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LOCALIZED CORROSION KINETICS IN HIGH STRENGTH AA2024 ALLOYS

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By

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2001

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ABSTRACT

Understanding of localized corrosion and its growth kinetics is critical from both scientific and practical points of view, since the high strength Al alloys widely used in aircraft structures are extremely susceptible to localized corrosion. In this work, the foil penetration technique, a non-electrochemical method for studying the growth kinetics of the fastest-growing localized corrosion site (pit, crevice, or intergranular attack), combined with electrochemical techniques, metallographic cross-sections, and other materials characterization tools such as SEM, TEM, and microfocal X-ray radiography, were used to address the effects of alloy microstructure, sample orientation, and artificial aging, potential, and environmental factors on the kinetics and morphologies of localized corrosion in AA2024 (Al-4.5%Cu-1.5%Mg).

AA2024 in the solution heat treated and water quenched condition, T3, and T3+ tempers exhibited two breakdown potentials, whereas overaged AA2024-T8, T8+, and solutionized and furnace cooled AA2024 exhibited only one breakdown potential. The breakdown potential decreased with increasing aging time at 190 °C. When two breakdown potentials were observed, the more active one was found to be related to the transient dissolution of S-phase Al2CuMg particles leading to pitting while the noble one
was thought to result primarily from initiation and growth of IGC. Localized corrosion was found to initiate at lower potentials as a result of artificial aging at 190°C, but the attack was in the form of selected grain dissolution rather than sharp IGC.

The growth kinetics of localized corrosion in T3 temper exhibited a strong anisotropy. Growth in the short transverse direction (through-thickness direction of a rolled plate) was found to be much slower than that in either the longitudinal or long transverse direction. The anisotropy occurred because pits that initiated on the surface often developed into intergranular corrosion (IGC) as they grew into the microstructure. Metallographic cross sections confirmed that the growth rate anisotropy was a result of microstructural anisotropy and a large difference in intergranular path length per nominal thickness for various orientations. The anisotropy of growth kinetics was found to be different for various forms of AA2024-T3 having different microstructures.

Localized corrosion kinetics were found to be almost independent of potential over a large range. Pitting was dominant only at low potentials where its growth rate was dependent on potential. Artificial aging had a strong effect on polarization and corrosion morphology of AA2024 in chloride, resulting in selected granular attack in T8 and T8+ tempers, but the aging did not have a significant effect on the localized corrosion kinetics at -580 mV SCE and open circuit. Both grain size and aspect ratio were found to be important factors in controlling the IGC growth kinetics. A statistical model was developed to explain anisotropic growth kinetics on the basis of the Al alloy microstructure. Finally, the influence of potential and nitrate or sulfate addition on the localized corrosion kinetics and morphology of T3 temper was also investigated.
TO MY WIFE, YONGMEI GAO
AND MY DAUGHTERS, YING-YING ZHANG,
JESSICA LING-LING ZHANG
ACKNOWLEDGMENTS

I am sincerely grateful to many people for their help and cooperation during the course of my graduate studies at the Fontana Corrosion Center (FCC) of the Ohio State University. First, I would like to thank my adviser Dr. Jerry Frankel, for his incredible and unconditional inspiration, encouragement, and advice in various aspects of my graduate studies. I appreciate the opportunity that he offered me as his graduate student to pursue my advanced study in the areas of electrochemistry and materials corrosion, which has not only helped me continuously learn and grow in my professional career, but also refined and developed my skills and experiences for my future career. I also wish to thank other committee members, Dr. Rudy Buchheit, Dr. Glenn Daehn, and Dr. Neil Falkner for their valuable comments and suggestions on my research and dissertation. I would like to acknowledge the US Air Force Office of Scientific Research for financially supporting this project.

I have received the endless assistance and cooperation in my experiments and result analysis from many former and current post doctoral researchers and senior graduates at FCC, and would like to thank them by listing their names here: Dr. Akshey Sehgal, Dr. Patrick Schmutz, Dr. Eiji Akiyama, Dr. Donghui Lu, Dr. Jian Zhang, Dr.
Mr. X, Mr. Derk Devecchio, Mr. Xiaodong Liu, and others. I would also like to thank Dr. Doug Wolfe and Ms. Shiling Ruan, from the Statistics Department at the Ohio State University, with whom I collaborated on the development of a statistical model for anisotropic intergranular corrosion growth. Microfocal x-ray radiographic analysis was performed by Mr. B. Zoofan in Prof. S. Rokhlin's lab in the department of Industrial Welding and Systems Engineering at the Ohio State University. Mr. Hendrick Colijn, Mr. Steve Bright, Mr. Cameron Begg, Mr. Gary Dodge, and Mr. Kenneth Kushner for help and training in use and operation of many MSE research facilities such as TEM, SEM, optical microscopy, and other tools. Ms. Cindy Flores and Ms. Dena Bruedigam, FCC administrative associates, for office supplies and other materials for the experiments, are also deeply appreciated.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abstract</td>
<td>ii</td>
</tr>
<tr>
<td>Dedication</td>
<td>iv</td>
</tr>
<tr>
<td>Acknowledgments</td>
<td>v</td>
</tr>
<tr>
<td>Vita</td>
<td>vi</td>
</tr>
<tr>
<td>List of Tables</td>
<td>xii</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xiii</td>
</tr>
<tr>
<td>Chapters:</td>
<td></td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>2. Literature Review</td>
<td>6</td>
</tr>
<tr>
<td>2.1 Pitting Corrosion</td>
<td>7</td>
</tr>
<tr>
<td>2.1.1. Characteristic potentials</td>
<td>7</td>
</tr>
<tr>
<td>2.1.2. Pit initiation</td>
<td>9</td>
</tr>
<tr>
<td>2.1.3. Metastable pits</td>
<td>11</td>
</tr>
<tr>
<td>2.1.4. Pit growth</td>
<td>13</td>
</tr>
<tr>
<td>2.2. Intergranular Corrosion (IGC)</td>
<td>23</td>
</tr>
<tr>
<td>2.2.1. IGC mechanisms</td>
<td>23</td>
</tr>
<tr>
<td>2.2.2. Relations between IGC, pitting and other forms of localized corrosion</td>
<td>30</td>
</tr>
<tr>
<td>2.3. Critical Factors in Controlling Localized Corrosion Kinetics</td>
<td>31</td>
</tr>
<tr>
<td>2.3.1. Alloy microstructure</td>
<td>32</td>
</tr>
<tr>
<td>2.3.2. Composition of electrolyte</td>
<td>38</td>
</tr>
<tr>
<td>2.3.3. pH effect</td>
<td>45</td>
</tr>
<tr>
<td>2.3.4. Inhibitors</td>
<td>48</td>
</tr>
<tr>
<td>2.4. Techniques for Studying Localized Corrosion Kinetics</td>
<td>51</td>
</tr>
<tr>
<td>2.5. Motivation and Objectives of the Thesis</td>
<td>54</td>
</tr>
</tbody>
</table>
   3.1 Introduction ................................................................. 83
   3.2 Experimental ............................................................. 85
   3.3 Results and Discussion .................................................... 87
      3.3.1 Microstructure .......................................................... 87
      3.3.2 Polarization curves .................................................. 91
      3.3.3 Types of corrosion ................................................... 93
      3.3.4 Effect of artificial aging ............................................ 101
      3.3.5 Effect of nitrate and sulfate additions ......................... 105
   3.4 Summary ........................................................................ 107

   4.1 Introduction ................................................................. 146
   4.2 Experimental ............................................................. 148
      4.2.1 Materials and samples .............................................. 148
      4.2.2 Foil penetration method ........................................... 149
      4.2.3 Characterization techniques ...................................... 151
   4.3 Results and Discussion .................................................... 152
      4.3.1 Localized corrosion growth at open circuit .................. 152
      4.3.2 Localized corrosion growth under potentiostatic conditions 158
      4.3.3 Effect of potential ................................................... 161
      4.3.4 Effect of artificial aging ............................................ 166
      4.3.4 Effect of nitrate or sulfate addition .......................... 169
   4.4 Summary ........................................................................ 170

5. Statistical Modeling for IGC Growth ................................................. 205
   5.1 Introduction ................................................................. 205
   5.2 Statistical modeling for IGC growth .................................. 206
   5.3 Summary ........................................................................ 223

6. Conclusions, Relevance of This Work, and Suggestions for Future Work ........ 235

Bibliography ............................................................................ 244
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Corrosion costs on US military aircraft in 1996</td>
<td>5</td>
</tr>
<tr>
<td>2.1</td>
<td>Electrochemical properties of intermetallic particles present in Al-Cu and Al-Cu-Mg alloys</td>
<td>65</td>
</tr>
<tr>
<td>3.1</td>
<td>Composition of as received AA2024-T3 plate and sheet materials (wt%)</td>
<td>110</td>
</tr>
<tr>
<td>3.2</td>
<td>Summary of observations obtained from potentiostatic polarization experiments</td>
<td>111</td>
</tr>
<tr>
<td>3.3</td>
<td>Influence of potential scan-rate on breakdown potentials for AA2024-T3, T8</td>
<td>112</td>
</tr>
<tr>
<td>3.4</td>
<td>Breakdown potentials for various tempered AA2024 (ST) alloys in Ar deaerated 1 M NaCl at scan rate of 0.1 mV/s. If one value is given, only one breakdown was observed</td>
<td>113</td>
</tr>
<tr>
<td>4.1</td>
<td>Methods for pit depth measurements</td>
<td>174</td>
</tr>
<tr>
<td>4.2</td>
<td>AA2024 materials and their heat treatments used in this work</td>
<td>175</td>
</tr>
<tr>
<td>4.3</td>
<td>Some open circuit foil penetration results for AA2024-T3 alloys</td>
<td>176</td>
</tr>
<tr>
<td>4.4</td>
<td>Penetration results for ST samples at low potentials in Ar-deaerated solutions</td>
<td>176</td>
</tr>
<tr>
<td>5.1</td>
<td>Average grain dimensions determined from ST, L and LT sections of AA2024-T3 plate</td>
<td>225</td>
</tr>
<tr>
<td>5.2</td>
<td>$\alpha$ and $\beta$ values of the gamma distribution estimated from the grain dimension measured from ST and L sections</td>
<td>225</td>
</tr>
</tbody>
</table>

xii
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Schematic cyclic potentiodynamic polarization curve to give $E_p$ and $E_r$</td>
<td>66</td>
</tr>
<tr>
<td>2.2</td>
<td>Schematic diagrams for pit initiation models. (a) adsorption mechanism; (b) anion penetration and ion migration model; (c) film breakdown theory.</td>
<td>67</td>
</tr>
<tr>
<td>2.3</td>
<td>Metastable pitting current transients observed on 302 stainless steel in 0.1 M NaCl at 420 mV SCE.</td>
<td>68</td>
</tr>
<tr>
<td>2.4</td>
<td>Mathematical transformation of an equi-concentration and equi-potential plane diffusion (a) into an equivalent plane problem (b).</td>
<td>68</td>
</tr>
<tr>
<td>2.5</td>
<td>Schematic anodic polarization curves for the pit and unpitted surface.</td>
<td>69</td>
</tr>
<tr>
<td>2.6</td>
<td>Galvanostatic potential transients; solid line represents experimental data; dashed line represents theoretical. (a) Fe in 1 M KCl, (b) Ni in 4 M KCl.</td>
<td>69</td>
</tr>
<tr>
<td>2.7</td>
<td>Influence of potential on the pit growth including pit depth and pit current density of Al foil in 0.01 M NaCl at pH 11.</td>
<td>70</td>
</tr>
<tr>
<td>2.8</td>
<td>Dependence of the product of pit depth and pit current on the ohmic potential drop.</td>
<td>70</td>
</tr>
<tr>
<td>2.9</td>
<td>Anodic and net current densities change as a function of potential for 100 nm Al film in 0.1 M NaCl.</td>
<td>71</td>
</tr>
<tr>
<td>2.10</td>
<td>Concentration of $Fe^{2+}$, $Fe(OH)^+$, and $H^+$ as a function of the product of the depth and current density in one-dimensional pit.</td>
<td>71</td>
</tr>
<tr>
<td>2.11</td>
<td>Corrosion potentials of the grains and grain boundaries for Al-4%Cu alloy as a function of aging time at 375 °F.</td>
<td>72</td>
</tr>
</tbody>
</table>
2.12 Effect of chloride concentration on the pitting potential of Al and Al-Cu alloys in deaerated NaCl solutions .................................................................................. 73

2.13 Potential-chloride concentration-type of corrosion relation for Al-4%Cu alloys ......................................................................................................................... 73

2.14 Two breakdown potentials observed in peak aged Al-4%Cu alloys ................................................................................................................................. 74

2.15 Anodic polarization curves for T1 (Al2CuTi) phase and Al in deaerated 0.6 M NaCl solution ........................................................................................................... 74

2.16 Effect of cooling rate during quenching between 400 to 315 °C on the susceptibility to IGC and SCC. IGC was tested in NaCl-H2O2, and SCC tested in 3.5% NaCl .................................................................................................................. 75

2.17 Effect of cooling rate on corrosion behavior of 2024Al alloys in 0.2 M NaCl .......................................................................................................................... 75

2.18 Effects of artificial aging on the corrosion and SCC behavior of AA2024 in NaCl solution........................................................................................................... 76

2.19 Pitting potentials of Al 99.99% in mixtures of NaCl + NaNO3 solutions .............. 76

2.20 Effects of Na2SO4 addition to 0.005M NaCl, and NaNO3 to 0.1 M NaCl on the number of pits formed on 99.4% Al samples (24 h immersion).............. 77

2.21 Effect of chloride concentration on pit growth rate .......................................................................................................................... 77

2.22 Influence of foreign anions addition to chloride on the perforation time and the electrolyte resistance (Foil thickness 0.2 mm, 0.01 M NaCl, pH=11 at -430 mV SCE) ........................................................................................................... 78

2.23 Pitting potentials of Al 99.99% in neutral deaerated mixtures of NaCl + Na2SO4 solutions ........................................................................................................ 78

2.24 Pit current-time curve for 7075 Al alloys in 0.1 M Na2SO4 added 1 x10^{-4} M F after 6 minutes ........................................................................................................ 79

2.25 Pitting potentials for Al as a function of pH in 0.1 and 1M chloride solutions. 79

2.26 Anodic polarization curves of AA2024-T3 in stagnant 0.1 M NaCl + 0.1M [Cr6+] solutions with varying pH ........................................................................... 80

2.27 Anodic polarization curves for AA2024-T3 in

xiv
2.28 Effect of pH on time to failure by stress corrosion cracking in AA7075-T6.  

2.29 Effect of chromate on the anodic current spikes associated with metastable pitting. On top left also shown is the cumulative number of pitting events/cm² verse exposure time.  

2.30 Microradiographs of 0.2 mm thick AA2024-T3 penetrated in an oxygen stirred 1 M NaCl + 0.3 %H₂O₂ + 10⁻⁴ M Na₂Cr₂O₇ solution.  

3.1 Microstructure of three orthogonal sections: (a) 1.9 cm thick AA2024-T3 plate, (b) AA2024-T8, (c) 0.2 mm thick AA2024-T3 sheet.  

3.2 SEM images of as-polished AA2024-T3 surface (a) BSE image showing aligned stringers of coarse intermetallic particles, (b) SE image showing two types of intermetallic particles: particles A-D are Al-Cu-(Fe,Mn) intermetallics, and particles 1-4 are Al-Cu-Mg intermetallics, (c) Typical EDS spectrum of the particles 1-4, (d) Typical EDS spectrum of the particles A-D in the micrograph (b).  

3.3 Transmission electron micrographs of AA2024-T3 showing (a) plate-like S' (Al₂CuMg) precipitates, (b) rod-like precipitates in matrix and grain boundaries.  

3.4 Transmission electron micrographs of AA2024-T8 showing (a) plate-like S' (Al₂CuMg) precipitates and rod shaped dispersoids in matrix, (b) Precipitate free zones around grain boundaries.  

3.5 Hardness-time curves for AA2024 aged at 190 °C.  

3.6 Optical micrographs of LT sections of AA2024-T3 (a), T8 (b) showing pancake-shaped grain structure, and fine sub-grain structure in T8 temper alloy.  

3.7 Anodic polarization curves for AA2024-T3 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV/s.  

3.8 Optical micrographs of the exposed surfaces of AA2024-T3 samples potentiostatically polarized at: (a) –690 mV SCE for 12 h, (b) –670 mV SCE for 2 h, (c) –660 mV SCE for 20 h, (d) cross section for the sample polarized at –660 mV SCE for 20 h.  

3.9 SEM images of the exposed surface for T3 samples potentiostatically deaerated solutions with varying pH.
3.10 Metallographic cross sections of AA2024-T3 (ST) potentiostatically polarized at, (a) -645 mV SCE for 5 h, (b) -645 mV SCE for 20 h, (c) -590 mV SCE for 5 h, (d) exposed surface of the sample polarized at -590 mV SCE for 5 h ................................................................. 123

3.11 Optical micrograph of the exposed surface of T3 sample potentiodynamically polarized to -560 mV SCE in Ar-deaerated 1 M NaCl. ................................. 124

3.12 Optical micrographs of AA2024-T3 surface, (a) sample potentiodynamically polarized to -560 mV SCE, (b) the same exposed surface area in (a) after potentiostatic polarization at -660 mV SCE for 12 h, (c) net current density changes during the potentiostatic experiment at -660 mV SCE ............................... 125

3.13 SEM images showing exposed surface of AA20245-T3 (ST) samples. (a) first potentiodynamically polarized to -560 mV SCE, and immediately followed by potentiostatic polarization at -660 mV SCE for 12 h, (b) first potentiodynamically polarized to -560 mV SCE, and immediately followed by potentiostatic polarization at -660 mV SCE for 65 h ....................... 126

3.14 Current density transients for AA2024-T3 (ST) samples held at potential range from -690 to -645 mV SCE, which is above the first breakdown and below the second breakdown potentials ........................................ 127

3.15 (a) Net current density transients for AA2024-T3 (ST) potentiostatically polarized at -660 mV SCE for 20 h, (b) the initial net current density transients at -660 mV SCE ........................................ 128

3.16 Net current density transients for AA2024-T3 (ST) samples held at -645 and -590 mV SCE, respectively ......................................................... 129

3.17 (a) Net current density changes with time for AA2024-T3(ST) when the potential was switched from -660 to -580 mV SCE, (b) Initial current density transient at -660 mV SCE ............................................ 130

3.18 Cyclic polarization curves for AA2024-T3 in deaerated 1.0 M NaCl at 0.1 mV/s scan rate ............................................................. 131

3.19 Metallographic cross sections of T3 samples cyclically polarized to (a) -620 mV on reverse scan, followed by potentiostatic polarization at the potential for 20 h, (b) -660 mV and held the potential for 20 h, (c) -800 mV SCE and held the potential for 20 h in deaerated 1 M NaCl ........ 132
3.20 The current densities as a function of time for the potentiostatic experiment at -620, -660, and -800 mV SCE, respectively.................................. 133

3.21 Cyclic anodic polarization curves for the same AA2024-T3 (ST) sample, first cyclic potential scanned twice from below OCP to -590 mV SCE, then potentiostatically polarized at -660 mV SCE for 15 h, followed by the third potential cycle in Ar-deaerated 1 M NaCl at 0.1 mV/s scan rate. ................................................................. 133

3.22 Anodic polarization curves for various tempers of AA2024 (ST) in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV/s. ......................... 134

3.23 (a) SEM image showing exposed surface and metallographic cross sections of ST orientated T8 samples potentiostatically polarized at (b) -740 mV SCE for 2 h, (c) -700 mV SCE for 12 h, and (d) -675 mV SCE for 3 h in Ar deaerated 1 M NaCl solutions................................. 135

3.24 SEM images of (a), and (b) showing exposed surface of T8 sample potentiodynamically polarized to -740 mV SCE, and followed by potentiostatic experiment at -740 mV SCE for 2 h, (c) EDS for un-dissolved Al-Cu-Mg particles on the exposed surface................................. 136

3.25 Optical micrographs showing exposed surface of T8 sample (a) potentiodynamically polarized to -660 mV SCE, (b) further held at -660 mV SCE for 2 h, (c) cross section................................................................. 137

3.26 Metallographic cross sections of L orientated T8 samples exposed at open circuit (-740 mV SCE) for 15.9 h, and (b) -580 mV SCE for 5.5 h in oxygenated 1 M NaCl solutions .................................................... 138

3.27 Current density changes with time for AA2024-T8 at different potentials. ...... 139

3.28 Cyclic polarization curves for AA2024-T3 and T8 tempers. ......................... 139

3.29 Metallographic cross sections of T8 samples (a) cyclic potentiodynamically polarized to -800 mV SCE on reverse scan without potentiostatic experiment, (b) followed by potentiostatic experiment at -800 mV for 15 h, (c) net current density changes during the potentiostatic experiment at -800 mV SCE. .............................................. 140

3.30 Cyclic polarization curves for AA2024-T3 (ST) in deaerated nitrate containing 1.0 M NaCl................................................................. 141

