth kinetics: the inhibiting effect of Cu is most clearly seen for the richest alloys and any inhibiting effect is small for Cu additions on the order of a few tenths of a weight percent.
Figure 5.7 shows pitting potentials of Al-5.0Mg-0.2Cu after the polarization cycles 2, 7, 12, and 17. Like the Al-Cu binary alloys, $E_{\text{pit}}$ measurements were scattered and increased just slightly with increasing cycle number. These electrodes were larger in area than the Al-Cu and Al-Mg binary APEs. This is believed to diminish the ennoblement in $E_{\text{pit}}$ observed in these experiments. It also precludes a direct comparison to the Al-5.0Mg binary alloy APE.

5.3.2 Repassivation of Al-Cu and Al-Mg-Cu APEs

During activation, APEs are polarized above the reversible potential of Cu and direct oxidation of Cu from the electrode surface is possible. For Cu-bearing APEs, repassivation occurs in the presence of Cu ion in the APE electrolyte. Figure 5.8 shows the repassivation behavior of Al 99.999, Al-5.0Mg, and Al-Cu binary alloys. The basis for comparison among these curves was nominal APE depth at the time the curve was collected, which was about 400 $\mu$m in this case. Although curves are from different cycle numbers are being compared, all have experienced about the same amount of prior dissolution. Using the data from Figure 5.3 and 5.4, the pit depth was about 400 $\mu$m after the third polarization cycle for Al 99.999 (small), and the fourth cycle for the other alloys. Repassivation potentials ($E_{\text{rep}}$) were taken at the inflection points in the repassivation scan noted in the figure. The plot shows that the repassivation response including $E_{\text{rep}}$ is ennobled for the binary Al-Cu solid solutions compared to pure Al and Al-Mg. Significant ennoblement exists for the Al-1.0Cu and Al-2.0Cu electrodes. Similar results have been reported for the ennobled Epit for Al-Cu solid solution in artificial crevice electrode cell [5].
In a similar fashion, a 0.2 wt.% addition of Cu to an Al-Mg solid solution ennobles repassivation kinetics. Figure 5.9 shows the repassivation scan for Al-5.0Mg and Al-5.0Mg-0.2Cu solid solutions dissolved to a depth of 400 µm (third polarization cycle for Al-5.0Mg and thirteenth for Al-5.0Mg-0.2Cu). It should be noted that the electrode areas in this comparison were different; the area of Al-5.0Mg was $1.1 \times 10^{-4}$ cm$^2$ and Al-5.0Mg-0.2Cu was $1.3 \times 10^{-3}$ cm$^2$. When the repassivation behavior of Al-5.0Mg-0.2Cu is compared to that of Al 99.999 of equal area, ennoblement is still detected (Figure 5.10). In this case, both the APEs have similar areas, on the order of about $10^{-3}$ cm$^2$ (Table 5.1). The pit depth was estimated about 100 µm after the third polarization cycle for both samples (Figure 5.4).

5.3.3 Cu enrichment by APE dissolution

Figure 5.11 is a scanning electron micrograph showing a cross section of an Al-5.0Mg-0.2Cu APE that was subjected to six polarization cycles in 0.1 M NaCl. In this image, the alloy electrode bears polishing marks and is on the left side of the image. Epoxy injected into the open space of the APE to preserve the corroded interface during sample preparation is on the right. The dissolved interface is irregular suggesting variations in dissolution rate develop along the electrode during the course of the experiment. EDX measurements were performed on this sample to analyze for evidence of Cu enrichment. Figure 5.12(a) shows a region on the corroded Al-5.0Mg-0.2Cu interface where EDX measurements were made. Measurements were made along the line indicated in the figure from left to right. EDX spectra for Al K, Cu L characteristic x-rays are plotted as intensity versus position in Figures 5.12(b) and (c). The ratio of Cu L to Al
K is shown in Figure 5.12(d). The peak in plot of the Cu to Al intensity ratio suggests Cu enrichment at this location along the APE surface. Similar evidence of Cu surface enrichment was found at various locations along this and other APE surfaces of Cu-bearing alloys.