3.31 Metallographic cross sections of T3 cyclic potentiodynamically
polarized to, (a) -630 mV SCE on reverse scan without potentiostatic experiment, (b) followed by potentiostatic experiment at -630 mV SCE for 20 h, (c) -600 mV SCE and followed by potentiostatic experiment for 20 h in deaerated 1 M NaCl + 0.2 M NaNO₃

3.32 Current density as a function of time for AA2024-T3 (ST) samples held at -600 and -630 mV on reverse scan in deaerated 1 M NaCl + 0.2 M NaNO₃

3.33 Cyclic polarization curves for AA2024-T3 (ST) in deaerated sulfate containing 1.0 M NaCl

3.34 Cyclic polarization curves for AA2024-T3 in deaerated 1.0 M NaCl with nitrate and sulfate additions

3.35 SEM images showing IGC of AA2024-T3 (L) potentiostatically polarized at -580 mV for 20 h in deaerated 1 M NaCl + 0.2 M NaNO₃

4.1 Metallographic sections of AA2024-T3. Also given is the terminology used for the different sections

4.2 Schematic of the electrochemical cell for the penetration experiment

4.3 Schematic of detection circuit diagram

4.4 Schematic of foil penetration experimental set-up

4.5 Schematic of microfocal X-ray radiography system

4.6 Localized corrosion morphologies for 1.9 cm thick AA2024-T3 (ST) at open circuit (a) after 89 h exposure, (b) after 332 h exposure, (c) after 450 h exposure

4.7 Penetration time for 1.9 cm thick plate and 0.21 mm as-received sheet alloys in oxygen-bubbled 1 M NaCl at open circuit

4.8 Localized corrosion morphologies for 1.9 cm thick AA2024-T3 L samples penetrated at open circuit

4.9 Penetration time for plate and as-received sheet alloys in 1 M NaCl + 5x10⁻² M Na₂S₂O₅ solution at open circuit

4.10 SEM picture showing unexposed surface of AA2024-T3 L (1.9 cm thick plate) penetrated in 1 M NaCl + 5 x 10⁻² M Na₂S₂O₅
4.11 Metallographic cross section of AA2024-T3 ST (1.9 cm thick plate) penetrated for 11.1 h in 1 M NaCl + 5x10^{-4} M Na_2S_2O_3 solution at open circuit (~ -610 mV SCE) ................................................................. 184

4.12 X-ray microradiograph for AA2024-T3 (LT) penetrated at OCP for 2.4 h ...... 185

4.13 Penetration rates for AA2024-T3 plate (1.9 cm thick plate) in oxygenated 1 M NaCl at -580 mV SCE .......................................................... 186

4.14 Optical micrographs of penetrated AA2024-T3 (ST) cross sections showing IG attack through thickness .................................................. 187

4.15 Optical micrographs of penetrated AA2024-T3 (L) cross-sections showing IG attack along grain boundaries .................................................. 188

4.16 Optical micrographs of penetrated AA2024-T3 (LT) cross-sections showing IG attack along grain boundaries .................................................. 189

4.17 Penetration rates for AA2024-T3 (8.9 cm thick plate) in oxygenated 1 M NaCl at -580 mV SCE ................................................................. 189

4.18 Penetration rates for various ST samples of AA2024-T3 in oxygenated 1 M NaCl at -580 mV SCE ................................................................. 190

4.19 Cross section of AA2024-T3 (ST) penetrated at -580 mV SCE showing pitting and IG attack. (a) ST sample prepared from close to the surface of 8.9 cm thick T3 plate, (b) Large magnification. .... 191

4.20 Cross section of as-received 0.22 mm thick AA2024-T3 (ST) penetrated at -580 mV SCE showing pitting and IG attack. (a) as-polished, (b) etched ................................................................. 192

4.21 Cross section of 1.9 cm thick AA2024-T3 (ST) penetrated at -580 mV SCE showing pitting, IG attack, and exfoliation. (a) heavy exfoliation, (b) IG attack ................................................................. 193

4.22 Penetration time for L sections of 1.9 cm thick AA2024-T3 in oxygen/Ar bubbled 1 M NaCl at potential range from -675 mV to + 500 mV SCE ................................................................. 194

4.23 Metallographic cross sections of AA2024-T3 L samples penetrated at + 500 mV SCE in oxygen bubbled 1 M NaCl solution .................................................. 194
4.24 Metallographic cross section of AA2024-T3 (ST) sample penetrated at +500 for 3.3 h in Ar-deaerated 1 M NaCl solution ................................................................. 195

4.25 X-ray microradiograph for AA2024-T3 (L) penetrated at +500 mV SCE for 1.1 h in oxygen-bubbled 1 M NaCl ................................................................. 195

4.26 SEM picture showing unexposed surface of AA2024-T3 L sample penetrated at +500 mV SCE in oxygen bubbled 1 M NaCl solution ........................................ 196

4.27 Cross sections of AA2024-T3 (L) penetrated, (a) 11.3 h at OCP (−630 mV SCE), (b) 16.5 hr at −650 mV SCE, (c) 267 h at −675 mV SCE. ... 197

4.28 Penetration rates for AA2024-T3 (ST) at different potentials ................................................................. 198

4.29 Cross sections of AA2024-T3 (ST) exposed in Ar-deaerated 1 M NaCl, (a) 260 h at -645 mV SCE, (b) 260 hr at −660 mV SCE ..................................... 198

4.30 Penetration rates of AA2024-T8 (L) samples at different potentials in O₂ bubbled 1 M NaCl solution ................................................................. 199

4.31 Metallographic cross section of AA2024-T8 (L) penetrated at OCP (−740 mV SCE) showing selected granular attack .................................................. 199

4.32 Metallographic cross section of AA2024-T8 (L) penetrated at -580 mV SCE showing heavy selected granular attack .................................................. 200

4.33 Penetration rates for various tempered AA2024 (L) samples at −580 mV SCE in O₂ bubbled 1.0 M NaCl ................................................................. 200

4.34 Penetration rates for various tempered AA2024 (L) samples in O₂ bubbled 1 M NaCl at open circuit potential (OCP). Open circuit potential is about −630 mV for T3 temper, −670 mV for T3+ temper, −740 mV SCE for T8 and T8+ tempers in oxygenated 1 M NaCl solutions ................................................................. 201

4.35 Metallographic cross sections of AA2024-T3+, T8+ L samples. (a) T3+ temper penetrated at OCP (−665 mV SCE) for 72 h; (b) T3+ penetrated at −580 mV SCE for 2.2 h; (c) T8+ penetrated at −580 mV SCE for 1.8h ................................................................. 202

4.36 Penetration rates for AA2024-T3 (L) samples in nitrate and sulfate containing 1 M NaCl solutions ................................................................. 203

4.37 Cross section of AA2024-T3 (L) penetrated at -520 mV SCE in xx
0.2 M NaNO₃ + 1.0 M NaCl solution  .................................................................................. 203

4.38 Cross section of AA2024-T3 (L) penetrated at -580 mV SCE in 
0.25 M Na₂SO₄ + 1.0 M NaCl solution ................................................................. 204

5.1 Optical micrographs for L and ST sections of 1.9 cm thick AA2024-T3 plate. 226

5.2 Histograms for grain width measured from an ST section
of 1.9 cm thick plate, (a) the original data distribution,
(b) the distribution after a logarithm transformation ........................................ 227

5.3 Histograms for grain thickness, b, measured from an L section of 1.9 cm
thick plate, (a) the original data distribution, (b) the distribution
after a logarithm transformation ........................................................................ 228

5.4 Schematic of brick wall model for IGC growth ................................................. 229

5.5 The uniform distribution of the horizontal distance Xⱼ(j) that
corrosion site could travel in the j th layer of the microstructure over
the [0, a] where a is the grain width .................................................................. 229

5.6 (a) Cumulative distribution functions for minimum total path length
for IGC normalized by the foil thickness for different values of m,
the number of corrosion sites. (b) Median minimum total distance/foil
thickness for different numbers of corrosion sites; the grain width and
thickness are assumed to be 0.3 and 0.05 mm ................................................... 230

5.7 (a) Cumulative distribution functions for minimum total path length
for IGC normalized by the foil thickness for different values of grain
widths, (b) Median minimum total distance/foil thickness for different
grain width a; the grain thickness is assumed to be 0.05 mm, and
the number of corrosion sites is assumed to be 1000 ....................... 231

5.8 Cumulative distribution functions for minimum total IG path length
normalized by the foil thickness for different values of m, the number
of corrosion sites. The grain width is assumed to have a normal
distribution with a mean of 0.3 mm and the standard deviation of 0.15 mm. 232

5.9 Cumulative distribution functions for minimum total path length for IGC
normalized by the foil thickness for different normal distributions of
grain width, a. The grain thickness is assumed to be 0.05 mm, and
the number of corrosion sites is 1000. ......................................................... 232

5.10 Cumulative distributions for the minimum total IG path length for
xxi
penetration in the ST direction normalized by the foil thickness from two gamma distributions: (a) $\alpha = 7$ and $\beta = 0.0675$; (b) $\alpha = 4$ and $\beta = 0.075$ .... 233

5.11 Cumulative distribution for the minimum total IG path length for penetration in the ST direction normalized by the foil thickness from the gamma distribution (4, 0.075) after the grain thickness is also assumed to have a gamma distribution .................................................. 233

5.12 Cumulative distributions for the minimum total IG path length for penetration in the ST direction normalized by the foil thickness from the gamma distribution (7, 0.0675) after the grain thickness is also assumed to have a gamma distribution .................................................. 234
CHAPTER 1

INTRODUCTION

Corrosion is reported to be the most costly problem in many industries. The economic costs of corrosion in USA alone were estimated at $296 billion, or 4.2% of the GNP in 1995\textsuperscript{1}.

High strength aluminum alloys are widely used as the main construction materials for aircraft. For example, 71wt% of F-16 components are made from Al alloys\textsuperscript{2}. Corrosion of Al alloys in aircraft structures is primarily localized in nature: pits, crevices and intergranular attack including exfoliation. Localized corrosion in these forms often interacts with stresses to result in a great loss of the mechanical properties because of stress corrosion cracking (SCC) or corrosion fatigue (CF). Therefore, the US Air Force spends a considerable amount of money on maintenance and corrosion control of its airplanes. For example, the corrosion costs were reported at more than $3 billion on US military aircraft in 1996, Table 1.1\textsuperscript{3}. This amount will surely increase as the required service life of aircraft is lengthened.
One of the most critical issues regarding the aging aircraft corrosion problem is the lack of experimental methods to quantitatively measure localized corrosion propagation rates. Current maintenance and inspection methods rely on qualitative measurement of the nominal amount of thickness reduction, which is clearly misleading for the quantification of localized corrosion damage. The lack of quantitative information on localized corrosion kinetics also to some extent hinders the development of predictive models for localized corrosion.

The objective of this work is to quantitatively characterize the kinetics and morphologies of localized corrosion in AA2024. The foil penetration technique used in this work provides a simple and direct way of measuring the fastest-growing localized corrosion site, be it a pit, crevice or intergranular attack. The fastest growing localized corrosion site can be considered to be the most important from a practical point of view since it would first penetrate a structure leading to component failure and might be associated with the highest stress intensity in the presence of stress.

This dissertation consists of 6 chapters including the current one. Each of the next 5 chapters is fairly independent. Chapter 2 covers a brief literature review on pitting and intergranular corrosion of Al alloys. Pitting and intergranular corrosion are two common forms of localized corrosion in high strength Al alloys. In the literature review, pitting corrosion is discussed on basis of its three major stages: pit initiation, metastable and pit growth. Three main mechanisms for intergranular corrosion will then be reviewed, followed by a discussion of the effects of some critical factors, including alloy
Chapters 3 through 5 contain the details of the technical findings of this thesis. They are written as stand-alone papers, and will be submitted individually for publication. As a result, there is no chapter in this thesis focused on experimental techniques. Chapters 3 through 5 each contain sections describing the relevant experimental methods.

Chapter 3 describes the electrochemical experiments on various tempers of AA2024 as a function of sample orientation relative to the rolling direction in deaerated 1 M NaCl. The breakdown potentials, associated with initiation of pitting and intergranular corrosion, were determined potentiodynamically. The types of corrosion morphology associated with different potential ranges in polarization curves were determined using metallography and SEM. Analytical TEM was also used to characterize the microstructure of T3 and T8 tempers. The effect of nitrate and sulfate on the localized corrosion behavior was also discussed.

Chapter 4 describes detailed quantitative studies on the localized corrosion kinetics of AA2024 using the foil penetration technique. The results for the localized corrosion growth at open circuit will be discussed first. Then the effects of microstructure, and sample orientation on the growth kinetics will be presented and discussed. Finally, the effects of potential, artificial aging as well as nitrate or sulfate addition on the growth kinetics will be addressed sequentially.
Chapter 5 describes the development of a statistical model for localized corrosion (mainly intergranular corrosion) growth kinetics. The aim of the statistical modeling is to explain the observed anisotropic growth kinetics of localized corrosion, and provide a prediction of localized corrosion kinetics on the basis of a given microstructure of Al alloys.

Chapter 6 summarizes the findings of this work and draws conclusions on the effects of microstructure, potential, artificial aging and solution environment on the kinetics and morphologies of localized corrosion in AA2024. Chapter 6 also highlights the relevance of this work, and lists a few suggestions for future work regarding the kinetics of localized corrosion.

REFERENCES


### TABLES

<table>
<thead>
<tr>
<th>Annual Corrosion Cost on Aircraft</th>
<th>$3 billion for Department of Defense (Navy 40%, Air Force 54%, Army 6%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Corrosion cost/Aircraft</td>
<td>$200,000/year</td>
</tr>
<tr>
<td>Avoidable cost</td>
<td>25% ($750 million/year)</td>
</tr>
<tr>
<td>Cost per flight hour (F-15)</td>
<td>$247</td>
</tr>
<tr>
<td>F-16 planes corrosion cost (Navy)</td>
<td>$24 million/year</td>
</tr>
</tbody>
</table>

Table 1.1    Corrosion costs on US military aircraft in 1996.
Corrosion is defined as “the destructive result of chemical reaction between a metal or metal alloy and its environment”\(^1\). Over the years, corrosion scientists and engineers have recognized that corrosion manifests itself in various forms. Corrosion is classified in a number of ways, and many of the forms are often interrelated, which makes exact distinction impossible. Broadly speaking, corrosion can be simply grouped into two categories: uniform corrosion and localized corrosion. Al and Al alloys are highly resistant to uniform corrosion due to the rapid formation of protective oxide films on the surfaces. The presence of the oxide films, however, makes them extremely susceptible to the localized corrosion such as pitting, crevice corrosion, intergranular corrosion (IGC), exfoliation, and stress corrosion cracking (SCC). Among all types of localized corrosion, pitting, crevice corrosion, and IGC including exfoliation hold special places in the corrosion of high strength Al alloys. Pitting and crevice corrosion share the same growth mechanism, and exfoliation is a special form of IGC in wrought Al alloys. Therefore this literature review will be mainly focused on pitting and IGC. The purpose
of this chapter is to provide a brief summary of literature work on pitting and IGC in Al
alloys, and discuss the critical factors that determine localized corrosion growth kinetics,
followed by the motivation and objectives of this thesis.

2.1 Pitting Corrosion

Pitting corrosion is defined as "localized accelerated dissolution of metal that
occurs as a result of a breakdown of the otherwise protective passive film on the
metal/alloy surface"\(^2\). One of the characteristic features of pitting corrosion is the
existence of characteristic potentials such as breakdown and repassivation potentials.
Determination of these characteristic potentials and changes with respect to
environmental factors such as chloride concentration, inhibitor concentration, etc., or
passive film composition/structure by alloying has been one of the primary goals of
pitting corrosion research in the past. So this review starts with an introduction of the
characteristic potentials.

2.1.1 Characteristic Potentials

Electrochemical studies of pitting corrosion have found that there exist
characteristic potentials. By means of the cyclic polarization technique, two characteristic
potentials can be determined related to pit initiation and repassivation (Fig. 2.1). One is
the pitting potential \(E_p\), sometimes referred to as the breakdown potential, above which
stable pits will initiate very rapidly. The other is the repassivation potential \(E_R\), which is
also referred to as the protection potential, below which growing pits will repassivate and
Numerous techniques have been developed to measure the characteristic potentials. It has been reported that the measured characteristic potential values may depend on methods as well as experimental parameters such as potential scan rate. For the past decades, both $E_p$ and $E_R$ have been used extensively to characterize metals and alloys with respect to the pitting corrosion susceptibility in a given environment or to establish the effects of environmental factors on pitting of a given metal or alloy. It is generally accepted that materials exhibiting higher values of $E_p$ and $E_R$ are more resistant to pitting corrosion.

For Al and Al alloys, however, the use of characteristic pitting potentials is not a very satisfactory criterion for the measurement of the susceptibility to pitting because of the microstructural heterogeneity on the alloy surfaces. For instance, in deaerated 1 M chloride solution, the pitting potential of AA2024-T3 ($E_p \sim -660 \text{ mV}_{\text{SCE}}$) is more noble than that of AA7075-T7 ($E_p \sim -760 \text{ mV}_{\text{SCE}}$). However, AA2024-T3 is generally more susceptible to pitting corrosion than AA7075-T7 in chloride solutions. In many cases, the local cathodic reactions determine the pitting susceptibility of Al alloys. It is now clear that the presence of the intermetallic particles and their electrochemical behavior can influence significantly both anodic and cathodic polarization behavior of Al alloys. For example, it was found that presence of Al$_2$Cu intermetallic phase in Al-Cu alloys not only raises potential of the alloy greatly to promote metastable pitting initiation, but also supports cathodic reaction to sustain metastable pit growth. There is a great deal of literature about the effect of the intermetallic particles on pitting corrosion of Al alloys, and some of them relevant to this thesis will be discussed later.
Pitting corrosion is a multi-step process, which can be divided into three stages: pit initiation, metastable pitting, and pit growth. So the following discussion will be developed on the basis of these three stages.

2.1.2 Pit Initiation

As mentioned above, pitting corrosion is a result of local breakdown of the passive film. Aggressive anions such as chloride anions are known to cause passive film breakdown, but the exact mechanism of the breakdown is still not quite clear. A number of models have been proposed to account for pit initiation, including competitive anion adsorption\textsuperscript{9-12}, anion penetration and migration through passive films\textsuperscript{13-15}, passive film dynamic breakdown and self-repair\textsuperscript{16,17}, localized acidification\textsuperscript{18}, and the point defect model\textsuperscript{19-22}. However, there is no agreement on the essential causes and mechanisms of pit initiation.

The existing models for pit initiation can be divided roughly into four categories:

(1) Adsorption mechanism (Figure 2.2(a))
(2) Anion penetration and ion migration model (Figure 2.2(b))
(3) Film breakdown theory (Figure 2.2(c))
(4) Stochastic model

These models have been extensively discussed in the literature\textsuperscript{2,3,23,24}, and a detailed discussion is beyond the scope of this review. Briefly, each group of models emphasizes different aspects of the pit initiation process. For example, the adsorption mechanism stresses the importance of adsorption of aggressive anions like chloride ions.
However, while it is generally believed that adsorption of chloride anions may be the first step, it is not a sufficient condition leading to pit initiation. The anion penetration and migration model introduces the important step of aggressive anions adsorbed in pit initiation process but requires the adsorbed aggressive anion transport through the passive film for the film breakdown. According to this model, smaller ions penetrate the film more readily, so Cl\(^-\) is more aggressive than Br\(^-\) and I\(^-\). The anion penetration model addressed well the specific effect of aggressive chloride anions on pit initiation in Al and Al alloys. But it is hard to explain pitting phenomenon in other environments with this theory, such as pitting of iron in SO\(_4^{2-}\) or ClO\(_4^-\), and pitting of aluminum in NO\(_3^-\) containing solution. These ions should be too large to migrate or diffuse through the oxide film. Furthermore, the anion penetration and migration model also fails to explain the fast pit initiation process\(^{25}\).

The film breakdown theory, Figure 2.2(c), assumes that a dynamic balance exists between breakdown and repair of the passive film. Electrostriction forces (dielectric deformation resulting from precipitating opposite charges by the electric field), the atmospheric pressure, and the interfacial tension drive the process to move in the breakdown direction\(^{17}\). The film breakdown theory correlates pit initiation with later pit growth stage. According to this model, breakdown will lead to pit initiation only when a pit is able to grow. It is generally accepted that pit growth stability largely depends on the electrochemical environment inside the pits, such as electrolyte composition and pit bottom potential. The criteria for pit growth stability will be discussed more detail later.
not only because it provides another approach to address the pit initiation phenomenon, but also because there is much literature on this subject. The stochastic model assumes that pit initiation is an unpredictable event. This model explains the randomness of pit initiation and the large scatter of pitting potential from a statistical point of view. The stochastic approach has also been used to address metastable pitting, which has further attracted a great deal of interest in the application of the stochastic approach to localized corrosion.

In summary, each pit initiation model is supported by certain experimental results, but none of them is able to provide a satisfactory explanation for all of the observations about pitting phenomena. The different experimental results and conditions for pit initiation reported in the literature lead to the opinion that no single mechanism governs passive film breakdown and pit initiation. In most situations, it is suggested that several mechanisms or combinations of these mechanisms may be responsible for pit initiation.

2.1.3 Metastable pits

Small pits that form either at potentials below the pitting potential or during the induction time prior to onset of stable pits above the pitting potential and then quickly repassivate are called metastable pits. Metastable pits are often manifested either by current transients under an applied potential or potential transits under an applied current (or at open circuit potential). Fig. 2.3 shows an example of typical metastable pit current transients observed in stainless steel in chloride solution. As shown in the figure, these
Metastable pits have following similar features: the current begins to increase when a metastable pit nucleates. The current keeps growing for a while as the metastable pit grows, and then quickly decreases after a short time because of repassivation of the pit.

The phenomenon of metastable pitting was first described qualitatively in the late 60s and early 70s. For example, Hisamatsu et al.\textsuperscript{32} observed the occurrence of current transients on stainless steel in 0.5 M $\text{H}_2\text{SO}_4 + 0.5$ M $\text{NaCl}$ solution. However, it was not until the 1980s that detailed studies of metastable pits were reported. Frankel et al.\textsuperscript{31} investigated metastable pitting phenomena in stainless steel, where they first used the term of metastable pitting for this type of pitting. In their work, the average metastable pit current density was found to increase with increasing applied potential. They also found that the metastable pits in stainless steels were covered by a layer of passive film remnant, and rupture of this cover resulted in the repassivation of these metastable pits.

It has been suggested that the early stage of stable pit growth is identical to that of metastable pits, and that the probability of stable pitting is directly related to the occurrence and intensity of metastable pitting. The difference between the stable and metastable pits is that “stable pits survive the metastable stage and continue to grow, whereas metastable pits repassivate and stop growing for some reason.”\textsuperscript{2}

Metastable pits are usually very small in size, only a few micrometers in diameter. They grow and repassivate in less than a few seconds. So transient techniques have been developed to study current transients under potentiostatic conditions\textsuperscript{33} or to examine potential transients at open circuit potential\textsuperscript{34}. These transient techniques are also applicable to the studies of inhibitor effects on metastable pitting\textsuperscript{35}. A considerable
in the metastable pitting in Al and Al alloys is to identify electrochemical factors that promote the transition from metastable to stable pit growth, and understand how corrosion inhibitors (chromate) affect this transition. More work is still necessary to understand these factors controlling metastable pit formation, and their transition into the stable pit growth.

2.1.4 Pit growth

Pit growth is another important aspect of pitting corrosion research in the past. To some extent, the understanding of pit growth is much more important than that of pit initiation since the growth of pits and other forms of localized corrosion can lead to early failure due to penetration or crack initiation.

In theory, pit growth can be controlled by one or some combination of following factors: charge-transfer process, mass-transport control, and ohmic drop control. For a hemispherical pit, different rate controlled pit growth would lead to specific relationships between current density $i$, pit radius $r$, time $t$, and potential $E$, which is often used for the determination of pit growth mechanism. In this section, pit growth is discussed in terms of the following three mechanisms:

(1) Charge transfer controlled growth,

(2) Mass transport controlled growth,

(3) Ohmic drop controlled growth.
Charge Transfer Controlled Growth

The electrochemical dissolution of metals is considered as charge transfer control when the charge transfer process is the slowest step in the whole dissolution process. In charge-transfer controlled dissolution, current is exponentially related to applied potential $E$, as given by the Butler-Volmer equation. Under some conditions, the Butler-Volmer equation simplifies to the Tafel equation:

$$\eta_a = b_a \log \frac{i}{i_0}$$

where $a$ denotes anodic properties, $i_0$ is the exchange current density, which is equivalent to the reversible rate for an electrochemical half-cell reaction at equilibrium, and $\eta$ is the overpotential ($E-E_{eq}$) where $E_{eq}$ is the equilibrium potential of the half cell reaction. $b_a$ is the anodic Tafel slope constant. For a simple one electron reaction, $b_a = 2.3RT/((1-\alpha)F)$ where $\alpha$ is the symmetry factor.

Several researchers suggested that metal dissolution might be charged transfer controlled at the very early stages of pit growth. The early stages of pit growth are generally referring to the process in the first $10^{-3}$ to $10^{-1}$ s after pit initiation. However, the pit initiation process and its subsequent growth stages are intimately related with each other, and hard to be separated individually, which makes it extremely difficult to study the early pit growth stage. Most of the literature work on the early stages of pit growth may include the later stages of pit growth as well.
growth in the early 70s. They proposed the concept of a thin salt layer to explain the early stages of metal dissolution. Once a stable pit is nucleated, its surface may be covered with a thin salt layer formed by the cations of the metal and the aggressive anions. According to Vetter and Strehblow, the pitted site has almost the same potential as the rest of passive surface at the very beginning of the pit growth.

Using a simple hemispherical pit and mathematical transformation (Fig. 2.4), Vetter and Strehblow calculated the concentration gradients \( \Delta c \) and ohmic drops \( \Delta \varepsilon \) within the pit as expressed by following:

\[
\Delta c = \frac{a \times i \times r}{z_m FD(1 + \frac{|z_m|}{|z_a|})}
\]

\[
\Delta \varepsilon = \frac{a \times i \times r}{k}
\]

where \( i \) is current density and assumed to be the same on the pit surface, \( k \) is the conductivity of the electrolyte, \( r \) is pit depth, \( a \) is a geometric factor, \( z_m \) and \( z_a \) are the valences of the metal ions and aggressive anions, \( D \) is the diffusion coefficient, and \( F \) is the Faraday constant.

For an initial current density of \( i = 9 \text{ A/cm}^2 \), and 2 \( \mu \text{m} \) diameter, initiated pits of iron in a chloride-containing sulfuric acid solution result in a concentration difference \( \Delta c = 0.9 \text{ moles/liter} \), which is far below the saturation of FeCl\(_2\) (\(~ 4.4 \text{ M} \)). The potential drop \( \Delta \varepsilon \) was about 9 mV. A maximum pH shift value \( \Delta \text{pH} < 0.85 \) was estimated from the
change in the concentration. Such a small pH shift and ohmic potential drop cannot explain the stability of the pit growth in the case of small pits. The authors concluded that the charge transfer controlled might be reasonable for initial pit growth since the potentiostatic results showed Tafel behavior.

The above mechanism for the early stages of pit growth is based on the initial high current densities, which was reported on iron and nickel in chloride and sulphuric acid by many researchers. At the very beginning of pitting corrosion, there is almost the same potential within the pits as that of the adjacent un-pitted surface. The only difference between the pitted sites and the rest of the surface is the highly localized current density, Fig. 2.5. Pit growth is controlled by an activated process similar to that associated with anodic polarization in the absence of a passive film. The local acidity increases as a result of the hydrolysis of metal ions. The field-induced migration of chloride ions or diffusion control must be taken into account for the following growth stages.

Strehblow and Wenners reported their experimental results on the early stages of pit growth on nickel and iron in 0.01 to 0.1 M KCl solutions. They concluded that pit growth began with the adsorption of Cl on the bare metal, followed by the ionization of complexes, which supported the above pit growth mechanism.

Popov et al. conducted a theoretical analysis of the experimental results obtained by Strehblow and Wenners, and proposed an extended model for the early stages of pit growth. As shown in Fig. 2.6, Popov et al. distinguished three successive stages of pit growth on iron and nickel in KCl solutions. During the first stage (t <
the high dissolution rate of metal, indicating that the metal dissolution is only charge transfer controlled. At $t \sim T_1$, the situation changes. The electrochemical kinetics are affected by the deficit of solvent concentration (water), and finally a dehydrated boundary layer at the pit bottom is formed. At $t = T$, the $E$ vs $t$ curve bends, indicating that the diffusion and ohmic drop controlled stage of pit growth begins. In the following stage ($t > T$), the thickness of the dehydrated layer (barrier layer or the resistive layer) increases until the entire volume of the pit is filled. However, Engell$^{42}$ argued that the pit growth was under mixed ohmic control and diffusion control even at the early stages, which is discussed next.

**Mass Transport Controlled Growth**

In contrast to Vetter and Strehblow's concept$^{36}$, Engell$^{42}$ demonstrated the possibility of the coexistence of active (pit surface) and passive surface after pit initiation by considering the Nernst diffusion layer at the metal surface outside the pit. Assuming a pit depth of 1 $\mu$m and 1 A/cm$^2$ dissolution current density, Engell$^{42}$ calculated that the change in concentration inside the pit could be as high as 15 M, which is sufficient for the precipitation of a metal salt. The precipitated salt layer causes a considerable potential drop inside the pit. Therefore, Engell$^{42}$ claimed that, even at the early stages, pit growth was controlled by diffusion or ohmic potential drop within the pits.

From the above discussion, it seems that salt films can form following pit initiation, although there exists some disagreement about the role that the salt film plays and the time when it is formed. According to Beck$^{43}$, the salt layer can form at the very
the formation of salt films in pits might be more important than a low pH for stable pit growth because repassivation of pits was observed even at a low pH (< 1) in Ti, Ni and Fe. The presence of salt films is also generally accepted as a requirement for the stable pit growth in stainless steels. Recently, Newman et al. proposed another explanation for the effect of salt film precipitation, arguing that the role of salt films depends on temperature. Below a particular temperature, the formation of salt films leads to passivation, while above the critical temperature, pits are stabilized by the precipitation of a salt film.

Considering the Tafel kinetics and ohmic resistance, Beck and Alkire found that the time for salt film formation was as short as $10^4$ to $10^8$ s on a pit with about the same size as thickness of the passive film. Based on their calculation, they proposed that pit growth be controlled by mass transport of metal dissolution species out of the pits. For a hemispherical pit growth controlled by a simple diffusion process, the limiting current dissolution, growth rates are given by:

$$i_t = \frac{2FDC_z}{d_p} \quad (2.4)$$

$$d_p = \left( r_1^2 + \frac{2DC_M}{\rho} t \right)^{1/2} \quad (2.5)$$

$$i_p = \frac{zFDC_z}{\left( r_1^2 + 2DC_M \frac{t}{\rho} \right)^{1/2}} \quad (2.6)$$

where $z$ is the valence, $d_p$ the pit radius, $D$ the diffusion coefficient, $r_1$ the radius of the
initial, pit-nucleus, M-molecular weight, \( \rho \)-density. From Equations (2.5) and (2.6), a parabolic growth law is obtained for pit growth under diffusion control.

It should be pointed out that the above model did not take into account the ohmic drop effect on the pit growth. Also, experimental data for this model at the early stage growth has not been attained yet, although at later stages a parabolic law was observed on Ni\(^{49} \), stainless steel\(^{32} \), and iron\(^{50} \). However, it is hard to prove if parabolic pit growth relations are attributed to only a simple diffusion process, since ohmic drop control also yields parabolic behavior.

It has been suggested that pitting of aluminum is different than that of iron, stainless steels or nickel. The large amounts of hydrogen bubbles generated within Al pits could impede the formation of salt film by drastically increasing the mass transport rate and continuously replacing the gas bubble volume with fresh bulk solution. As indicated by Hunkeler and Bohni\(^{51} \), for a hemispherical 0.2 mm deep pit, growing in a 1 M Cl\(^{-}\) solution at -720 mV SCE, the solution inside the pit can change six times a minute. Therefore, Hunkeler and Bohni\(^{51-53} \) suggested that the pit growth was governed by the ohmic drop control in Al.

**Ohmic Drop Controlled Growth**

It has been long argued that the pit bottom potential will be lower than the outside surface potential if at least part of the cathodic reaction occurs outside of the pit, which is typically the case for pits. Large ohmic potential drops as high as 1 V or more were reported in iron between the bulk electrolyte and the electrolyte at the bottom of large pits\(^{54-57} \). Based on their experiments on iron in chloride-free solutions of varying pH,
Pickering and coworkers proposed that the ohmic potential drop is the critical factor stabilizing pit growth because it shifts the potential of the pit bottom into the active region. If the IR drop is less than a critical value, pit growth may stop due to repassivation.

However, in the case of Al alloys and stainless steels in neutral chloride environments, there may not be an active/passive transition in the polarization. The ohmic potential drop decreases the potential at the pit bottom, which destabilizes the pit growth, rather than ohmically stabilizes its growth because of the low dissolution rate. In other words, pit growth in these systems is ohmically-limited, not ohmically-stabilized.

Using an artificial pit in a flowing chloride solution, Beck observed that pitting of aluminum under potentiostatic conditions grew under ohmic drop control, because there was considerable agitation due to hydrogen evolution during pitting. Later, Bohni demonstrated that the ohmic drop controlled pit growth in Al occurred at open circuit potential as well.

In the early 80s, Hunkeler and Bohni developed a non-electrochemical method to study the pit growth in Al. They measured the time for pits to perforate Al foils of varying thickness (10, 50, and 200 μm) as a way to determine pit growth rate for the fastest growing pits. They found that pit growth is not only time-dependent but is also influenced by the applied potential. Figure 2.7 shows pit growth depth and current density of Al as function of the potential difference. The conductivity values obtained from the slope in the Figure 2.8 correspond reasonably well with dilute and moderately concentrated bulk solutions. So they claimed that pit growth is ohmically controlled

20
under both open circuit and potentiostatic conditions because the pit growth rate is related to the conductivity of the bulk electrolyte. The pit depth, current density and time follow a parabolic law given by:

\[ d_p = at^{1/2} \]  

(2.7)

\[ i_p = i_p^0 t^{-1/2} \]  

(2.8)

where \( a \) is constant depending on potential, temperature, electrolyte, \( i_p^0 \) is the initial pit current density at \( t = 1 \) minute.

Frankel and coworkers\(^{59,60}\) developed another non-electrochemical approach to study the pit growth in sputter-deposited thin metallic films. Pits in thin metallic film samples with thickness less than 1 \( \mu \)m will quickly penetrate to the inert substrate, and then grow in a two dimensional fashion. As shown in Fig. 2.9, the pit current density increases linearly with potential in the low potential range. The pit surface was extremely rough, and the results indicated that pit growth in Al thin film in pure chloride was under ohmic drop or mixed ohmic/charge-transfer control until very high potential range where mass transport controlled growth resulted in potential-independent current density.

This section has shown that the critical factors controlling the stable pit growth are not completely understood. In addition to salt film precipitation and IR drop, other factors such as the concentrations of metal ions, chloride ions, and \( H^+ \), have all been proposed as the critical factors stabilizing pit growth. For example, some authors\(^{61,62}\) have suggested that there may exist a critical concentration of electrolyte inside the pit, \( C^* \), above which the pit can grow, and below which the pit will repassivate. For
The critical concentration, $C^*$, can be calculated from mass transport equations. Since the local ion concentration $C$ is proportional to the product of pit dissolution current density $i_p$ and pit size $r_p$ from mass transport theory, a critical pit size must be exceeded for stable pit growth to occur. For example, Buzza and Alkire$^{63}$ reported that pit stability of pure Al in NaCl depends on the critical pit size.

However, there is no agreement as to which ion ($H^+$, or halide ion/metal ion) is responsible for pit growth stability. Some$^{61,62}$ suggested that the aggressive anion is more important while others$^{64,65}$ believed that the $H^+$ ion buildup or localized acidification is more important. According to Galvele$^{18,64,65}$, localized acidification is the decisive criterion for pit growth stability as well as for pit initiation. Galvele$^{18,64}$ calculated the concentration of various ionic species inside a one dimensional pit in Fe as shown in Fig.2.10. The author found that, although the chloride ion changes were not significant in the initial stages, the pH changes were very important even in the earliest stages of pit growth. The critical acidification was reached at the pH where the product of the depth $X$ and current density $i$ reached approximately $10^5$A/cm for Fe. Since chloride is a strong acid anion, its concentration is proportional to solution acidity. It is possible that both local concentration change in chloride ions and local pH change might be connected to the same factor.

In summary, pit growth is a critical, but not well understood, aspect of pitting corrosion. The local potential and electrochemical environment inside the pits determine whether, once initiated, pits grow or repassivate. There might exist a number of factors that could have effects on the pit growth and its stability, but the combination of these
2.2 Intergranular Corrosion (IGC)

Intergranular corrosion is a term used to describe a type of corrosion in which preferential attack takes place in grain boundaries or adjacent regions without appreciable attack of the grain bodies. The intergranular corrosion susceptibility of high strength Al alloys is well known. This section will discuss the causes of susceptibility to IGC, and the relationship between IGC, pitting, and other forms of localized corrosion in high strength Al alloys.

2.2.1 IGC mechanisms

The problem of intergranular corrosion in high strength aluminum alloys has been studied for many years. Several mechanisms have been proposed to explain IGC of Al alloys. It is generally accepted that IGC susceptibility is attributed to the development of a preferential anodic path along grain boundaries, resulting from localized precipitation in the vicinity of the grain boundaries. However, the exact nature and causes of this anodic path are still not quite clear. Generally speaking, there are three different explanations for IGC susceptibility of Al alloys, which can be referred to as:

(1) Galvanic couple theory
(2) Precipitate free zone breakdown model
(3) Anodic dissolution of grain boundary precipitates
Galvanic Couple Theory

The galvanic couple theory is the most classical electrochemical explanation of IGC in Al alloys. The theory was first proposed by Dix et al. to describe intergranular stress corrosion cracking of Al-Mg and Al-Cu alloys\(^{66,67}\). According to this theory, IGC susceptibility is attributed to the action of local galvanic corrosion between the noble grain matrix and anodic grain boundary regions. More specifically, in Al-Mg and Al-Mg-Zn alloys, IGC is considered to be a result of galvanic corrosion between anodic grain boundary particles (\(\text{Al}_8\text{Mg}_2\), \(\text{MgZn}_2\)) and the grain matrix\(^{68}\). In Cu-containing alloys, such as Al-Cu, Al-Cu-Mg, and Al-Zn-Mg-Cu, IGC is explained as a result of galvanic corrosion between copper-depleted (precipitate free) zones and the grain matrix\(^{68}\).

An early and important contribution to the development of galvanic couple theory was the work by Mears, Brown, and Dix on Al-4\%Cu\(^{69}\). By using a unique technique, they measured the corrosion potentials for the grain boundary regions and the grain centers on a large grained Al-4\%Cu alloy in NaCl-H\(_2\)O\(_2\). The Al-4\%Cu alloy was first solution heat treated at 930 °F (499 °C), followed by quenching in cold water, and then aging at 375 °F (191 °C) for different times. The corrosion potentials for both grains and grain boundaries were measured as a function of aging time, Figure 2.11. The data in Fig. 2.11 indicate that the grain boundaries became anodic with respect to the grain bodies once the aging started. The corrosion potential difference reached a maximum after aging for about 4 to 8 h at 191 °C. It is also shown in Figure 2.11 that 5\% plastic deformation reduced the time for maximum potential difference because of the acceleration of precipitation. With more aging, the difference decreased and finally it almost became
It was found that the Al-4\%Cu was most susceptible to intergranular attack when the corrosion potential difference was a maximum. In their work, the authors explained that anodic grain boundary regions were due to the formation of copper deleted zone around the grain boundaries. The copper deleted zones were later observed in aged Al-4\%Cu alloys by TEM\textsuperscript{70}, but the authors failed to take into account the effect of Al\textsubscript{2}Cu precipitation, which is cathodic with respect to the grain matrix, on their grain boundary potential measurement.

Interestingly, Cocks and Brummer reported a different IGC picture in Al-4\%Cu alloys\textsuperscript{71}. They found that copper depleted zones were present virtually from the beginning of age-hardening process. The only difference as the aging continued, was some growth of grain boundary precipitates and widening of the Cu-depleted zones. Importantly, they found not only that aging had not much effect on IGC susceptibility of Al-4\%Cu alloys, but also that aging appeared to increase the rates of IG attack. Cocks and Brummer did not report how long the Al-4\%Cu was aged, but the findings suggest that the aging effect on IGC susceptibility of Al-Cu may not simply result from the potential difference between grain matrix and grain boundary regions.

In Al-Zn-Mg-Cu alloys, IGC susceptibility is known to depend on aging. A small change in temper can result in marked differences in the susceptibility to IGC. For example, 7xxx series alloys in the T6 temper are usually more susceptible to IGC than in the T7 temper. Sprowls and Brown attributed the high resistance to IGC in the T7 temper to similar potentials of the grain bodies and grain boundary regions\textsuperscript{72}. 

25
The galvanic couple theory fails to explain why chloride ions are necessary for intergranular corrosion of Al alloys, since galvanic corrosion should occur in any electrolyte with comparable ionic conductivity. However, experiments in sulfate solution did not reveal IGC susceptibility of Al-4%Cu. Later, Galvele and DeMicheli proposed that it was breakdown potential difference, not corrosion potential difference that produced IGC susceptibility of aged Al-Cu alloys. Nevertheless, the concept of galvanic couple theory is still relevant to IGC studies in Al alloys. It may not directly contribute to IGC initiation, but could affect IGC growth kinetics.