5.3.4 Behavior of APEs during repassivation and cathodic polarization

Figure 5.13 shows the 1st, 2nd, 3rd, 4th, 5th, and 6th polarization cycles for Al-5.0Mg-0.2Cu, and the 3rd polarization cycle for Al-5.0Mg (dashed line). In the cathodic branch of the polarization curve, a significant increase in current density was observed at potentials between $-1.0$ and $-1.3$ V. Overall, this figure shows two important effects of Cu on the reaction kinetics of Al alloys. These are retarded kinetics in the anodic regime, perhaps due to surface film formation, and enhanced kinetics in the cathodic regime (to potentials of $-1.3$ V in this case), again possibly related to Cu-rich surface film formation.

Sasaki and Issacs have also reported reduction peaks in cathodic branches of APE cyclic polarization curves carried out with 99.999 % and 99.9 % purity Al [9]. They considered the possibility of impurity metal ion reduction as the origin of the peak, but argued that it resulted from the reduction of protons accumulated in the APE. In our experiments, the cathodic peak was observed for each of the Cu-bearing alloys used, but not for Al 99.999 or Al-5.0Mg. Figures 5.14 and 5.15 plot the magnitude of the cathodic peak current density versus polarization cycle number for each of the alloys in this study. In the case of the binary alloys, the highest current densities were observed for the alloys with the highest Cu content. The peak current densities recorded for Al-5.0Mg-0.2Cu approached those for the Al-2.0Cu binary alloy.
In our experiments, the possibility of metal ion reduction giving rise to the cathodic peak cannot be ruled out easily. To determine if hydrogen reduction could fully account for the observed peak, the necessary pH was estimated. Hydrogen reduction was assumed to occur as:

\[
2H^+ + 2e^- \rightarrow H_2
\]  
Eqn. 5.4

The total charge associated with the peak charge was estimated from Faraday’s law and integration of the polarization curve in the region of interest:

\[
Q = nmF
\]  
Eqn. 5.5

\[
m = \frac{Q}{nF} = \frac{I \times time}{nF}
\]  
Eqn. 5.6

where \(n\) is equivalent number (1 equiv/mol for hydrogen ion), \(m\) is mass of hydrogen ions (mol), \(F\) is Faraday’s constant (96,487 C/equiv). Once the hydrogen mass (m) is known, concentration of hydrogen ions is calculated using the following equation.

\[
\left[ H^+ \right] = \frac{m}{V}
\]  
Eqn. 5.7
where \( V \) is volume of artificial pit that can be estimated from the known value of electrode area and the estimated pit depth as shown in Figure 5.3 and 5.4. Assuming no diffusion of protons from the APE and no significant contribution to the cathodic current from oxygen reduction, a pH of 1.7 is needed to allow the cathodic peak of the 1\textsuperscript{st} polarization cycle shown in Figure 5.13. A pH of 0.11 is needed to allow the peak in the 17\textsuperscript{th} polarization cycle. Neither of these pH values is unreasonable for this experiment.

Conversely, if the cathodic peak was due to only Cu ion reduction, then what Cu ion concentration is needed to support the observed peaks and might that be achieved by prior dissolution? To answer the question we estimated the maximum possible charge associated with reduction of Cu ions produced by APE dissolution to the integrated charge in the cathodic peak. The mass of Cu ions from APE dissolution was:

\[
\text{mass} = 0.002 \rho V \quad \text{Eqn. 5.8}
\]

where \( \rho \) is density of Al (2.7 g/cm\(^3\)) and \( V \) is volume of the APE dissolved calculated from the known electrode area and the pit depth. The factor of 0.002 accounted for the concentration of Cu in the APE. The associated charge from reduction of these ions, \( Q_{\text{Cu}^{2+}/\text{Cu}^-} \), was calculated using Faraday’s law:

\[
Q_{\text{Cu}^{2+}/\text{Cu}^-} = nmF \quad \text{Eqn. 5.9}
\]
where \( n \) is 2 (equiv/mol) for Cu ions, \( m \) is mol of Cu ions equals to mass divided by atomic mass of Cu (63.546 g/mol), and \( F \) is Faraday’s constant (96,487 C/equiv). Assuming no diffusion of \( \text{Cu}^{2+} \) from the APE and perfect reduction efficiency, the \( \text{Cu}^{2+} \) reduction charge is 4.5 times greater than that of the charge from integrating the cathodic peak in the first polarization cycle. By the eighth cycle, \( \text{Cu}^{2+} \) reduction charge fell to 97% of the charge from peak integration and by the 17th cycle it was only 22% of the needed peak charge.