**Precipitate Free Zone (PFZ) Breakdown Model**

The PFZ breakdown model is based on the breakdown potential difference between the grain matrix and the solute depleted zones adjacent to the grain boundaries. The model was first presented by Galvele and DeMicheli for IGC susceptibility of aged Al-4%Cu. In order to determine the electrochemical relationships in aged Al-4%Cu, Galvele and De Micheli measured the breakdown potentials for Al-4%Cu solid solution, Al2Cu intermetallic phase, Al-0.2%Cu, and two pure Al alloys with 99.99% and 99.9999% purity, respectively, Figure 2.12. They found that the breakdown potential of Al-4%Cu solid solution alloy was similar to that of the intermetallic Al2Cu, particularly in dilute NaCl solution. There were no differences in the breakdown potentials of the Al-0.2%Cu and high purity Al. However, both Al-4%Cu solid solution and intermetallic Al2Cu exhibited about 100 mV higher breakdown potential than the Al-0.2%Cu and high purity Al. Based on this result, they predicted that IGC of aged Al-4%Cu occurred only...
had a copper depleted PFZ present along the grain boundaries, which had a lower breakdown potential than grain matrix (Al-4%Cu solid solution) and grain boundary precipitate (Al₂Cu). That was why there were two breakdown potentials in the anodic polarization curves of the peak-aged alloy, Figure 2.14. When the corrosion potential is higher than PFZ breakdown potential, but lower than that of matrix, localized attack on PFZ results in IGC. The same Al-4%Cu in the overaged condition is not susceptible to IGC because the PFZ disappears. The overaged Al-4%Cu was found to have only one breakdown potential, which is consistent with their explanation. It was found that the differences in pitting potential between grain boundaries and grain bodies changed with aging time. The maximum susceptibility of aged Al-4%Cu alloys to IGC occurred when their pitting potential difference reached a maximum.

The PFZ breakdown model has also been applied to IGC of other Al alloys, such as Al-Cu-Mg, Al-Zn-Mg, Al-Zn-Mg-Cu, Al-Mg-Si-Cu, Al-Li-Cu. It is still not clear whether the PFZ breakdown is the only cause of IGC susceptibility in age-hardening Al alloys, however, this model correlates the phenomenon of IGC with pitting corrosion in Al alloys from electrochemical point of view.

More recently, Ramgopal et al. investigated electrochemical behavior of PFZ and MgZn₂ precipitates present in AA7150-T6, and -T7 tempers using the artificial pit/crevice technique, and found that thin film analogs of the PFZ had similar electrochemical behavior to that of the matrix in neutral chloride solution. On the other hand, the authors found that there was a significant difference in the composition of grain
boundary precipitates between T6 and T7 temper, but both dissolved below the breakdown potential of the alloys. They suggested that the dissolution of the high Cu enriched grain boundary precipitate in T7 temper created different microchemistries containing very high Cu around the grain boundary regions, which suggested that the dissolution of the PFZ in the T6 and T7 tempers may occur under different environments. The PFZ is active in the microchemistry formed in the T6 temper whereas in the T7 temper microchemistry it is noble, which makes T6 susceptible to IGC and T7 resistant. The authors suggested that it is anodic dissolution of grain boundary precipitate that leads to IGC susceptibility of AA7150-T6 alloys. The anodic dissolution of grain boundary precipitates is another explanation for IGC and intergranular stress corrosion (IGSCC) in Al alloys as discussed below.

Anodic dissolution of grain boundary precipitates

This theory suggests that the existence of a preferential anodic path along grain boundaries results from anodic dissolution of grain boundary precipitates. The evidence supporting this mechanism has been derived mainly from intergranular corrosion stress corrosion cracking (IGSCC) studies of Al-Mg\textsuperscript{82,83} and Al-Li-Cu alloys\textsuperscript{84,85}.

In Al-Mg (5xxx series) alloys, the formation of a continuous grain boundary precipitate Mg\textsubscript{5}Al\textsubscript{8} is believed to be responsible for IGC and IGSCC since the precipitates Mg\textsubscript{5}Al\textsubscript{8} are strongly anodic to the Al-Mg solid solution matrix in most electrolytes\textsuperscript{82}. Recent work on AA 5083 alloys has indicated that IGSCC behavior of the alloy was related to the anodic dissolution of the continuous grain boundary precipitate.
get IGC, which is not widely observed in other Al alloys.

In Al-Li-Cu alloys, it has been established that T1 (CuAl$_2$L$_i$) is the most active phase present in the subgrain boundaries and matrix\textsuperscript{83}. In peak aged AA2090 (Al-2.1%Li-2.6%Cu), T1 is preferentially precipitated at the subgrain boundaries. Electrochemical studies of simulated bulk T1 phase show that T1 phase has high dissolution rate ($10^{-4}$A/cm$^2$) over a wide range of potential in 3.5% NaCl, Figure 2.15. Buchheit et al.\textsuperscript{85} claimed that the anodic dissolution of T1 (CuAl$_2$L$_i$) at the grain boundaries controls the IGC and SCC behavior of the Al-Li-Cu alloys. Since the selective dissolution of T1 phase not only exposes subgrain faces, but also lowers local pH in the occluded environment, aggressive subgrain boundary attack occurs leading to IGC in the peak aged AA2090.

In summary, there are essentially three different theories proposed to explain IGC susceptibility of Al alloys from electrochemical point of view. It is generally accepted that susceptibility to IGC results from the precipitation of intermetallic phases in the vicinity of the grain boundaries. The specific electrochemical roles of the grain boundary precipitates and the adjacent PFZ zones vary from one alloy system to another. However, it should be pointed out that, in addition to above three electrochemical mechanisms of IGC, that there is another theory for the causes of IGC, referred to as the grain boundary theory. The grain boundary theory considers that IGC depends on the grain boundary energy and structure\textsuperscript{86}. The high energy of grain boundaries makes them favorable sites for solute segregation and precipitation, either of which might cause localized corrosion.
One important concept of this theory is coincidence site lattice (CSL) interface\(^87,88\) (grain boundary is one kind of interface). Coincident sites are those at the boundary where atoms of the adjacent grains forming the grain boundary exactly match or coincide. According to grain boundary theory, the misorientation angle and structure of a grain boundary (characterized by CSL model) determine whether it is intrinsically susceptible to or immune to intergranular attack\(^88-90\). The grain boundary theory has been used to explain IGC phenomena in stainless steel and other nickel based alloys\(^91,92\). However, this theory is not widely accepted in the corrosion of high strength Al alloys.

### 2.2.1 Relationships between IGC, pitting, and other forms of localized corrosion

More and more work has shown that a strong correlation exists among different forms of localized corrosion. The relationships can be illustrated from following aspects:

First, pitting and IGC have been reported to be dependent on each other in AA6056-T6 (Al-Mg-Si-Cu),\(^78\) AA6013-T6 (Al-Mg-Si-Cu),\(^79\) AA2024-T3 (Al-Cu-Mg),\(^93\) AA2090 (Al-Li-Cu),\(^80\), although how pitting and subsequent IGC are related to each other is still not well understood. One mechanism proposed to account for the dependence of IGC and pitting is as follows. Pits occur first, as they grow into microstructure; IGC nucleates on pit walls and spreads along anodic solute depleted zones\(^78\). According to this mechanism, whether pits can subsequently develop into IGC depends on two factors. One is the local pH within occluded pits, which must be maintained very low for the stable IGC growth. The other is the presence of solute...
(mainly Cu) depleted zones along the grain boundaries. These two are necessary for IGC to occur.

Second, it has been reported that there is a correlation between the susceptibility to IGC and exfoliation in Al alloys. Exfoliation is essentially a directional attack along elongated grain boundaries. In most cases, IGC susceptibility combined with elongated grain structure will lead to exfoliation.

Finally, stress corrosion cracking (SCC) could also be related to IGC since SCC sometimes is intergranular. For example, Al-Cu alloys were reported to be susceptible to both IGC and SCC in chloride environments. However, there are exceptions, indicating a complicated relationship between IGC and IGSCC. For example, AA2024-T8 was reported susceptible to IGC, but not susceptible to IGSCC.

2.3 Critical Factors in Controlling Localized Corrosion Kinetics

Once initiated, localized corrosion grows at a rate that depends on many factors such as alloy composition, microstructure, electrolyte concentration, local pH, potential, solution flow, etc. The critical factors to be addressed in this review are the following:

1. Alloy microstructure.
2. Composition of electrolyte.
3. pH effect.
4. Inhibitors.
2.3.1 Alloy microstructure

The alloy microstructure can have strong effects on the susceptibility of Al alloys to the initiation of localized corrosion as well as its development. In principle, the microstructure including surface structure determines whether localized corrosion will occur, what type of localized corrosion will take, and how fast the localized corrosion will propagate once initiated.

High strength Al alloys often contain one or more alloying elements added to increase strength. As a result, one of key features of these Al alloy microstructures is a dispersion of various intermetallic particles in the grain matrix and the grain boundaries. Most alloying additions and impurity elements are concentrated in these particles because of their low solid solubility in aluminum. These intermetallic particles can be grouped broadly into two categories. One is formed during the heat treatment by the reaction of Al with alloying elements. The other group typically contains impurities such as Fe, Si, and forms from the melt during solidification. The electrochemical behavior of these intermetallic particles can be totally different from that of solid solution Al matrix. It is widely known that intermetallic particles play an important role in localized corrosion behavior of Al alloys. For example, the intermetallic phase particles are often reported to be the common sites for pit initiation in Al alloys. The anodic dissolution of intermetallic particles at the grain boundaries can lead to IGC and SCC. Al alloys that do not form intermetallic particles at grain boundaries, or those in which the intermetallic particles have potential similar to the grain matrix, have high resistance to localized corrosion. Obviously, a clear understanding of intermetallic particles, such as
the amount, size, and spatial distributions, and their electrochemical properties is critical in understanding the relationship between microstructure and localized corrosion behavior of Al alloys. It is still not clear whether intermetallic particles can directly affect the localized corrosion growth kinetics. However, the presence of intermetallic particles in the microstructure may indirectly influence localized corrosion growth kinetics by changing the type of localized corrosion such as pitting into IGC since pits and crevices have been shown to develop into IGC as they grow into the microstructure. Furthermore, it has been reported that long time immersion of AA2024-T3 in NaCl solution caused individual intermetallic particle-nucleated pits to grow laterally and in depth, producing larger pits through pit coalescence rather than merely through single pit growth. The clustering of intermetallic particles often occurs in wrought alloys. Therefore, intermetallic particles are expected to have some effects on the localized growth kinetics.

The most important intermetallic particles presented in Al-Cu and Al-Cu-Mg alloys are \( \theta - Al_2Cu \) and \( Al_2CuMg \) (S phase), respectively. Their electrochemical behavior has been extensively studied and characterized. Table 2.1 summarizes the electrochemical properties of these two intermetallic phases in various environments. It is generally accepted that \( Al_2CuMg \) (S phase) is active, while \( \theta - Al_2Cu \) is noble with respect to the matrix. There is a considerable amount of work about the effect of these intermetallic particles on localized corrosion behavior of Al-Cu-Mg alloys. For example, Buchheit et al. investigated local dissolution phenomena associated with \( Al_2CuMg \) S phase particles in AA2024-T3. They found that \( Al_2CuMg \) (S) particles were dominant in
themCTotructiure Jrhese S-phase particles induced two types of pit morphologies in the matrix at their periphery by S phase dealloying. Another recent study\textsuperscript{95} indicated that two types of particles were identified in AA2024-T3. One type contained Al, Cu and Mg (which was believed to be the Al\textsubscript{2}CuMg particles, and the other contained Al, Cu, Mn and Fe. The pitting was found to be associated with these two types of particles. Guillaumin and Mankowski\textsuperscript{93} reported similar results. More recently, Leblanc and Frankel\textsuperscript{103} found that some small Al\textsubscript{2}CuMg particles in AA2024-T3 do not corrode without the presence of Al-Cu-Fe-Mn particles. Only large Al\textsubscript{2}CuMg particles corroded, leaving a high potential Cu-rich remnant around the particles. Surprisingly, such Cu-rich remnants do not cause further pitting as expected. They also found that the size and location of Al-Cu-Fe-Mn particles have a strong influence on the localized corrosion of AA2024-T3. As the area ratio of the Al-Cu-Fe-Mn particles increases with respect to the surrounding exposed matrix, the pitting mechanism changes dramatically from the dissolution of Al\textsubscript{2}CuMg particles to the attack of the matrix\textsuperscript{103}.

For heat treatable Al alloys, the microstructure is affected not only by alloy composition, but also by the mechanical and thermal treatments used to develop desired mechanical properties. Therefore, variations in thermal treatment such as solution heat treatment temperature, quenching rate, and artificial aging can also have a significant effect on localized corrosion behavior of Al alloys. For instance, in the case of Al-Cu and Al-Cu-Mg, it was found that the microstructure, which is directly controlled by the quenching rate, determined the degree of susceptibility to pitting, IGC, as well as stress corrosion cracking (SCC)\textsuperscript{104}. Figure 2.16 shows the effect of quenching rate on the
resistance to localized corrosion in Al-4.5%Cu, Al-4.3%Cu-1.25%Mg and a commercial Al-4.5%Cu-1.5%Mg-0.6%Mn alloy (AA2024) in NaCl-H2O2 solution. At the fastest quench rates, only pitting attack occurred. As quenching rate decreased, IGC susceptibility increased. For AA2024, the quench rate must be kept above about 1000 °F/s in order to avoid IGC susceptibility. The data in the figure also show that SCC resistance of the as-quenched Al alloys depends on quench rates as well. Figure 2.17 shows another work on the effect of quenching rate on the localized corrosion and corrosion potential of AA2024 in NaCl. The result is almost the same as that in NaCl-H2O2. Only pitting attack occurred at a high cooling rate above 280 °C/s. In the range of cooling rates between 167-70 °C/s, both pitting and intergranular attack were observed. Below 70 °C/s, only intergranular attack occurred. The increasing IGC susceptibility with slow quenching is generally explained on the basis of electrochemical effects associated with the change of the microstructure, where copper-rich grain boundary precipitates and Cu-depleted zones adjacent to the grain boundaries form during the quench.

The effect of artificial aging on localized corrosion behavior in Al alloys is also related to the change in the microstructure. Figure 2.18 shows the effects of artificial aging on the corrosion and SCC behavior of AA2024 in NaCl. The susceptibility to IGC and SCC was found to increase initially, reach a maximum, and then decrease during artificial aging. As was discussed earlier, Mears, Brown and Dix explained this aging effect on the basis of corrosion potential difference between grains and grain boundary regions during aging, while Galvele et al. believed it was breakdown potential difference that caused the susceptibility to IGC. Despite this disagreement on the detailed
understanding as to the exact electrochemical mechanism of localized corrosion, it is clear that change in the microstructure around the grain boundaries can greatly influence IGC susceptibility, which illustrates the importance of microstructure in determining localized corrosion behavior.

Most Al alloys are used in the wrought form, and have an elongated grain structure. The grains are elongated in both the long transverse and longitudinal directions, forming a pancake-like microstructure. Such a directional microstructure is thought to be an important factor for Al alloy susceptibility to exfoliation. The variations in grain structure such as grain shape have been reported to affect the susceptibility of AA2024-T3 and AA2014-T6 alloys to exfoliation. It was found that the severity of the exfoliation was related to the grain aspect ratio of the alloys, with the most severe exfoliation occurring on the mid-plane (T/2 section) as a result of the more elongated shape of the grains in this plane. The directionality of microstructure is also important for localized corrosion development. For example, an orientation dependent corrosion fatigue crack growth and SCC was reported in 8090 Al-Li plate and Al-Zn-Mg-Cu alloys, respectively. Unfortunately, little is known about these microstructure orientation effects on localized corrosion susceptibility and its growth.

There is no quantitative or qualitative data on the influence of grain size on localized corrosion kinetics in Al alloys. In stainless steels, it has generally been accepted that sensitization (susceptibility to IGC) increased with grain size because the density of Cr carbides per unit surface area of the grain boundary is a function of grain size. However, as localized corrosion (mainly IGC) grows into a microstructure, superfine-
Grain steel exhibited a relatively higher corrosion rate than normal- and coarse-grained steels. So the influence of grain size must also consider other factors, such as intermetallics and their distribution, solute depleted zones and environments. Since sheet and plate alloys exhibit different microstructure in grain shape and grain size, different localized corrosion growth kinetics are expected in sheet and plate Al alloys.

Precipitate-free zones (PFZ’s) are another important microstructural feature in age hardening Al alloys. It is well established that preferential precipitation at the grain boundaries during aging of Al alloys can lead to the formation of PFZ’s adjacent to grain boundaries. There are two explanations for the formation of PFZ’s\textsuperscript{1,11}. First, there is a narrow (~100 nm) region at grain boundary, which is depleted of solute because of the rapid diffusion of solute atoms into the boundary where large precipitate particles are formed. Second, relatively low vacancy concentration makes nucleation of precipitates impossible at this narrow region. The width of the PFZ’s depends on many factors, such as alloy composition, solution treatment temperature, quenching rate, aging temperature and period of natural aging before artificial aging. For higher solution treatment temperature, faster quenching rate, and lower aging temperature, narrower PFZ’s are formed. The existence of PFZ’s has been reported in many Al alloy systems, such as Al-4\text% Cu\textsuperscript{72}, AA2024 (Al-Cu-Mg)\textsuperscript{72}, AA2090 (Al-Li-Cu)\textsuperscript{80}, and AA6056-T6 (Al-Mg-Si-Cu)\textsuperscript{78}, and AA6013-T6 (Al-Mg-Si-Cu)\textsuperscript{79}, Al-Zn-Mg\textsuperscript{76}, Al-Zn-Mg-Cu (7xxx)\textsuperscript{5}. Interestingly, all of the above alloys all are susceptible to IGC, which explains the correlation between PFZ’s and IGC in Al alloys. However, there is still some controversy over the dependence of IGC susceptibility on the formation of PFZ’s. For example,
Ramgopal\textsuperscript{81} studied IGC of AA7150, and found that PFZ has similar or slightly noble electrochemical behavior with respect to Al matrix in both T6 and T7 tempers. The relationship between PFZ width and SCC resistance was also studied in Al-Zn-Mg\textsuperscript{82} and Al-Li-Cu, but it seems that there is no direct relationship between the PFZ width, IGC, and SCC in Al-Zn-Mg and Al-Li-Cu alloys.

It should be pointed out that localized corrosion might take the form of both IGC and pitting in long transverse and short transverse directions of AA2024-T3 plate. It was reported that the localized corrosion of the AA2024-T3 lap joint, taken from a KC-135 tanker aircraft includes IGC, pitting, as well as exfoliation\textsuperscript{96}. The exact reason for such corrosion morphology of different forms of localized corrosion is not explored.

3.3.2 Composition of electrolyte

Most of literature work on localized corrosion has been conducted mainly in chloride solution. Nevertheless, it has been observed that localized corrosion can occur in other environments as well. For Al and Al alloys, nitrates ($\text{NO}_3^-$)\textsuperscript{73}, perchlorates ($\text{ClO}_4^-$)\textsuperscript{11,73}, thiocyanates ($\text{SCN}^-$)\textsuperscript{112}, and other types of halides including fluorides ($\text{F}^-$)\textsuperscript{113}, bromides ($\text{Br}^-$)\textsuperscript{114}, and iodides ($\text{I}^-$)\textsuperscript{114} were reported to cause pitting. More importantly, according to the recent work on real crevice environments taken from actual lap joints of Air Force planes\textsuperscript{115}, it was found that these environments are quite different from what had been assumed, i.e. chloride is not the only major component. Sulfate, nitrate, and fluoride are also found in abundance. Also, it is quite surprising that the pH in the real lap
Chloride:

The influence of chloride on the pitting of Al and Al alloys has been well documented\textsuperscript{11,73,112,116-120}. It has been reported that the chloride ion concentration changes the pitting potential according to the following equation\textsuperscript{117}:

\[
E_p = E_p^0 + 2.3 \, n \,(RT/3F) \log [Cl^-]
\]

(2.9)

where \(E_p^0\) = pitting potential at \([Cl^-] = 1\) M, and \(n\) is the number of Cl\(^-\) ions in the aluminum chloride complex or reaction order in the pitting reaction.

A plot of \(E_p\) against \(\log [Cl^-]\) should be linear with a slope of \(2.3n(RT/3F)\) and an intercept of \(E_p^0\). Bohni and Uhlig\textsuperscript{11} reported a slope of 124 mV/decade and an intercept of -746 mV\textsubscript{SCE} for pure Al, which is in agreement with results determined early by Kaesche\textsuperscript{121}. Stirrup et al.\textsuperscript{117} found a slope of 100 mV/decade and a -757 mV\textsubscript{SCE} intercept for pure Al, and Rinker and Duquette\textsuperscript{118} obtained a slope of 106 mV/decade and an intercept of -843 mV\textsubscript{SCE} for an Al-4.2Mg-2.13Li alloy.

The qualitative effect of chloride concentration on pitting corrosion is well known. Pitting corrosion damage increases with increasing chloride concentration. There is little attempt to measure its effect quantitatively\textsuperscript{51-53}. According to Hunkeler and Bohni\textsuperscript{51-53}, pit growth of pure Al in chloride solution is under ohmic control in both cases, which under ideal conditions results in a square root growth law. Increase in chloride concentration increases the electrolyte conductivity, resulting in accelerating pit
growth. However, Cheung reported that the pit growth was independent on applied potential. The difference was believed as a result of a crevice effect.

**Nitrate:**

Galvele et al. studied localized corrosion of Al and Al-4%Cu alloys in nitrate solutions. They found that both Al and Al-4%Cu showed hemispherical pit morphology, which is completely different from that observed in chloride solution. As described above, IGC was found for the aged Al-4%Cu alloy in 1 M NaCl. However, no IGC was observed in 1 M NaNO₃. It appeared that, in nitrate solutions, pits nucleated at the grain boundaries, but could not develop along the narrow depleted zone as in chloride solution. The authors suggested that this difference in IGC behavior could be attributed to the different pit morphology. However, it is still not clear how different anion actions give rise to different pit morphologies in Al and Al-Cu alloys.

Galvele et al. also studied pitting corrosion behavior of Al in mixtures of NaCl and NaNO₃ solutions, and found that both pitting potentials and pit morphology were strongly dependent on composition of the solution. For a small (0.05 M) addition of NaCl into 1 M nitrate, the pit morphology was almost the same as that observed in pure NaNO₃. As the concentration of NaCl increased to 0.1 M NaCl, the pits tended to lose their hemispherical shapes and became like the NaCl type although the pitting potential was almost the same as that of pure NaNO₃, Fig. 2.19. The pitting potential showed a sharp drop with further increasing NaCl concentration. It is generally accepted that the high pitting potential of Al in pure nitrate solutions is attributed to the interference by a cathodic reaction with the localized acidification process, i.e. reduction of the nitrate
ions as given by\textsuperscript{112,113}:

\[ 2 \text{NO}_3^- + 12 \text{H}^+ + 10e^- = \text{N}_2 + 6\text{H}_2\text{O} \] \hspace{1cm} (2.10)

Such a cathodic reaction will consume a great amount of protons, preventing the formation of localized acidity.

Bohni and Uhlig also studied the effect of nitrate addition on the pitting of Al in chloride solution\textsuperscript{11}. They found that NaNO\textsubscript{3} addition to NaCl solution raised the pitting potential to more noble values, and inhibited pitting corrosion. Fig. 2.20 shows the effect of nitrate addition on the number of pits on 99.4\% Al samples in 0.1 M NaCl after 24 h immersion. The effect of sulfate addition is also shown in the figure. As can seen, when the nitrate concentration increased above 0.28 M in 0.1 M NaCl solution, no pits were observed on 99.4\% Al. The minimum concentration of nitrate required for inhibiting pitting of pure Al in aerated sodium chloride solutions is given by the following relationship\textsuperscript{11}:

\[ \log(\text{Cl}) = 0.65\log(\text{NO}_3^-) - 0.78 \] \hspace{1cm} (2.11)

It should be pointed out that in both studies discussed above, the pH of the electrolyte mixtures was not reported, and it was assumed that there were no appreciable pH changes after addition of nitrate, which may not be the case.

AA7075 alloys in nitrate-containing chloride solutions were reported to show different localized corrosion susceptibility from that of Al-Cu alloys. AA7075-T6 temper is known to be susceptible to IGC. However, Maitra et al.\textsuperscript{77} found that the addition of nitrates to chloride solutions caused IGC of T7 temper alloys as well. It was found that addition of nitrate addition greatly increased the difference in the pitting potential.
the reason for the increased IGC susceptibility of AA7075-T7 in chloride plus nitrate solutions. In their work, the effects of solution pH and sulfate additions on localized corrosion of AA7075-T7 were found to be relatively small.

Although it was reported about 30 years ago that both chloride and nitrate can cause pitting and IGC on Al and Al alloys, quantitative studies of the effect of nitrate and chloride on localized corrosion growth kinetics of Al were not reported until the early 80s. Hunkeler and Bohni\textsuperscript{51-53} developed a metal foil technique to study the pit growth kinetics on Al in various electrolytes. According to their work\textsuperscript{51-53}, the pit growth rate is strongly affected by the chloride concentration as well as the applied potential. Fig. 2.21 shows pit depth as a function of time for two different chloride concentrations at \(-470 \sim -480\) mV SCE potentials. It is obvious that lowering the chloride concentration reduces the growth rate. Fig. 2.22 shows influence of nitrate as well as other foreign anions on the penetration time, indicating \(10^3\) and \(10^1\) M additions of \(\text{NO}_3^-\) and \(\text{CrO}_4^{2-}\), respectively, are needed to inhibit the pit growth in 0.01 M NaCl at pH 11. They claimed that localized corrosion occurred in the form of pit growth, not other forms of localized corrosion.

Sulfate:

There are no reports that localized corrosion occurs naturally in Al and Al alloys in pure sulfate solution since Al alloys have a very high pitting potential in pure sulfate solutions. It was reported that the pitting potential of pure Al was as high as 2.0 V SHE in 1 M Na\(_2\)SO\(_4\) solution\textsuperscript{112}. Several investigations have reported the effects of sulfate addition on the pitting potential of Al and Al alloys in chloride solutions\textsuperscript{112,123}. Galvele
et al. have shown that addition of sulfate to chloride slightly increased the pitting potential, Fig. 2.23\textsuperscript{112}. Pit morphology was very similar to that of the NaCl type. Only at very high sulfate concentration, the pitting potential increased significantly. At high sulfate solution, pits appeared as cluster of small pits. Bohni and Uhlig\textsuperscript{11} found similar results as shown in Fig. 2.20. Pit number per specimen decreased with increasing sulfate concentration. There is no doubt that addition of sulfate will inhibit pit initiation on Al. However, it has been found that addition of sulfate to chloride solution increased anodic current, which indicated that addition of sulfate accelerated localized corrosion growth rate\textsuperscript{52}. Maitra et al.\textsuperscript{77} also found the IGC rate of AA7075 was significantly higher in chloride with nitrates and sulfate additions than in pure chloride solution. The exact reason for this effect is not clear. However, another study of pit growth in 2-D sputter-deposited thin Al film indicated that addition of sulfate (low concentration) to chloride has only small effect on the pit growth rates at low potential\textsuperscript{123}. It has been reported that in some cases pits grow faster in width than in depth, while in other cases the opposite trend is observed. So pit growth behavior in 2-D may differ from that of pit growth in bulk alloys, which justifies that more work is needed on the role of sulfate in localized corrosion growth.

**Fluoride:**

Among all the halide ions (F\textsuperscript{-}, Cl\textsuperscript{-}, Br and I), fluoride ion has the smallest radius (r=1.36 Å). Because the ionic radius of F\textsuperscript{-} is close to that of O\textsuperscript{2-} (r=1.40 Å), it is possible for F\textsuperscript{-} to replace the O\textsuperscript{2-} in the oxide film. Furthermore, the tendency for adsorption on some oxide surfaces normally increases in the following order\textsuperscript{3}:  

\textbf{43}
Therefore, it has been suggested that mechanism for fluoride-induced pitting on the passive metals may differ from that of other halogen anions.

Dallek and Foley investigated the effect of fluoride addition on pit initiation and pit growth behavior of AA7075 alloys in 0.1 M Na₂SO₄ solution by recording the induction time and the current-time curve after injecting a specific concentration of fluoride solution. It was found that the current increased for a while and reached a plateau, Fig.2.24. The current plateau observed on the current-time curve was explained by the formation of insoluble AlF₃ compound on the Al alloy surface. Using x-ray diffraction analysis technique, Katoh identified the formation of AlF₃·3H₂O and AlF₃·2H₂O on Al corroded in NaF solution. Straumanis et al. studied the corrosion of Al in hydrofluoric acid with varying water, and reported the formation of AlF₃ according to the following reaction:

$$2\text{Al} + 6\text{HF} \Rightarrow 2\text{AlF}_3 + 3\text{H}_2 \quad (2.12)$$

It should be noticed that the above work was conducted in high concentration fluoride (>1M). Little is known about localized corrosion of Al alloys in dilute aqueous fluoride solutions. Scully et al. studied localized corrosion of sputtered Al and Al-0.5%Cu alloy thin films in dilute HF solution. The authors found that no intermediate phases (GP zone, 0' phase) were observed in sputtered Al-0.5%Cu alloy film as would be expected in bulk Al-Cu binary alloys. But the corrosion behavior (metastable pitting) was observed to be similar to that bulk Al-Cu alloys. Little work has ever been reported on localized corrosion of Al-Cu-Mg alloys in diluted fluoride solutions.
Although HF is a weakly-dissociating acid when concentrated, it behaves as a
strong acid when diluted\textsuperscript{127}. The presence of F\textsuperscript{-} in real aging aircraft lap joints\textsuperscript{115}
justifies the importance of understanding the localized corrosion behavior of AA2024-T3
in diluted fluoride containing chloride solutions.

2.3.3 pH effect

The idea that local pH changes can lead to pit initiation and growth is not new. It
dates back to the early "autocatalytic" pitting mechanism\textsuperscript{128}. However, there is no
general agreement on the effect of pH on the pitting potential. It has been reported in
several systems and in a wide range of pH values, that the pitting potential is not affected
by the pH of the solution\textsuperscript{18}. On the other hand, several authors reported that pitting
potential depends on solution pH\textsuperscript{18,129}.

For Al and Al alloys in neutral chloride solutions, it is generally accepted that
solution pH has no marked effect on the pitting potential. The earliest observation that
pitting potential is independent of pH appears to be work by Kaesche\textsuperscript{121}. Foroulis et
al.\textsuperscript{130} studied the kinetics of the breakdown of passivity of preanodized Al in chloride
solution. They found that pitting potential is independent of solution pH in the range 5-
10. In another study, Carroll and Breslin\textsuperscript{131} found that the pitting potential of pure Al in
0.5 M NaCl is independent of pH between values of 2 to 10. More recently, McCafferty
et al.\textsuperscript{132} have shown that the pitting potential of pure Al is independent of pH in buffered
0.1 M and 1.0 M NaCl solutions with pH values between 4 and 8, but there is a slight
The pitting potential was measured for Al alloy 8090 and 2014 in 1-10wt% NaCl solutions at pH 2, 6, and 11. The controversy over the effect of solution pH on pitting may be attributed to different experimental conditions used. Some used buffered chloride solutions under the assumption that buffers will not interfere with the pit initiation and growth under investigation, which may not be the case for some systems. Others used non-buffered solutions (pH adjusted by addition of HCl or NaOH), which are commonly used in measuring pitting potential by polarization technique. Another important fact is that the pitting potential is mainly determined by local pH within the pits, not by bulk solution pH. From the early stress corrosion cracking study on AA7075-T6 in 4.4% KCl solution, it was found that the pH at the crack tip changed only slightly when the pH of the bulk solution was varied in the range of 2 to 10. Therefore, pH change in bulk solutions should not have much effect on the pitting potential in chloride solution if it is true that the local pH within the pits is not influenced much by the pH of bulk solution. But for intermetallic particle-induced pitting in AA2024-T3, it was found that pitting corrosion was dependent on solution pH.

Our polarization work has shown that solution pH influences the pitting potential of AA2024-T3 in chromate containing chloride solutions, particularly for solutions with high Cr ion concentration. Fig. 2.26 shows a set of anodic polarization curves of AA2024-T3 in stagnant 0.1 M NaCl + 0.1 M Cr solution. Clearly, the pitting potential increased with increasing pH. Similar results were observed in deaerated solutions, Fig. 2.27. However, in the chromate-free solutions, the pitting potential changed...
little with pH, which is agreement with other work reported for Al corrosion in neutral chloride solutions. It appears that chromate/dichromate ions and hydroxyl ion have a synergistic effect on the pitting of Al alloys. The pH dependent pitting behavior of Al alloys in chromate containing may be attributed to the solubility of the reduction product chromium (Cr$^{3+}$) in the solutions. But the exact mechanism is not clear yet.

There is a lot of work about the effect of pH on SCC of high strength Al alloys. It is generally accepted that the occurrence of intergranular stress corrosion cracking (IGSCC) of Al alloys in chloride solution is greatly reduced as the solution becomes increasingly alkaline. Figure 2.28 shows some typical results about the effect of pH on failure time by SCC of AA7075-T6. There is sharp increase in failure time with pH around 10. The reason for the pH effect on SCC is not clear yet.

In AA6013-T6 (Al-Mg-Si-Cu alloy), IG attack was found to be dependent on the local pH. IGC was not initiated on TEM foils of the alloy in neutral oxygenated salt water (NaCl-H$_2$O$_2$), but was produced in dilute HCl solution. In AA2090 (Al-2Li-3Cu), local low pH environment was reported to stimulate aggressive subgrain boundary dissolution, which caused IGC.

It is known that the solubility of the corrosion product of Al and Al alloys is very dependent on solution pH. Insoluble corrosion product precipitated on the top of the pits may influence the mass transport and ohmic potential drop, both of which control later stages of pit growth process. Therefore, it is possible that solution pH may have an effect on localized corrosion growth. More work is necessary to clarify pH effect on the localized growth kinetics.
The most-studied and most important inhibitors for Al and Al alloys are chromate/dichromate. So the discussion of inhibitors will be focused on chromate/dichromate effects.

The effect of chromate on localized corrosion has been studied since the early 60's. It has been well established that the pitting potential is shifted in noble direction with addition of chromate. A critical ratio of chromate to aggressive anion (Cl\(^-\)) concentration must be exceeded in order to inhibit pitting of Al. The following empirical equation for the relationship between critical concentration of chromate and chloride has been obtained for Al:

\[
\log [\text{Cl}^-] = 0.56 \log [\text{CrO}_4^{2-}] - 1.11
\]

The above results can be explained by the competitive adsorption of Cl\(^-\) and CrO\(_4^{2-}\) ions. It has been suggested that the inhibition mechanism of chromate ions in chloride solutions involves blocking of Cl\(^-\) incorporation into the oxide film by the presence of chromate ions. However, others claimed that no Cl\(^-\) concentration changes in the oxide film were observed with addition of chromate to chloride solutions.

X-ray absorption studies of the interaction of chromate on the surface of Al with air-formed and anodic films showed that different valency Cr species (Cr\(^3+\) and Cr\(^6+\)) were observed in the oxide layer. The ratio of Cr\(^6+\)/Cr\(^3+\) depended on thickness of oxide film and type of film. In Al with a thick anodic film, Cr\(^6+\) dominated, while both Cr\(^6+\) and Cr\(^3+\) were present for thin anodic film samples. The presence of Cr\(^3+\) was attributed to rapid reduction of chromate species at flaw bases and their gradual penetration into...
Other studies also showed that both \( \text{Cr}^{6+} \) and \( \text{Cr}^{3+} \) species were present in the passive film of Al\(^{138}\).

It is worth mentioning that the ratio of \( \text{Cr}^{6+} \)/total \( \text{Cr} \) in chromate conversion coatings on Al also depends on the thickness of coating\(^{139}\). The reason for this was attributed to fact that thinner coating contains more numerous surface defects, so more \( \text{Cr}^{6+} \) reduction is expected to occur at flaws.

The effect of chromate on metastable pitting is an interesting and important aspect of pitting corrosion. Pride et al.\(^{35}\) studied the chromate effect on metastable pits on pure Al in chloride solutions \((10^{-4} \text{ to } 1 \text{ M})\). They found that a small amount of chromate addition significantly changed the metastable pitting behavior of pure Al. Chromate inhibitor acts in several ways to affect metastable pitting, such as reducing the metastable pit nucleation frequency, peak pit current, apparent pit radii, apparent pit current density. Fig. 2.29 shows the effect of the \( \text{CrO}_4^{2-} \) concentration on the anodic current spikes, which are associated with metastable pitting, in \( 10^{-3} \text{M NaCl at } -0.5 \text{ V}_{\text{SCE}} \). It is clear from the Fig. 2.29 that metastable pit transients were absent when \( 5 \times 10^{-5} \text{ M Na}_2\text{CrO}_4 \) was added to \( 10^{-3} \text{ M NaCl solution. More importantly, chromate also lowered the pit growth rate. The authors suggested that the criterion for pit stabilization (}I_{\text{pit}}/I_{\text{pit}} > 10^2 \text{ A/cm}) \text{ that was difficult to maintain with addition of chromate to chloride solutions. However, the exact role of chromate during pit growth is still unclear from their work}^{35}.\)

Very little has been reported on the effect of chromate on pit growth. Hunkeler and Bohni\(^{51-53}\) studied the effect of chromate anion on pit growth on pure Al using the foil penetration technique and found that about \( 10^{-1} \text{M} \) addition of chromate is needed to
inhibit the pit growth in 0.01 M NaCl solution with pH of 11. Surprisingly, based on the results on 2-D pit growth studies in 0.1 M chloride\textsuperscript{123}, it was found that low concentrations of dichromate (if dichromate is assumed to provide the same inhibition as does chromate) has no effect or even increases the pit growth. Only very high concentrations inhibited the pit growth. It was suggested that chromate enhances indirectly the pit growth by increasing the tenacity of the passive film, which results in an increasing of the mass transport barrier\textsuperscript{133}. Nevertheless, the reason for different behavior of chromate in 2-D (not much effect on pit growth rate at low concentration) and 3-D pit growth (reduces pit growth rate even at very low concentration) is not clear. But it appears that the factors greatly affecting 3-D pit growth do not necessarily influence the 2-D pit growth to the same extent as usually expected. Further work is very necessary to clarify this effect.

It should be pointed out that most of the past work on chromate effects on pitting was not performed at constant solution pH under the assumption that solution pH has no effect on pitting as usually observed in neutral chloride solution. However, our preliminary work\textsuperscript{133} has shown that there might exist a synergistic effect between chromate and hydroxyl ions. Solution pH needs to be taken into account for the chromate inhibition mechanism. Unfortunately, no studies of pH effect in chromate inhibition have been reported.

In conclusion, chromate can act in different ways to inhibit pitting corrosion. Considerable work has indicated without a doubt that when added to chloride solution, chromate increases the pitting potential, decreases metastable pits nucleation, inhibits pit
growth rate, and accelerates (or does not much affect) the repassivation process. The prevalent explanations for chromate inhibition effects include the following:

(1) Competitive adsorption of chromate anion with chloride anion for the defect sites in the passive oxide, or through adsorption of chromate anions to block the incorporation of chloride anion into the oxide film\textsuperscript{11,140-142}.

(2) Incorporation of chromate or its reduction product into the passive film in the oxide film changes the electronic properties of passive film to make it more resistant to chloride attack\textsuperscript{143}.

(3) Dynamic repair of newly initiated breaking areas or defect areas by its reduction\textsuperscript{133,144}.

(4) Self-healing of defect or flaw areas by migration and altering the local electrochemical conditions for repassivation\textsuperscript{133,139,145}.

(5) Passivating intermetallic particles, and reducing metastable nucleation rate\textsuperscript{133}.

(6) Acting as a cathodic inhibitor at open circuit\textsuperscript{146}.

In summary, the exact mechanism by which chromate acts is still not clear. More systematic work needs to be done to elucidate the effects of chromate/dichromate on localized corrosion initiation and growth kinetics.

2.4 Techniques for Studying Localized Corrosion Kinetics

As discussed above, studies of localized corrosion kinetics is an important part in the area of Al alloy corrosion. A fundamental understanding of kinetics of dissolution in localized corrosion sites is critical for the development of predictive models. However, it
is often quite difficult to quantitatively study localized corrosion kinetics. For example, in order to determine the pit growth rate ($i \sim E$ relationship), one must know the active pit area and number of pits, which are generally hard to measure and count. Pits often are assumed as hemispherical for the simple calculation of active pit areas, which sometimes is not the case in practice. On the other hand, the measured current may come from different pits on the same surface with different growth rates or different forms. Furthermore, hydrogen evolution in the pit site consumes a portion of the current so that the current measured under potentiostatic conditions is only a fraction of the true anodic dissolution current. All of these factors make it extremely difficult to quantitatively measure localized corrosion kinetics using electrochemical techniques. The study of single pits, formed by various approaches such as masked techniques, implantation\textsuperscript{147}, laser irradiation\textsuperscript{63}, or the use of artificial pit electrode\textsuperscript{148}, provides a practical way to study the pit growth kinetics. But there is no assurance that the behavior of artificial pit growth is the same as that of real pits that occur in practice. Another new electrochemical technique for pit growth rates is electrochemical impedance spectroscopy (EIS)\textsuperscript{7}. However, EIS can only deal with early stages of pit growth. Furthermore, reliable impedance measurement requires a linear relationship between the input and output signals, and determination of pit growth rates from EIS data involves some assumptions as well.