Because the Cu ion reduction charge is not well correlated to the peak charge, the peak is well below the reversible potential for Cu, and the APE solution is likely to be sufficiently acidic, we conclude that the cathodic polarization response on Cu-bearing APEs is dominated by proton reduction from the corrosion potential on the reverse scan to about \(-1.3 \text{ V}\). Furthermore, we conclude that proton reduction is facilitated by a Cu-enriched layer that has formed on the APE surface during the repassivation process. The nature of these experiments do not reveal what specific effects Cu reduction has on the pit repassivation process, but these experiments do suggest the possibility that pit repassivation in Cu-bearing alloys is fundamentally different than that in Cu-free alloys.

### 5.3.5 The effect of Cu on dissolution characteristics

The dissolution behavior of several Al binary alloys related to commercial alloy compositions have been characterized and reported [3-5, 13]. In particular, the results of this study compare most closely with a study reported by Ramgopal and Frankel who used an artificial crevice electrode cell to study the dissolution kinetics of sputter deposited Al-Cu alloy thin films. This study showed that Cu alloying additions ennobled
dissolution kinetics resulting in an increased repassivation potential [5]. A voltage component calculation was used to show that the primary effect of Cu on pit dissolution kinetics was to increase the surface overpotential for alloy dissolution. A specific linkage to Cu surface enrichment or a surface film of any type was not made in this work. This study noted that ennobling effects were insignificant for Cu concentrations under 0.2 wt.% and were most significant for Cu concentrations approaching 4.0 wt.% This general trend is reflected in many facets of the present study including pit growth, ennoblement of dissolution kinetics and $E_{\text{rep}}$ and $E_{\text{pit}}$, and catalysis of hydrogen reduction on repassivated APE surfaces.

In a separate study focused on metastable pitting in Al-Cu alloys, Cu additions have been shown to inhibit pit growth kinetics [6]. Evidence for local Cu surface enrichment due alloy dissolution has been developed, and the idea that this is connected to ennobled dissolution kinetics has been explored [12]. The cyclic polarization approach used in this study was expected to lead to, and perhaps even enhance Cu surface enrichment. In fact, characterization of the APE interface indicates Cu surface enrichment occurs for alloys with both small and large Cu concentrations.

Across the range of cases studied here, three main features are demonstrated in the electrochemical response of APEs made with Cu-bearing Al alloys: 1) an increase in the APE pitting potential, 2) ennobled dissolution kinetics and retarded pit growth, and 3) increased ability to catalyze reduction reactions on passivated APE surfaces. We suggest that these behaviors are associated with Cu enrichment at the active pit surface. Given these features, the essential characteristics of Cu-rich surface films that form under pit-like conditions are that they confer protective properties by limiting alloy dissolution and
can support reduction reactions at enhanced rates compared to passivating or passivated pure Al surfaces. These essential behaviors associated with Cu are likely to affect the course of localized corrosion in Al-Cu alloys with consequences for the temporal evolution and morphology of corrosion damage accumulation.

5.4 CONCLUSIONS

1. In cycle polarization experiments with Al-Cu-X solid solution alloys artificial pit electrodes pit growth rates were observed to be slower than comparative pure Al and Al-Mg solid solution electrodes. Growth rates were significantly slowed for alloys with about a Cu content of about 2.0 wt.%, and were slightly slowed for alloys containing only 0.2 wt.% Cu.

2. In electrochemical measurements Cu-bearing solid solutions demonstrated elevated pitting potential and repassivation potentials. Dissolution kinetics in repassivation polarization scans were also ennobled. Consistent with the findings of Ramgopal and Frankel, the magnitude of this ennoblement was dependent on the solid solution Cu content.