Non-electrochemical techniques offer another approach to address localized corrosion kinetics. There are two kinds of non-electrochemical techniques available in the literature. One is thin film pitting technique for the study of 2-D pits in thin metal
films, and other is foil penetration technique for the study of fastest growing localized corrosion sites in bulk alloys. Both techniques show many advantages over electrochemical techniques for the study of localized corrosion growth kinetics. For example, in thin film pitting technique, the pit current density is easily and accurately determined by measuring pit wall velocity from the image analysis. The anodic pit current density, $i$, is proportional to the velocity of the pit wall according to Faraday's law:

$$i = \rho n F \left( \frac{\partial r(t, \theta)}{\partial t} \right)$$

where $r(t, \theta)$ is the radius as a function of time, and angle around the perimeter, $\theta$, $\rho$ is the density, $n$ is the number of electrons in the dissolution reaction, $F$ is the Faraday constant, $M$ is molecular weight.

In the case of the foil penetration technique, growth kinetics are determined by measuring the time for the fastest growth localized corrosion site to perforate foils of varying thickness. The penetration time is measured by detecting a resistance change of filter paper, which is sandwiched between the sample and a backing Cu foil. This technique can be used to study the effects of environmental factors, such as electrolyte composition and applied potential on localized corrosion kinetics. More details about foil penetration and its experimental set-up will be discussed in Chapter 4.

The foil penetration technique was first developed by Hunkeler and Bohni for the study of pit growth kinetics in Al foils. As discussed earlier, they found that pit growth was under ohmic control in Al as the electrolyte resistance had a direct effect on
The foil penetration technique has been used recently to address localized corrosion behavior of AA2024-T3 alloys\textsuperscript{146}. In that study, 0.2 mm thick AA2024-T3 sheets were tested in chloride + dichromate, and chloride + dichromate + other oxidizers (such as H\textsubscript{2}O\textsubscript{2}, Na\textsubscript{2}S\textsubscript{2}O\textsubscript{7}) solutions. It was found that localized corrosion can take circuitous paths while penetrating through the wrought foil. Microfocal X-ray radiography indicated that the attack morphology was much more convoluted than a hemispherical pit, Figure 2.30. The convoluted growth morphology of localized corrosion underscores the usefulness of the foil penetration technique for the measurement of growth kinetics. In fact, it was subsequently found that the form of localized corrosion was not simple pitting corrosion. Localized corrosion that starts outs as pits can transition to other forms of attack such as IGC and exfoliation. Unfortunately, there is no quantitative information regarding the effect of microstructure on the morphology and localized corrosion kinetics. All of these have motivated this thesis work.

2.5 Motivation and Objectives of the Thesis

As discussed above, there are a number of key issues that are still not clear with respect to localized corrosion susceptibility and kinetics of AA2024-T3, such as microstructure effects including intermetallic particles, heat treatment and aging, sample orientation, local pH effect as well as various environmental conditions. The motivation of this thesis is to develop quantitative information on localized corrosion kinetics in
AA2024. Listed below are some of objectives that will be addressed in this thesis:

(1) Measurement of localized corrosion kinetics in different directions relative to the rolling direction.

One of the needs in the field corrosion is a quantitative measurement of growth kinetics of various forms of localized corrosion. For example, pit depths are often measured using mechanical probes or optical methods. Clearly these methods are not applicable to convoluted growth pits observed in 2024-T3 sheets. The foil penetration technique is a suitable approach to study localized corrosion growth kinetics of AA2024-T3 under a variety of conditions. Growth rates along three alloy directions, longitudinal (L), long transverse (LT), and short transverse of wrought AA2024-T3 plate will be quantitatively measured to have a better understanding of microstructural orientation effect on the kinetics.

(2) The effects of microstructure, grain shape, and heat treatment, artificial aging, applied potential, and environments on localized corrosion susceptibility, morphology, and kinetics.

Localized corrosion in wrought Al alloys is closely associated with the microstructure. Wrought Al alloys have a typical elongated grain structure, which is thought to be an important factor in localized corrosion, but the effect of this structure directionality has never been measured quantitatively. The qualitative effect of heat treatment condition of the alloy on IGC susceptibility is also well known, however, the exact reason for it is still not understood. The effect of nitrate/sulfate addition has been shown to have a beneficial effect on the pitting potential, but little work has addressed
their influence on growth kinetics. Plate and sheet alloys exhibit different grain structure.

No comparison has made for growth kinetics of plate and sheet alloys. The characterization of microstructure, localized corrosion morphologies under different conditions is also important part of the thesis work. The optical microscopy, SEM, TEM, and microfocal X-ray radiography and other analytical techniques will be employed in this work.

(3) Statistical modeling of localized corrosion growth kinetics

The lack of quantitative data of localized corrosion growth to some degree impedes the development of a predictive corrosion model. The results of the proposed penetration work are expected to provide some quantitative information in the development of localized growth kinetics model. The aim of the statistical modeling for localized corrosion is to explain observed penetration results for the given microstructure of Al alloys.

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### Table 2.1 Electrochemical properties of intermetallic particles present in Al-Cu and Al-Cu-Mg alloys.

<table>
<thead>
<tr>
<th>Intermetallic Phases</th>
<th>Alloys</th>
<th>Nobility</th>
<th>$E_{\text{corr}}$ (mV SCE)</th>
<th>Solution, pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta$-Al$_2$Cu</td>
<td>Al-Cu</td>
<td>Cathodic</td>
<td>-580$^{98}$</td>
<td>1 M NaCl (deaerated)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-500$\sim$1600$^{99}$</td>
<td>Na$_2$B$_4$O$_7$10H$_2$O + H$_3$BO$_3$, C$_4$H$_6$O$_6$, H$_2$SO$_4$, NaOH, PH=2~12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-250$\sim$1100$^{102}$</td>
<td>0.5 M Na$_2$SO$_4$, H$_2$SO$_4$, 1 M NaCl, pH=0.4~12</td>
</tr>
<tr>
<td>S-Al$_2$CuMg</td>
<td>Al-Cu-Mg</td>
<td>Anodic</td>
<td>-920$^{101}$</td>
<td>1 M NaCl, pH=11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>-880$^{99}$</td>
<td>1 M NaCl, pH=11</td>
</tr>
</tbody>
</table>

Table 2.1 Electrochemical properties of intermetallic particles present in Al-Cu and Al-Cu-Mg alloys.
Figure 2.1. Schematic cyclic potentiodynamic polarization curve to give $E_p$ and $E_r$. 
Figure 2.2 Schematic diagrams for pit initiation models: (a) adsorption mechanism, (b) anion penetration and ion migration model, and (c) film breakdown theory.
Figure 2.3 Metastable pitting current transients observed on 302 stainless steel in 0.1 M NaCl at 420 mV SCE\textsuperscript{31}.

Figure 2.4 Mathematical transformation of an equi-concentration and equi-potential plane diffusion (a) into an equivalent plane problem (b)\textsuperscript{36}.
Figure 2.5 Schematic anodic polarization curves for the pit and unpitted surface$^{41}$.

Figure 2.6 Galvanostatic potential transients; solid line represents experimental data; dashed line represents theoretical. (a) Fe in 1 M KCl, (b) Ni in 4 M KCl$^{39,40}$. 
Figure 2.7 Influence of potential on the pit growth including pit depth and pit current density of Al foil in 0.01 M NaCl at pH 11\textsuperscript{52}.

Figure 2.8 Dependence of the product of pit depth and pit current on the ohmic potential drop\textsuperscript{51}.
Figure 2.9 Anodic and net current densities change as a function of potential for 100 nm Al film in 0.1 M NaCl\textsuperscript{59}.

Figure 2.10 Concentration of Fe\textsuperscript{2+}, Fe(OH\textsuperscript{+}), and H\textsuperscript{+} as a function of the product of the depth and current density in one-dimensional pit\textsuperscript{18}.
Figure 2.11 Corrosion potentials of the grains and grain boundaries for Al-4\%Cu alloy as a function of aging time at 375 \(^{\circ}\)F.\(^{72}\)
Figure 2.12 Effect of chloride concentration on the pitting potentials of Al and Al-Cu alloys in deaerated NaCl solutions\textsuperscript{73}.

Figure 2.13 Potential-chloride concentration-type of corrosion relation for Al-4\%Cu alloys\textsuperscript{73}.  

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\textsuperscript{73} Reference number.
Figure 2.14 Two breakdown potentials observed in peak aged Al-4%Cu alloys.\textsuperscript{73}

![Anodic polarization curves for T1 (Al\textsubscript{2}CuTi) phase and Al in deaerated 0.6 M NaCl solution.\textsuperscript{85}]

Figure 2.15 Anodic polarization curves for T1 (Al\textsubscript{2}CuTi) phase and Al in deaerated 0.6 M NaCl solution.\textsuperscript{85}
Figure 2.16 Effect of cooling rate during quenching between 400 to 315 °C on the susceptibility to IGC and SCC. IGC was tested in NaCl-H₂O₂, and SCC tested in 3.5% NaCl.

Figure 2.17. Effect of cooling rate on corrosion behavior of AA2024 alloys in 0.2 M NaCl.
Figure 2.18 Effects of artificial aging on the corrosion and SCC behavior of AA2024 in NaCl solution.\textsuperscript{82}

Figure 2.19 Pitting potentials of Al 99.99\% in mixtures of NaCl + NaNO\textsubscript{3} solutions.\textsuperscript{112}
Figure 2.20 Effects of Na$_2$SO$_4$ addition to 0.005M NaCl, and NaNO$_3$ to 0.1 M NaCl on the number of pits formed on 99.4% Al samples (24 h immersion)$^{11}$. 

Figure 2.21 Effect of chloride concentration on pit growth rate$^{52}$. 

77
Figure 2.22 Influence of foreign anions addition to chloride on the perforation time and the electrolyte resistance (Foil thickness 0.2 mm, 0.01 M NaCl pH=11 at -430 mV_{SCE})\textsuperscript{52}.

Figure 2.23. Pitting potentials of Al 99.99% in neutral deaerated mixtures of NaCl + Na\textsubscript{2}SO\textsubscript{4} solutions\textsuperscript{112}.  

1000
SOD
9H tm  m
CIIIIOWII tM l/U

Figure 2.22. Influence of foreign anions addition to chloride on the perforation time and the electrolyte resistance (Foil thickness 0.2 mm, 0.01 M NaCl pH=11 at -430 mV_{SCE})\textsuperscript{52}.

Figure 2.23. Pitting potentials of Al 99.99% in neutral deaerated mixtures of NaCl + Na\textsubscript{2}SO\textsubscript{4} solutions\textsuperscript{112}.  

78
Figure 2.24 Pit current-time curve for 7075 Al alloys in 0.1 M Na$_2$SO$_4$ added 1 x 10$^{-4}$ M F$^-$ after 6 minutes$^{113}$.

Figure 2.25 Pitting potentials for Al as a function of pH in 0.1 and 1 M chloride solutions$^{132}$. 
Figure 2.26 Anodic polarization curves of AA2024-T3 in stagnant 0.1 M NaCl +0.1 M [Cr$^{6+}$] solutions with varying solution pH$^{133}$. 

Figure 2.27 Anodic polarization curves for AA2024-T3 in deaerated 0.1 M NaCl +0.1 M [Cr$^{6+}$] solutions with varying solution pH$^{133}$. 

80
Figure 2.28 Effect of pH on time to failure by stress corrosion cracking in AA7075-T6.  

Figure 2.29 Effect of chromate on the anodic current spikes associated with metastable pitting. On top left also shown is the cumulative number of pitting events/cm² verse exposure time.  

81
Figure 2.30 Microradiographs of 0.2 mm thick AA2024-T3 penetrated in an oxygen stirred 1 M NaCl + 0.3 %H₂O₂ + 10⁻⁴ M Na₂Cr₂O₇ solution[46].
CHAPTER 3

BREAKDOWN POTENTIALS AND MORPHOLOGY
OF LOCALIZED CORROSION IN AA2024

3.1 Introduction

Pitting and intergranular attack, including exfoliation, are two common forms of localized corrosion in high strength Al alloys such as AA2024-T3 in chloride-containing aqueous environments. Pits and intergranular attack can be sites for initiation of cracks, resulting in catastrophic failure by stress corrosion cracking or corrosion fatigue. A mechanistic understanding of pitting and intergranular corrosion (IGC) susceptibility in Al alloys and quantification of their growth kinetics, therefore, are of scientific interest and technological importance.

The problem of pitting and IGC susceptibility in high strength Al alloys has been studied for many years. In principle, both pitting and IGC result from a local breakdown of the passive film that forms on the surface, but the exact mechanism of the breakdown is still not clear. Attack that occurs at intermetallic particles, or in the matrix of a grain is called pitting, whereas attack on grain boundary regions is called IGC. From an

83
electrochemical point of view, both pitting and IGC processes seem to be very similar in nature. For example, chloride ions have been reported to be necessary for both pitting and IGC in Al alloys. The growth of pits and IGC is believed to depend on potential. As pits grow into the microstructure, they can develop into IGC or exfoliation (a form of intergranular corrosion found in wrought alloys), which can penetrate deeply into the microstructure. To some extent, IGC can be regarded as a special kind of pitting corrosion occurring preferentially at the grain boundaries for Al alloys since the mechanism of IGC was found to be of the same nature as the process of pitting. However, differences clearly exist between pitting and IGC. For example, artificial aging is thought to minimize intergranular corrosion susceptibility, but may not necessarily improve pitting resistance. Furthermore, the growth kinetics for IGC may be different than for pitting.

Many questions regarding the nature of pitting and IGC in Al alloys are still unclear. Little is known about the transition between pitting and IGC and the factors responsible for this transition process. Another unresolved issue is how artificial aging affects the susceptibility of alloys to pitting and IGC. In this chapter, the pitting and IGC behavior of AA2024 in different tempers is discussed based on the results of electrochemical tests, corrosion morphology, and microstructure characterization using optical metallography, SEM and TEM. The effect of nitrate and sulfate ions on the localized corrosion behavior was studied. The purpose of the investigation is to identify the electrochemical factors that govern the susceptibility to IGC and control the transition.
from pits to IGC, and determine how artificial aging, solution environment, and anodic potential affect the initiation and growth of IGC from a microstructural point of view.

3.2 Experimental

Most specimens were prepared from commercial 1.9 cm (3/4 in.) thick AA2024-T3 plate stock. A few samples were taken from commercial 0.2 mm thick AA2024-T3 sheet. The chemical compositions of AA2024 plate and sheet are shown in Table 1. For the plate material, samples with three different orientations i.e. longitudinal (L), long transverse (LT) and short transverse (ST) sections were prepared using a band saw or diamond saw. The T3+, T8, and T8+ tempers were produced by artificially aging AA2024-T3 slices, previously cut from the plate, at 190 °C in an air furnace for 2.5 h, 12 h, and 36 h, followed by air cooling, respectively. Solution heat-treated (SHT) AA2024 samples were also prepared from the original AA2024-T3 plate and sheet. The solution heat treatment was conducted in an air furnace at 492 °C for 1 h, followed by either water quenching or furnace cooling. The effect of artificial aging on the mechanical properties was determined using microhardness measurements. All samples for electrochemical experiments were ground mechanically and polished through a series of silicon carbide (SiC) papers (up to 800 grit) in ethanol. No water was used during polishing in order to minimize corrosion. After polishing, the samples were degreased with ethanol before attachment to the bottom of an acrylic cell by pressing against a teflon knife-edge O-ring to expose an area of about 1 cm² for the experiments. The solution for most experiments was 1 M NaCl, prepared by mixing A.C.S. grade NaCl crystals with 18 MΩ-cm
Anodic potentiodynamic polarization experiments were performed in deaerated 1.0 M NaCl to determine the breakdown potentials of various tempers (SHT, T3, T3+, T8 and T8+) of AA2024 as a function of sample orientation relative to the rolling direction. A three-electrode electrochemical cell was used for the measurements using a Pt mesh counter electrode and a saturated calomel reference electrode (SCE). A Princeton Applied Research Model 273 potentiostat/galvanostat corrosion measurement system was used to perform the potential scan. The solution was Ar-deaerated for at least 24 h before the polarization experiment, and was continuously purged with Ar during the measurement. Each sample was exposed to the solution for 35 min prior to the start of the measurement. The sample was then potentiodynamically polarized from −30 mV vs. the open circuit potential to a potential above the breakdown potentials at 0.1 mV/s. No IR compensation or correction was performed during polarization measurement. The breakdown potentials were taken as the points in the anodic polarization curve at which the current increased sharply. Cyclic polarization was performed on some samples to examine the repassivation behavior of localized corrosion (pitting and intergranular corrosion) in Ar-deaerated 1.0 M NaCl.

In order to correlate the anodic polarization behavior to the forms of localized corrosion occurring on the samples, potentiostatic polarization experiments were conducted on both AA2024-T3 and T8 tempers. In one group of experiments, samples were first potentiodynamically polarized to various anodic potentials and then held at this
metallographic cross-sections of these potentiostatically polarized samples were subsequently examined by optical microscopy or scanning electron microscopy (Philips XL30 FEG-SEM) to determine the form of corrosion attack. In another group of experiments, the potential of the samples in deaerated 1.0 M NaCl was switched every 20 to 60 min from a low (below the second breakdown potential) to high value (above the second breakdown potential), and the current was recorded to correlate localized corrosion growth with potential changes.

The microstructures of AA2024-T3 and T8 were characterized using optical metallography, scanning electron microscopy (SEM) and transmission electron microscopy (Philips CM200 TEM). Samples with the three different orientations (ST, L, and LT) were polished to 1 μm diamond paste followed by etching in Keller’s reagent for about 30 to 50 s. Foils for transmission electron microscope (TEM) examination were first thinned mechanically to a thickness of 0.1 mm, and then electropolished to perforation in a twin-jet electropolishing apparatus using a 30% nitric acid in methanol at -30 to -50 °C.

3.3 Results and Discussion

3.3.1 Microstructure

The microstructures of AA2024 plate and sheet are shown in Figure 3.1 (a, b, c). All tempers (SHT, T3, T3+, T8 and T8+) of the AA2024 plate have a typical elongated pancake-shaped grain structure. Grains were elongated in both the longitudinal and long
transverse directions. This directionality of elongated grain structure is particularly important in regard to localized corrosion growth kinetics, which will be discussed in chapter 4. The average grain dimensions for AA2024-T3 plate at the ¼ T section were approximately 50 μm in the short transverse (ST) direction, 2000 μm in the longitudinal (L) direction, and 300 μm in the long transverse (LT) direction. Grains were a little more elongated at the midsection of the plate. In contrast, the 0.2 mm thick AA2024-T3 sheet material exhibited a completely recrystallized structure, as evidenced by an almost equiaxed grain structure along three alloy directions with an average grain size of 30-50 μm, Figure 3.1(c).

One of the principle microstructural features associated with wrought AA2024 is the existence of coarse intermetallic particles (often called constituent particles) in the structure. They are aligned as stringers in the rolling direction, and can be easily identified in back-scattered electron imaging due to their high content of transition metals, Figure 3.2 (a). As reported by others, SEM-EDX analysis indicates that there exist two main types of large constituent intermetallic particles: smaller and spherically shaped Al-Cu-Mg particles (S phase, marked 1-4, Figure 3.2(b)), and larger and blocky Al-Cu-(Fe,Mn) particles (labeled A-D, Figure 3.2(b)). These coarse intermetallic particles have been extensively studied and well characterized. It is generally accepted that these constituent particles are the main cause of the corrosion problems for AA2024-T3 as they often lead to pitting and intergranular corrosion. In addition to these large sized intermetallic particles, smaller submicron particles (often called dispersoids) that form during solidification of the ingots, and the finest hardening precipitates, which
form during aging, are also present in the microstructure. Features of these particles and precipitates can only be studied using high resolution TEM. In naturally aged AA2024-T3, it is believed that the matrix contains homogeneous coherent precipitates, denoted as GP zones, as well as some hardening precipitates $\text{S'Al}_{2}\text{CuMg}^{8,13}$. Figure 3.3 are TEM micrographs showing the high density of plate-like (Widmanstatten) hardening precipitates ($\text{S'Al}_{2}\text{CuMg}$) in AA2024-T3. In addition, there are a lot of large and rod shaped particles scattered through the matrix, containing Al, Mn, and Cu (possibly $\text{Al}_{20}\text{Mn}_3\text{Cu}_2$). There was little evidence for the existence of precipitate free zones (PFZ) around the grain boundaries in the T3 temper although the formation of precipitate–free zones adjacent to the grain boundaries during quenching has been reported$^8$. However, a lot of rod shaped precipitate particles can be seen in grain boundary regions, Figure 3.3 (b). They all had a very similar shape, but were identified by EDS as having one of the following compositions: very close to $\text{Al}_2\text{Cu}$ (very little Mg), $\text{Al}_2\text{CuMg}$, or $\text{Al}_{20}\text{Mn}_3\text{Cu}_2$ particles with no Mg. Occasionally, Al-Cu-Mn-Fe particles appeared at the grain boundaries as well. It is believed that the rod shaped precipitate particles containing Mn and Cu formed during solidification, not from aging, whereas others were believed to precipitate during natural aging$^{14}$. The Mn and Cu-rich particles are thought to pin grain boundaries, thus retarding recrystallization, and resulting in the retention of the elongated grain structure.

Microstructural changes that occur during solution heat treatment and artificial aging create corresponding changes in mechanical properties and electrochemical behavior. The detailed microstructural changes can be quite complicated including
and density, as well as changes of composition and structure in subgrain and grain
boundaries. In general, artificial aging will not have much effect on the coarse constituent
particles. The rod-like dispersoids, once formed, usually resist either dissolution or
coarsening as well. However, GP zones and the plate-like hardening precipitates
(S'Al₂CuMg) will change with aging. Solution heat treatment will dissolve these
hardening precipitates. The blocky Fe, Mn-rich and coarse Al-Cu-Mg constituent
particles are also not soluble at solution treatment temperature. It is generally believed
that artificial aging at 190 °C allows more precipitation of S' from GP zones in the
matrix. Figure 3.4 shows such fine and numerous precipitate S' platelets in AA2024-T8.
The S' precipitate platelets are still partially coherent with the matrix, and they can grow
to more than 10 nm in thickness before transforming into incoherent S phase
particles. No significant changes in matrix composition were revealed by EDS
analysis as a result of artificial aging. Artificial aging will also cause preferential
precipitation in the grain/subgrain boundaries, leading to the formation of precipitate-free
zones (PFZ) around the grain boundaries. Figure 3.4 (b) is a TEM micrograph illustrating
such copper depleted zones adjacent to the grain boundary precipitates.

The effect of artificial aging on mechanical properties was evaluated using
microhardness measurements. Figure 3.5 shows the hardness changes for AA2024 aged
for different times at 190 °C, which is in agreement with values reported in literature⁸,¹³.
Hardness initially decreased during artificial aging due to partial reversion of the GP and
GPB zones. After 12 h at 190 °C, a maximum in hardness was reached when the alloy
contained a critical dispersion of GP zones and S' precipitates in the matrix. The overaged T8+ alloy showed a slight decrease in hardness because more incoherent S particles transform from S' precipitates.

As mentioned above, the AA2024-T3 sheet had a recrystallized equiaxed grain structure and the plate had an elongated grain structure. Interestingly, fine sub-grain structure was also seen in the etched section of overaged AA2024-T8 plate, Figure 3.6. Generally, a fine sub-grain structure is the result of a re-crystallization process (partially or fully) during alloy metallurgical and thermal processing\(^\text{14}\). However, recrystallization seems unlikely at the artificial aging temperature (190 °C). One alternative explanation is that artificial aging increased heterogeneous precipitation along subgrain boundaries, leading to changes in the subgrain boundary structure or composition so that they are revealed by chemical etching. The existence of precipitate-free zones adjacent to the grain boundaries as revealed by TEM observation on T8 temper also supports this view. From the above discussion, it is clear that artificial aging at 190 °C changes the grain and grain boundary composition, and microstructure of AA2024 alloys.

3.3.2 Polarization curves

Potentiodynamic polarization experiments were performed on AA2024-T3 ST, L, and LT samples to test the influence of sample orientation. Figure 3.7 shows that the current increases sharply above the first breakdown potential \(E_1\). However, instead of increasing monotonically with increasing potential, the current reaches a maximum at a potential labeled \(E_c\) and then decreases by as much as a factor of 10. Above a second
almost independent of the sample orientation and potential scan rate. The more active
one, $E_1$, occurs at about $-670 \sim -700$ mV SCE, and the more noble one, $E_2$, occurs at about
$-590 \sim -610$ mV SCE. $E_c$ was in the range of $-630$ to $-650$ mV SCE. This current
maximum is a reproducible feature of the potentiodynamic polarization curves for the
three alloy directions of AA2024-T3.

Recently, Ramgopal et al.\textsuperscript{17} investigated IGC susceptibility of 7xxx series Al-Zn-
Mg-Cu alloys (AA7075, AA7150) in 0.5 M NaCl + 0.001 M HCl solutions. They found
that those alloys in the T6 temper exhibited two breakdown potentials in the anodic
polarization curves while the same alloys in the T7 temper exhibited only one breakdown
potential. The breakdown potentials were almost independent of the sample orientations.
However, the nature of corrosion attack associated with each breakdown potential was
found to be very complex and dependent on exposure time. After a short potentiostatic
polarization at $E_1$, only pitting was observed whereas IGC was observed for a similar
experiment at $E_2$. Following long 24 h potentiostatic tests at $E_1$, both T6 and T7 tempers
exhibited IGC and pitting. Interestingly, the same T6 temper alloy did not exhibit two
breakdown potentials following three-year storage at room temperature.

Two breakdown potentials have also been reported for aged Al-4%Cu\textsuperscript{1,6}, Al-Zn-
Mg-Cu (AA7075)\textsuperscript{18,19}, and Al-Cu-Mg (AA2017, AA2024)\textsuperscript{4,11}. In aged Al-4%Cu,
Galvele and DeMicheli\textsuperscript{1} reported that first breakdown potential was associated with the
dissolution of the Cu-depleted zone along the grain boundary (i.e. intergranular
corrosion), and the noble one corresponded with pitting of the grain bodies. Sugimoto et
Maitra and English\textsuperscript{18,19} proposed a similar mechanism for two breakdown potentials observed for AA7075-T6 in deaerated 3.5\% NaCl solution. In addition, they found a much larger difference between these two breakdown potentials in a mixture of chloride, nitrate, and sulfate solutions compared to that in pure chloride solutions. In Al-Cu-Mg alloys (AA2017 and AA2024) alloys, Urushino and Sugimoto\textsuperscript{4} also concluded that two breakdown potentials corresponded to pitting at the grain boundaries and the grain matrix, respectively. More recently, Guillaumin and Mankowski\textsuperscript{11} proposed a different view, arguing that the first breakdown potential of AA2024-T3 was related to the dissolution of coarse intermetallic Al\textsubscript{2}CuMg particles, while the second breakdown potential corresponded to the matrix breakdown potential. Our experimental results for AA2024-T3 are in agreement with the earlier study by Guillaumin and Mankowski\textsuperscript{11} regarding the first breakdown potential, but suggest that the second breakdown potential may result from initiation and growth of IGC. It should be pointed out that two breakdown-potential polarization curve is a summation of current from two different localized dissolution processes. Even though the second breakdown potential results primarily from IGC growth, IGC may initiate below the second breakdown potential.

### 3.3.3 Types of corrosion

The presence of two breakdown potentials in the anodic polarization curves is an important feature of localized corrosion of AA2024-T3 in chloride solution. Generally speaking, a breakdown potential corresponds to the dissolution potential of a
metallurgical phase. So, two breakdown potentials may indicate that there are two phases in AA2024-T3 microstructure, with different dissolution potentials, responsible for two different forms of localized corrosion. The reason for the current peak, i.e. the decrease in current with increasing potential above $E_1$ must also be explained. In order to determine the causes responsible for each of the breakdown potentials in the polarization curves of AA2024-T3, potentiostatic polarization experiments were performed. Samples were first potentiodynamically polarized at 0.1 mV/s scan rate from the open circuit potential to a final potential ranging from the first breakdown potential ($E_1$) to the second breakdown potential ($E_2$), and then held at the final potential for certain times. The exposed surfaces of the samples were subsequently examined by optical microscopy and SEM to determine corrosion morphology. In addition, some samples were metallographically cross-sectioned for further information. Table 3.2 summarizes the observations made from the potentiostatic experiments and metallography. No IGC was found at the first breakdown potential for the T3 temper. Figure 3.8 shows the exposed surfaces of the samples after polarization to $-690$ mV SCE (held for 12 h), $-670$ mV SCE (held for 2 h), and $-660$ mV SCE (held for 20 h). The initial attack was associated with the intermetallic particles at the sample surface. Figure 3.9 shows SEM images of a sample polarized to $-660$ mV SCE and then held for 20 h. EDS analysis indicated that attacked Al-Cu-Mg particles (particles marked A-C in Figure 3.9 (a) and (b)) contained Cl and O, but almost no Mg. No IGC was found on either the exposed surface or cross section, but a large number of small pits were found on the exposed surface, Figure 3.8 (c). These pits were so shallow that it was hard to locate them in the cross section, Figure
These results suggest that both matrix and grain boundary regions remained unattacked around the first breakdown potential.

The corrosion morphology changed as the potential increased to the transition potential, $E_c$. IGC was still not observed after 5 h at $-645$ mV SCE (which is about $E_c$), Figure 3.10 (a). However, IGC did occur after 20 h at $-645$ mV SCE, Figure 3.10 (b), indicating that IGC can initiate below $E_2$ but an induction period for IGC formation may exist. After 5 h at $-590$ mV SCE, which is about equal to $E_2$, sharp IG attack was observed on both the exposed surface and the cross section, Figures 3.10 (c), (d). At potentials above the second breakdown potential, $E_2$, much less time was needed for IGC to initiate and grow into the microstructure. Figure 3.11 shows the exposed surface morphology of a sample that was potentiodynamically polarized to $-560$ mV and then removed from solution. This potential is well above the second breakdown potential, and IG attack appeared in addition to pits on the surface.

In order to determine whether IGC can continue to grow when the potential is decreased back to $-660$ mV SCE, a sample was first potentiodynamically polarized at 0.1 mV/s scan rate from OCP to $-560$ mV SCE in deaerated 1 M NaCl, and removed from the solution. The morphology of the exposed surface was recorded under optical microscopy. The sample was then exposed to the deaerated 1 M NaCl again but at $-660$ mV for 12 h. Figure 12 (b) shows the same surface area in Figure 12 (a) after the sample was exposed to the solution at $-660$ mV SCE for 12 h. The three darker lines in the picture are polishing scratches, which are used as markers for the area identification. There was no clear evidence for increasing IGC attack on the exposed surface after the 12
boundaries occurred on the surface. The current density change with time during the second exposure is shown in Figure 3.12(c). It was very similar to those for samples potentiostatically polarized at a potential just below the second breakdown potential without a prior treatment at high potentials, as will be discussed later. The exposed surface of the sample was also examined under SEM. Because the corrosion behavior of the alloy was found to be altered considerably by prior SEM examination, attempts to compare the surface morphology of the same sample exposed at different times had to be abandoned. Figure 3.13 shows the exposed surface morphologies for different samples after they were first potentiodynamically polarized to -560 mV SCE, and then immediately polarized potentiostatically at -660 mV SEC for 12 h and 65 h, respectively. Both samples show similar attack morphology, which suggests that IGC may stop growing if the potential is decreased to a certain low value. These observations are evidence for assigning pitting corrosion to $E_1$, and IGC to $E_2$.

The current density vs. time curves obtained during the potentiostatic polarization experiments show different behavior for the T3 temper samples held at different potentials. Figure 3.14 shows the current density transients for the samples held at -690, -670, -660, and -645 mV SCE, respectively. Clearly, the curves are similar for potentials below the second breakdown potential. The current density increased initially due to the onset of pitting, but then decreased to the order of $\mu$m/cm$^2$ within minutes. The final current density seemed to increase with the applied potential. At -645 mV SCE, which is about equal to $E_c$, the current density first dropped to a low level, but increased slightly.
As shown in Figures 3.14 and 3.15 (a), at -660 mV SCE, the current density reached a peak in few minutes, and then dropped quickly. However, at longer times, Figure 3.15 (b), the current density increased again, but the final current density was still on the order of $\mu$A/cm$^2$, a little higher than the passive current density. Recall that Figure 3.8 showed the presence of numerous small pits after 20 h at -660 mV SCE. This suggests that there exists a kind of pitting, probably due to intermetallic particles such as (Al$_2$CuMg) or surface defects, which initiates quickly but grows very slowly in the potential range from $E_1$ to $E_c$. It is possible that the pits are simply dissolved-out S phase particles that do not lead to stable pits. This behavior is a kind of metastable pit growth. At -590 mV SCE, which is just above $E_2$, however, the current density showed totally different behavior. There was no initial peak in current density. Instead, the current density increased slowly with time until a very high value was reached, Fig. 3.16.

The behavior of the current density with time under potentiostatic polarization was consistent with the observation of a current maximum in the potentiodynamic polarization curves. Pits formed at the first breakdown potential, not IGC as reported in the literature$^{1,18}$. These pits might be metastable, in that they form from the transient dissolution of S phase particles and then stop growing, or they might continue to grow very slowly. Like pitting, IGC has an incubation stage during its initiation. At the second breakdown potential, $E_2$, IGC initiated and grew very rapidly. Corrosion morphology that can be termed pitting is also evident at the higher potentials, suggesting that the metastable dissolution of S phase particles can lead to stable pits if the potential is further increased.
A second type of potentiostatic experiments was performed, in which the potential was switched every 20 to 60 min between a low (above \( E_1 \) but below \( E_c \)) and high value (above \( E_c \) or \( E_2 \)). Figure 3.17 shows some typical anodic current density curves for AA2024-T3 (ST orientation) in Ar-deaerated 1 M NaCl when the potential was switched from \(-660 \text{ mV SCE} \) (below \( E_c \)) to \(-580 \text{ mV SCE} \) (above \( E_2 \)). The sample was initially held at \(-660 \text{ mV SCE} \) for 30 minutes, during which time a lot of small pits formed, as described above. The current density increased sharply upon polarization to \(-660 \text{ mV SCE} \), but then dropped quickly to very small values (on the order of \(10^{-5} \text{ A/cm}^2 \)) in less than 10 min. When the potential was then switched to \(-580 \text{ mV SCE} \), which is in the fast-growth IGC range, the current density increased rapidly by three orders of magnitude. IGC occurred on the surfaces and started to grow into the microstructure. When the potential was switched back to the initial value of \(-660 \text{ mV SCE} \), the current density decreased sharply but still was much higher than the initial current level. The current density decrease could have resulted from two causes. It is possible that localized corrosion growth (both in the form of pitting and IG attack) is dependent on potential under these conditions. Alternatively, the current density decrease might be due to repassivation of IGC or transition of IGC to pits if the growth in the later \(-660 \text{ mV SCE} \) steps was only due to pitting. It is not exactly clear if the localized corrosion grew in the form of pits or IGC in this experiment during the later \(-660 \text{ mV SCE} \) steps. However, based on the discussion above on the potentiostatic experiment at \(-660 \text{ mV \( \text{SCE} \))}, it is reasonable that it was more pit-like attack than IGC since the current density measured at the later \(-660 \text{ mV SCE} \) step was on the same order of magnitude as that of the potentiostatic experiment.
at -660 mV SCE. Other approaches such as X-ray microradiography might be helpful to gain a better picture of corrosion form in-situ at later -660 mV stage. Sorting this out will also help interpret the presence of $E_{\text{re}}$ in the backward scan curve during cyclic polarization where the rate of current density decrease changed, as discussed presently.

Cyclic polarization experiments were also performed to study the repassivation of localized corrosion. Figure 3.18 shows typical cyclic polarization curves for AA2024-T3 ST and L samples tested at a scan rate of 0.1 mV/s in Ar-deaerated 1 M NaCl. As expected, a current hysteresis is observed upon reversing the potential scan direction. In addition, a transition potential occurs on the reverse scan, which we have designated reverse critical potential, $E_{\text{re}}$. Generally, this transition potential has been defined as the protection potential or repassivation potential below which pits (or other form of localized corrosion) cannot stabilize and propagating pits repassivate. However, it is clear that relatively high currents still flow during the reverse scan at potentials between $E_{\text{re}}$ and the zero current potential. In addition, $E_{\text{re}}$ is a little higher than the first breakdown potential, $E_1$. So $E_{\text{re}}$ might be indicative of the repassivation of one form of localized corrosion or the first stage of repassivation of localized corrosion on the reverse scan. This reverse transition potential is also reproducible in the three orientations of AA2024-T3.

Cyclic polarization experiments, followed by potentiostatic polarization, were used to examine the repassivation of localized corrosion during the reverse scan. Samples were first potentiodynamically polarized from open circuit potential to -500 mV SCE, which is well above $E_2$, and then scanned in the reverse direction to -620, -660, or -800
mV. The samples were held at the final potentials for 20 h, and then metallographically
cross-sectioned to determine corrosion morphology. Figure 3.19 shows some typical
metallographic cross sections of those samples. It is clear that IG attack depth decreased
with decreasing potential during the reverse scan, which suggests that IGC growth was
not sustained when the potential was decreased below a certain value (referred to as the
repassivation potential for IGC). The attack morphology was more like pitting at -660
and -800 mV SCE compared to that at -620 mV SCE, which is consistent with lower
measured net anodic current densities during the potentiostatic experiments, Figure 3.20.
The measured net current density remained at a relatively high level during the
potentiostatic experiment at -620 mV SCE, but decreased gradually to lower levels for
the samples held at -660 and -800 mV SCE. The results also suggest that there are two
repassivation potentials and that the repassivation potential for pitting is very low.

Figure 3.21 shows cyclic anodic polarization curves obtained on the same
AA2024-T3 ST sample. The sample was first scanned from 50 mV below OCP to -590
mV SCE, back to the starting potential and then scanned again through the same potential
cycle. Following those two cycles, the sample was potentiostatically polarized at -660
mV SCE for 15 h, and then scanned again through another cycle. The first breakdown
potential, $E_1$, was not observed in the second scan or the one after the potentiostatic
treatment at -660 mV SCE. This is further evidence that $E_1$ is associated with a transient
process such as S phase dissolution, and not from a process that should be repeatable,
such as IGC or matrix pitting.
The influence of artificial aging on the localized corrosion behavior of AA2024 in 1 M NaCl solution was studied. Tempers used in this study include as-received T3, T3+ (2.5 h at 190 °C), T8 (12 h at 190 °C), and T8+ (36 h at 190 °C). The solution heat-treated AA2024 (SHT) condition was also prepared from as-received 1.9 cm thick T3 plate by heating at 490 °C for 1 h. Some SHT samples were quenched in water after the solution treatment. Others were purposely furnace cooled at a very slow rate from the solution heat treatment. Standard powder X-ray diffraction analysis, using Cu Kα radiation on Scintag PAD-V X-ray diffractometer, confirmed no phase differences among AA2024-T3, water quenched SHT, and furnace cooled SHT samples.

The breakdown potentials were measured for aged AA2024 in three directions relative to the rolling direction after solution heat treatment and artificial aging. Figure 3.22 shows some typical anodic polarization curves for various tempers of AA2024 (ST) samples obtained in 1 M NaCl at a scan rate of 0.1 mV/s. Tables 3.3 and 3.4 summarize the polarization experiment results. The reported values are the average of at least three separate experiments. As can be seen from the Table 3.3, the breakdown potentials were almost independent of the sample orientation relative to the rolling direction. It is clear that artificially aging AA2024-3 at 190 °C resulted in significant changes in the anodic polarization curves. The breakdown potentials decreased with increasing aging time. Like AA2024-T3, T3+ and water-quenched SHT alloys exhibited two breakdown potentials, while only one breakdown potential was found for T8, T8+, and furnace-cooled AA2024-SHT alloys. Muller and Galvele reported that aging Al-4%Cu could produce a decrease
of more than 100 mV in the breakdown potential as a result of formation of Al₂Cu intermetallic particles and depletion of copper from the matrix. In the case of AA2024, it is expected that aging allows more precipitation of fine intermetallic particles such as S phase from matrix, leaving a copper-impoverished matrix and forming copper-depleted zones along the subgrain and grain boundaries, both of which decrease the breakdown potentials of the alloys. However, as described above, it is believed that $E_1$ and the corresponding current peak associated with $E_c$ are a result of transient dissolution of large constituent S phase particles. This was proven for the T3 temper, but it is not expected that aging will affect the composition or behavior of these large constituent particles, or that fine newly precipitated S phase particles have a lower breakdown potential. The metallographic evidence presented below indicates that copper depletion of the matrix with aging causes a reduction in the matrix breakdown leading to selected granular attack at low potentials for T8 and T8+ tempers. It is expected that transient dissolution of large constituent S-phase particles would still occur in the overaged tempers. However, the current associated with this behavior might be buried under the current associated with the dissolution of select grains.

Figure 3.23 shows cross sections and the exposed surface for T8 ST oriented samples after potentiostatic polarization at -740 mV for 2 h, -700 mV for 12 and -675 mV SCE for 3 h, respectively. As seen from exposed surface SEM image, Figure 3.23(a), the initial attack is scalloped in appearance as a result of dissolution of select grains. The evidence for selective grain dissolution is much clearer from the cross sections, Figure 3.23 (b, c, d). The form of localized corrosion is neither S phase particle dissolution nor
intergranular attack as the case of T3 temper. S phase particles did not dissolve at this potential as indicated by EDS analysis of S phase particle composition, Figure 3.24. At \(-660 \text{ mV SCE}\), which is well above the T8 breakdown potential, the initial attack is still scalloped, pit-like, Figure 3.25 (a). After 2 h exposure, severe dissolution of selected grains occurs as indicated from the exposed surface and the cross section, Figure 3.25 (b) and (c). There is a little intergranular attack, but for some reason the intergranular attack cannot propagate deeply into the microstructure. Further evidence for the selected granular attack can be seen in cross sections of L oriented T8 samples exposed at open circuit \((\sim-740 \text{ mV SCE})\) for 15.9 h in oxygenated 1 M NaCl solution, Figure 3.26 (a). Based on the attack morphology on as-polished and etched cross sections, it is assumed that wide and directional attack results from dissolution of individual elongated grain. The selected granular attack does not spread across the grain boundaries, but only propagates along the elongated grain direction, which is totally different mechanism from that of T3, where attack is initiated at grain boundaries and the attack remains sharp at the grain boundaries. At a much higher potential such as \(-580 \text{ mV SCE}\), more selected granular attack occurred, Figure 3.26 (b).