3. Ex-situ SEM/EDX characterization of pit surfaces showed evidence of Cu enrichment. Surfaces of Al-Cu-X electrodes were irregular suggesting that differential dissolution rates developed during the course of dissolution experiments.
4. Distinctive reduction peaks were found in cathodic polarization scans on passivated Cu-bearing electrodes. Such peaks were absent in pure Al and Al-Mg solid solution electrodes. These peaks are attributed to the reduction of protons from the acid APE environment on a Cu-enriched surfaces as well as Cu ion reduction reaction.
Figure 5.1: A schematic drawing of the artificial pit electrode cell.
Figure 5.2: Cyclic polarization curve of Al-5.0Mg-0.2Cu from its 3rd cycle.
Figure 5.3: Estimated pit depth using Faraday’s law for Al 99.999 (small), Al-0.1Cu, Al-1.0Cu, and Al-2.0Cu as a function of number of polarization cycles.
Figure 5.4: Estimated pit depth using Faraday’s law for Al 99.999 (Both of large and small), Al-5.0Mg and Al-5.0Mg-0.2Cu.
Figure 5.5: Part of potentiodynamic curves for Al 99.999 (small), Al-0.1Cu, Al-1.0Cu, and Al-2.0Cu after the 10th polarization cycle.
Figure 5.6: Pitting potentials of Al 99.999 (small), Al-0.1Cu, Al-1.0Cu and Al-2.0Cu as a function of number of polarization cycles.
Figure 5.7: Plot of current density in terms of potential during anodic polarization scanned from –1.4 to 0.4 V (vs. SCE) for Al-5.0Mg-0.2Cu.
Figure 5.8: Repassivation behavior of Al 99.999 (small), Al-5.0Mg and Al-Cu alloys.
Figure 5.9: Repassivation behavior of Al-5.0Mg and Al-5.0Mg-0.2Cu.
Figure 5.10: Repassivation behavior of Al 99.999 (large) and Al-5.0Mg-0.2Cu.
Figure 5. 11: Image of artificial pit of Al-5.0Mg-0.2Cu after six polarization cycles.
Figure 5.12: (a) Pit morphology of Al-5.0Mg-0.2Cu and EDX spectra for (b) Al K, (c) Cu L and (d) ratio of Cu L to Al K.
Figure 5.13: Repetitive polarization cycles of Al-5.0Mg-0.2Cu (1st, 2nd, 3rd, 4th, 5th and 6th) and Al-5.0Mg (3rd).
Figure 5.14: Cathodic peak current density in terms of polarization cycle number for Al 99.999 and Al-0.1Cu, Al-1.0Cu and Al-2.0Cu.
Figure 5.15: Cathodic peak current density in terms of polarization cycle number for Al-5.0Mg and Al-5.0Mg-0.2Cu.
Table 5. 1: Sample dimensions and electrode areas of materials used in the artificial pit electrode cell experiment.

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</tr>
<tr>
<td>Al 99.999 (large)</td>
<td>500</td>
<td>$2.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Al-0.1Cu</td>
<td>160</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Al-1.0Cu</td>
<td>160</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Al-2.0Cu</td>
<td>170</td>
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</tr>
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REFERENCES

CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 CONCLUSIONS

In this study, the effect of alloying Cu on Al-Cu and Al-Mg-Cu solid solution alloys were investigated with aims to elucidate role of Cu on localized corrosion of aluminum alloys. The followings are key findings:

1. Cu additions to Al alloys will increase $E_{\text{pit}}$ measured electrochemically provided that the Cu is retained in solid solution and the density of heterogeneous pit initiation sites is low. A multi-electrode approach was used to collect statistically large populations of pitting potential measurements on Al 99.999, Al-0.2Cu, Al-2.0Cu, and Al-2.0Zn solid solution alloys (area $\approx 10^{-4}$ cm$^2$) with different passive dissolution periods. Results confirmed that Cu dissolved in solid solution ennobles pitting compared to Al 99.999, while Zn activates it. But the ennobled pitting potential is dependent on the electrode area and occurs regularly only on small electrode ($10^{-4}$ cm$^2$), but not on large ones ($10^{-2}$ cm$^2$).
2. A study of individual metastable pit transients showed that Cu in solid solution depresses the metastable pit initiation rate. The initiation rate is decreased by an order of magnitude by the addition of 0.2 wt.% Cu and is essentially eliminated by addition of 2.0 wt.% Cu over the duration of our experiment.

3. Cu in Al-Cu solid solution inhibits the dissolution kinetics of metastable pits by reducing the growth rate \( (i.e., \frac{I_{\text{peak}}}{I_g}) \). Considering probabilistic frameworks describing formation of stable pits from metastable ones, the decrease in the metastable pit initiation and growth rates lower the probability of formation of stable pits resulting in the observed increases in the pitting potential due to alloying Al with Cu.

4. Cu additions do affect the repassivation behavior of metastable pit in Al, resulting in a distinctive two-stage repassivation process. Two-stage repassivation consists of a rapid initial repassivation event and a much slower second stage of repassivation. A comparison of first stage repassivation kinetics in Al-0.2Cu with those of Al 99.999 shows that rates are essentially identical; hence the effect of Cu on repassivation behavior is not expected to affect stable pit formation.

5. Electrochemically stimulated dissolution ennobles the subsequently measured pitting potential for Al-Cu alloys provided that the dissolution does not lead to localized corrosion in the first place. The ennobling effect is diminished or absent in large area electrodes containing heterogeneous defects that are not healed by during stimulated
dissolution. STEM shows that Cu surface enrichment by dissolution under conditions of aggressive, uniform electrochemical dissolution, cathodic polarization (alkaline cathodic corrosion) and pitting. In the case of metastable pitting or passive dissolution, localized Cu enrichment may occur leading to the observed ennoblement of Epit.

6. Copper in Al-Mg-Cu solid solutions ennobles the dissolution kinetics of the alloy. Pit growth rates of Al-Mg-Cu solid solutions is lower than that of an Al-Mg solid solution or pure Al. It is also determined that Cu reduces the pit growth rate of Al-Cu solid solutions. The repassivation potential is higher for Al-Mg-Cu solid solutions than for pure Al and Al-Mg solid solutions. Pitting potential (E_{pit}) measurements after cyclic polarization show that E_{pit} is generally higher for higher Cu-content alloys. In cyclic polarization experiments, E_{pit} is also proportional to the number of polarization cycles for Al-Cu and Al-Mg-Cu solid solution alloys. As the pit deepens after each polarization cycle more Cu is enriched at the pit surface, which decreases susceptibility to subsequent pit initiation. Diagnostic evaluation on cathodic peak rise indicates that the peak rise is due to the increased rate of hydrogen reduction reaction as well as Cu ion reduction reaction. Cu enrichment at the artificial pit surface sustains a higher hydrogen evolution rate. The EDS analysis on the bottom of one of local pits indicates locally Cu enriched layer.

6.2 FUTURE WORK

While the role of Cu in Al-Cu solid solution was systemically characterized in this study, there exist unresolved issues. The critical issues are as following:
1. The local acidification model associated with local Cu enrichment still cannot explain the inhibiting effect of Cu on metastable pit initiation rate. In order to achieve local acidification, the metal should begin to dissolve in any mechanism that has not been explained in this study.

2. Reduced initiation rate of metastable pits by Cu addition in Al-Cu solid solution can be further considered by observing pit morphologies and its densities on pure Al, Al-Cu solid solution and Cu-bearing Al alloys. Metastable pit initiation rate can be dependent on surface roughness. Study on relationship between surface roughness and pit initiation rate for pure Al and Al-Cu solid solution will elucidate the mechanism of pit initiation further.

3. Measurement on growing pit’s pH should support the local acidification model. The local pH on Cu enriched layer is plus.

4. Technical development on the needle sample preparation for STEM/EDS analysis should be carried out in an attempt to reduce initial Cu enrichment on the electropolished sample surface.

5. Dissolution kinetic should be further studied by applying potentiostatic polarization instead of repetitive polarization. Measuring the pit depth by using optical microscopy through the transparent film should help to obtain real pit depth in terms of charge passed and Cu contents.
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