The two breakdown potentials appeared again after solution heat treatment and water quenching of T8 temper, which further suggests the single breakdown potential appeared in T8 temper is not associated with dissolution of newly precipitated S phases, but from a process that is reversible by heat treatment such as matrix dissolution.

The current densities obtained during the potentiostatic experiment were very different for T8 samples than for T3 samples held around the first breakdown potential,
The current densities increased gradually with time, reaching high values, depending on the applied potential. This is similar to that found for T3 samples potentiostatically polarized around the second breakdown potential, Figure 3.16. However, unlike T3 temper, no sharp IGC was observed in T8 samples polarized above the breakdown potential. The selective grain attack in T8 temper suggests that artificial aging produces Cu-depleted matrix and enhance the nobility of grain boundary regions, reducing the IGC susceptibility in AA2024-T8.

As mentioned earlier, the AA2024-T3 alloy in sheet form had a different grain structure than the AA2024-T3 plate alloy. Artificial aging also resulted in the same effect on polarization curves of AA2024-T3 sheet material.

Figure 3.28 shows typical cyclic polarization curves for AA2024-T8 tested at a scan rate of 0.1 mV/s in Ar-deaerated 1 M NaCl. A current hysteresis was observed upon reversing the scan. It is clear that the polarization curves of T8 temper also exhibited different behavior on the reverse scan than those of T3 temper. There was no clear abrupt potential transition occurring on the reverse scan, which was found for the T3 temper, as discussed earlier.

Potentiostatic polarization was performed to examine the morphology of localized corrosion at low potentials on reverse scan direction. As before, samples were first potentiodynamically polarized to −600 mV SCE, and then scanned in the reverse direction to −800 mV SCE, at which the sample was either removed from the solution immediately or further held for 15 h. Figure 3.29 shows the metallographic cross sections and the current density transient for the potentiostatic experiment at −800mV SCE. The
attack morphology was almost the same for both samples, but more selective grain attack occurred on the sample held 15 h at −800 mV SCE, which suggests that this form of attack can still grow at potential as low as −800 mV SCE. As shown in Figure 3.29 (c), the measured net current density decreased quickly, and became negative during the potentiostatic polarization at −800 mV SCE, which suggests that anodic dissolved surface may produce an extremely high local cathodic reaction.

3.3.5 Effect of nitrate and sulfate addition

The effect of nitrate and sulfate addition on localized corrosion behavior was also studied since it was reported that, in addition to chloride ion species, a relatively large amounts of nitrate and sulfate was present in real lap joints taken from airplanes. It is generally accepted that nitrates can inhibit the pitting corrosion of Al and Al alloys in chloride solutions. On the other hand, sulfates are reported to have little effect on the pitting of Al alloys unless they are present at a very high concentration. As in the case of pure chloride solution, the breakdown potentials were almost independent of sample orientation relative to the rolling direction in nitrate or sulfate containing chloride solutions. Figure 3.30 shows cyclic polarization curves for AA2024-T3 ST in 1 M NaCl + 0.05 M NaNO₃, and 1 M NaCl + 0.2 M NaNO₃ solutions, respectively. The anodic polarization curves for L and LT samples were similar to these of ST samples. As expected, addition of nitrate increased both the open circuit potential (OCP) and breakdown potential. It was also found that both the OCP and breakdown potential increased with increasing nitrate concentration. As compared to pure chloride solution,
the nitrate addition also changed the polarization behavior of AA2024-T3 on the reverse
scan, which suggests that nitrate may affect the repassivation behavior of localized
corrosion.

Potentiostatic experiments were performed to further examine the type of
corrosion during the reverse scan in nitrate containing chloride solutions. Again, samples
were potentiodynamically polarized to a high value of −400 mV SCE, and then the scan
was reversed. Figure 3.31 shows that much deeper IG attack was observed for the sample
held at −630 mV SCE for 20 h than for the sample given the same cyclic polarization
treatment but without the subsequent potentiostatic polarization at −630 mV SCE. This
suggests that IGC can still grow at −630 mV SCE in 1 M NaCl + 0.2 M NaNO₃. On the
other hand, there was not much difference in the depth of IGC between the samples held
at −600 mV SCE and at −630 mV SEC for 20 h after cyclic polarization. Both were
primarily IGC and exfoliation with a similar IGC depth into the microstructure. However,
the measured net current densities were very different, Figure 3.32. The larger amount of
anodic charge obtained at −600 mV SCE did not lead to deep and heavy IGC, which
suggests that the measured current density may not represent well the metal anodic
dissolution kinetics under those conditions. It is possible that the local cathodic reaction
greatly affects the net current measurement under potentiostatic conditions in nitrate
containing chloride solutions. This will be discussed further in the next Chapter.

Figure 3.33 shows anodic polarization curves for AA2024-T3 (ST) in 0.5 M
Na₂SO₄ + 1.0 M NaCl solutions. The high concentration sulfate addition produced little
difference in anodic polarization behavior except that only one breakdown potential was exhibited. The polarization curve on the reverse scan appeared to be unchanged.

The disappearance of the second breakdown potential in nitrate or sulfate addition may be a result of an increase in the first breakdown potential, since two breakdown potentials were still visible in a chloride solution containing a amount of nitrate and sulfate, Figure 3.34 (b). The addition of nitrate may only affect S phase particle dissolution process by increasing its dissolution potential, but had little effect on IGC growth kinetics as will be discussed more detail in Chapter 4. Potentiostatic polarization at -580 mV also results in IG attack as shown in Figure 3.35. However, the density of IG attack on the cross section was obviously much lower compared to heavy IG attack at -580 mV SCE in pure chloride solution. This suggests that initiation of IG corrosion is more difficult in nitrate containing chloride environment. In contrast, addition of sulfate up to 0.5 M appeared to have little effect on anodic polarization behavior of AA2024-T3. The effect of sulfate addition on IGC growth kinetics will also be discussed in Chapter 4.

3.4 Summary

Polarization experiments and metallographic examination of various tempers of AA2024 were performed, and the following observations were made:

1. The anodic polarization curves of AA2024 in the solution heat treated and water quenched condition, T3, and T3+ tempers exhibited two breakdown potentials. The breakdown potentials were found to be independent of sample orientation for any given temper. When two breakdown potentials were observed, the more
active one was related to transient dissolution of S phase intermetallic particles while the noble one was a result of initiation and growth of IGC.

2. Artificial aging had a strong effect on polarization curves and localized corrosion morphology of AA2024. AA2024-T8, T8+ exhibited only one breakdown potential. Unlike T3 temper, no sharp IGC was found in the T8 temper. Selected grain attack resulting from breakdown of copper depleted matrix phase was believed to be the cause for localized corrosion in the T8 and T8+ tempers.

3. A corrosion morphology transition between pitting and intergranular attack was found at critical potentials on the upward or reverse scans in T3 temper. IGC only initiated and grew at high potentials while pitting dominated at low potentials. Like pitting, there may exist an induction stage period for IGC to initiate. Once initiated, IGC repassivated at a much higher potential than pits.

4. Addition of nitrate to chloride solution increased the first breakdown potential for S phase dissolution, and changed the repassivation behavior of AA2024-T3. Sulfate addition appeared to have little influence on the polarization curves.

5. TEM observations did not provide much evidence that precipitate free zones (PFZ’s) were present at the grain boundaries of AA2023-T3. However, the PFZ’s were observed in the T8 temper. Artificial aging resulted in localized precipitation of intermetallic phase at the grain boundaries, which greatly changed the localized corrosion behavior of AA2024.

6. AA2024-T3 plate and sheet exhibited different grain structures, but both had similar localized corrosion characteristics.
REFERENCES


### TABLES AND FIGURES

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<tr>
<th>Form</th>
<th>Si</th>
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Table 3.1 Composition of as received AA2024-T3 plate and sheet materials (wt%)
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<th>Time (h)</th>
<th>Attack Types</th>
<th>Notes</th>
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<td><strong>AA2024-T3</strong></td>
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<td>-645 (~E(_c))</td>
<td>20</td>
<td>IGC + pits</td>
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<tr>
<td></td>
<td>-620 (&gt;E(_c))</td>
<td>5</td>
<td>IGC + pits</td>
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Table 3.2 Summary of observations obtained from potentiostatic polarization experiments.
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<td>LT</td>
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Table 3.3 Influence of potential scan-rate on breakdown potentials for AA2024-T3, T8.
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<th>$E_2$ (mV SCE)</th>
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<td>As-received</td>
<td>-691±17</td>
<td>-610±15</td>
</tr>
<tr>
<td>-T3+</td>
<td>2.5h at 190 °C</td>
<td>-691±12</td>
<td>-640±13</td>
</tr>
<tr>
<td>-T8</td>
<td>12h at 190 °C</td>
<td>-739±6</td>
<td></td>
</tr>
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<td>-T8+</td>
<td>36h at 190 °C</td>
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Table 3.4 Breakdown potentials for various tempered AA2024 (ST) alloys in Ar deaerated 1M NaCl at scan rate 0.1 mV/s. If one value is given, only one breakdown was observed.
Figure 3.1 Microstructures of three orthogonal sections of (a) 1.9 cm thick AA2024-T3 plate, (b) AA2024-T8, (c) 0.2 mm thick AA2024-T3 sheet.
(a) BSE image of aligned stringers of coarse intermetallic particles

(b) SE image of two types of intermetallic particles A-D and 1-4.
Figure 3.2 SEM images of as-polished AA2024-T3 surface, (a) BSE image showing aligned stringers of coarse intermetallic particles, (b) SE image showing two types of intermetallic particles: particles A-D are Al-Cu-(Fe,Mn) intermetallics, and particles 1-4 are Al-Cu-Mg intermetallics, (c) Typical EDS spectrum of the particles 1-4, (d) Typical EDS spectrum of the particles A-D in the micrograph (b).
Figure 3.3 Transmission electron micrographs of AA2024-T3 showing (a) plate-like S' (Al\textsubscript{2}CuMg) precipitates, (b) rod-like shape precipitates in matrix and grain boundaries.

Figure 3.4 Transmission electron micrographs of AA2024-T8 showing (a) plate-like S' (Al\textsubscript{2}CuMg) precipitates and rod shaped dispersoids in matrix, (b) Cu-depleted zones around grain boundaries.
Figure 3.5 Hardness-time curve for AA2024 aged at 190 °C.
Figure 3.6 Optical micrographs of LT sections of AA2024-T3 (a), T8 (b) showing pancake-shaped grain structure, and fine sub-grain structure in T8 temper.
Figure 3.7 Anodic polarization curves for AA2024-T3 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV/s.
Figure 3.8 Optical micrographs of the exposed surfaces of AA2024-T3 (ST) samples potentiostatically polarized: (a) at $-690\text{ mV SCE}$ for 12 h, (b) at $-670\text{ mV SCE}$ for 2 h, (c) at $-660\text{ mV SCE}$ for 20 h, (d) cross section of the sample polarized at $-600\text{ mV SCE}$ for 20 h in Ar-deaerated 1 M NaCl solutions.
Figure 3.9 SEM images of the exposed surface for T3 (ST) sample potentiostatically polarized at -660 mV SCE for 20 h, (a) SE image of exposed surface, (b) BSE image of surface, (c) EDS spectrum of the attacked S particles A-C.
Figure 3.10. Metallographic cross sections of AA2024-T3 (ST) potentiostatically polarized at (a) -645 mV SCE for 5 h, (b) -645 mV SCE for 20 h, (c) -590 mV SCE for 5 h, (d) exposed surface of the sample polarized at -590 mV SCE for 5 h in Ar-deaerated 1 M NaCl solutions.
Figure 3.11 Optical micrograph of the exposed surface of T3 (ST) sample potentiodynamically polarized to -560 mV SCE in Ar-deaerated 1 M NaCl solution.
Figure 3.12 Optical micrographs of AA2024-T3 sample surface, (a) potentiodynamically polarized to -560 mV SCE, (b) the same exposed surface area in (a) after potentiostatic experiment at -660 mV SCE for 12 h, (c) net current density changes during the potentiostatic experiment at -660 mV SCE.
Figure 3.13 SEM images showing exposed surfaces of AA2024-T3 (ST) samples, (a) first potentiodynamically polarized to \(-560\) mV SCE, and immediately followed by potentiostatic polarization \(-660\) mV SCE for 12 h, (b) first potentiodynamically polarized to \(-560\) mV SCE, and immediately followed by potentiostatic polarization at \(-660\) mV SCE for 65 h in Ar-deaerated 1 M NaCl.
Figure 3.14 Net current density transients for AA2024-T3 (ST) samples potentiostatically polarized at potential range from -690 to -645 mV SCE, which is above the first breakdown and below the second breakdown potentials.
Figure 3.15 (a) Net current density transients for AA2024-T3 (ST) potentiostatically polarized at -660 mV SCE for 20 h, (b) the initial portion of the current density transients.
Figure 3.16 Net current density transients for AA2024-T3 (ST) samples potentiostatically polarized at -645 and -590 mV SCE, respectively.
Figure 3.17 (a) Net current density changes for AA2024-T3(ST) when the potential was switched from -660 to -580 mV SCE, (b) The initial current density transients at -660 mV SCE.
Figure 3.18 Cyclic polarization curves for AA2024-T3 in deaerated 1.0 M NaCl at 0.1 mV/s scan rate.
Figure 3.19 Metallographic cross sections of T3 samples cyclically polarized to (a) -620 mV for 20 h on reverse scan, followed by potentiostatic polarization at -620 mV SCE for 20 h, (b) -660 mV and held the potential for 20 h, (c) -800 mV SCE and held the potential for 20 h in deaerated 1 M NaCl.
Figure 3.20 net measured current densities as a function of time for the potentiostatic experiment at -620, -660, and -800 mV SCE, respectively.

Figure 3.21 Cyclic anodic polarization curves for the same AA2024-T3 (ST) sample in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV/s. The sample was cyclically polarized twice from 50 mV below OCP to -590 mV SCE. Following the prior two cycles, the sample was scanned again through another cycle after 15 h exposure at -660 mV SCE.
Figure 3.22 Anodic polarization curves for various tempers of AA2024 (ST) in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV/s.
Figure 3.23 (a) SEM image showing exposed surface and metallographic cross sections of ST orientated T8 samples potentiostatically polarized at (b) -740 mV SCE for 2 h, (c) -700 mV SCE for 12 h, and (d) -675 mV SCE for 3 h in Ar-deaerated 1 M NaCl solutions.
Figure 3.24 SEM images (a), and (b) showing exposed surface of T8 sample potentiodynamically polarized to $-740$ mV SCE and followed by potentiostatic experiment at $-740$ mV SCE for 2 h, (c) EDS for un-dissolved Al-Cu-Mg particles.
Figure 3.25 Optical micrographs showing exposed surface of T8 sample, (a) potentiodynamically polarized to -660 mV, (b) further held at -660 mV SCE for 2 h, (c) cross section.
Figure 3.26 Cross sections of L oriented T8 samples exposed at (a) open circuit (−740 mV SCE) for 15.9 h, and (b) −580 mV SCE for 5.5 h in oxygenated 1 M NaCl solutions.
Figure 3.27 Net current density changes with time for AA2024-T8 at different potentials.

Figure 3.28 Cyclic polarization curves for T3 and T8 tempers in Ar-deaerated 1 M NaCl.
Figure 3.29 Metallographic cross sections of T8 samples, (a) cyclic potentiodynamically polarized to -800 mV SCE on reverse scan, (b) followed by potentiostatic experiment at -800 mV for 15 h, (c) net current density changes during the potentiostatic experiment at -800 mV SCE in Ar-deaerated 1 M NaCl solutions.
Figure 3.30 Cyclic polarization curves for AA2024-T3 (ST) in Ar-deaerated nitrate containing 1.0 M NaCl solutions.
Figure 3.31 Metallographic cross sections of T3 (a) cyclic potentiodynamically polarized to −630 mV SCE on reverse scan without potentiostatic experiment, (b) followed by potentiostatic experiment at −630 mV SCE for 20 h, (c) to −600 mV, and followed by potentiostatic experiment at −630 mV for 20 h in deaerated 1 M NaCl + 0.2 M NaNO₃.
Figure 3.32 Net current density as a function of time for AA2024-T3 (ST) samples held at -600 and -630 mV SCE on reverse scan in deaerated 1 M NaCl + 0.2 M NaNO₃.

Figure 3.33 Cyclic polarization curves for AA2024-T3 (ST) in deaerated sulfate containing 1.0 M NaCl solution.
Figure 3.34 Cyclic polarization curves for AA2024-T3 in Ar-deaerated 1.0 M NaCl with nitrate and sulfate additions.
Figure 3.35 SEM images showing IGC of AA2024-T3 (L) potentiostatically polarized at 
-580 mV for 20 h in Ar-deaerated 1 M NaCl +0.2 M NaNO$_3$. 

(a) SE image, 20 h at -580 mV

(b) BSE image, 20 h at -580 mV
4.1 Introduction

There is increasing scientific and practical interest in quantitatively measuring localized corrosion growth rates in Al alloys, since most high strength Al alloys widely used in aircraft structures are extremely susceptible to localized corrosion. The development of predictive models for localized corrosion calls for a fundamental understanding of the growth kinetics, including the effects of microstructure, potential, and solution environment on the development of localized corrosion. For instance, any predictive model for corrosion will need to be based on real data on the propagation rates of localized corrosion. Unfortunately, there are currently no standard methods for quantitative measurement of localized corrosion kinetics. Many assumptions regarding the number and morphology of pits are needed to translate measured current transients into pit growth rate. Pit growth kinetics also have been evaluated optically by using a microscope to focus on the bottom of the pit, and thereby determine pit depth. Table 4.1
summarizes a number of methods for pit depth measurements. Clearly, microscopic and micrometer depth gauge methods are only accurate when the pit bottom is visible from the top. However, microfocal x-ray radiography shows that pits in thin AA2024-T3 can take circuitous paths as they grow into AA2024-T3 so that much of the pit is not visible from the surface. Metallographic sectioning may reveal a portion of such pit morphologies and generate a pit depth, but it is tedious and time consuming, and there is no assurance that the sectioning will reveal the deepest pits, which are more important than the average pit depth from a practical point of view. Mechanical machining and optical observation may give more reliable information on pit depth but are tedious as well. Therefore, the development of meaningful corrosion damage metrics for characterization of pit depth is critical from both scientific and practical points of view.

On the other hand, pits and crevice corrosion have been shown to develop into other forms of localized corrosion, such as exfoliation or intergranular corrosion (IGC). For example, Arrowood et al. reported the occurrence of heavy exfoliation corrosion in KC-135 aging aircraft body skin, made from AA2024-T3 alloys. In another work, Koch studied the localized corrosion on aging KC-135 tanker aircraft AA2024-T3 lap joints, and found severe local intergranular corrosion under the surface of the lap joints. Since the growth kinetics of IGC or exfoliation corrosion might be very different from pit growth kinetics, it is important to understand their growth kinetics independently. Unfortunately, only a few reports of quantitative measurements of the kinetics of IGC in Al alloys exist, and little is known about the influence of alloy microstructure on localized corrosion kinetics. In this chapter, localized corrosion kinetics are quantitatively
measured. The foil penetration technique\textsuperscript{2,8} was used to study localized corrosion kinetics in various tempers of AA2024 (i.e. SHT, T3, T3+, T8, and T8+) in different orientations relative to the rolling direction. The quantitative data of localized corrosion kinetics can be used to further develop the predictive model for localized corrosion in aging aircraft.

4.2 Experimental

4.2.1 Materials and samples

Three types of AA2024-T3 alloys were used for the foil penetration experiments. AA2024-T3 in the form of plates with 1.9 cm and 8.9 cm thickness were purchased from Metalmen Sales, Inc., NY, and 0.2 mm thick AA2024-T3 sheet alloy was obtained from Heinzen Metals, Inc., Palatine IL. Unless stated otherwise, the results were obtained from the 1.9 cm thick plate. Samples with three orthogonal orientations (i.e. longitudinal (L), long transverse (LT) and short transverse (ST) sections) were prepared from the 1.9 cm and 8.9 cm thick AA2024-T3 plates using a band saw or electrical discharge machining (EDM). The convention utilized for the various sections is given in Figure 4.1, along with the microstructure of the 1.9 cm thick plate in the as-received T3 temper. The ST direction is the through-thickness direction in the rolled plate, and the L direction is along the rolling direction. The sections are labeled according to the perpendicular direction. Other tempers were obtained by artificially aging AA2024-T3 plate to 190 °C for different times. Table 4.2 lists the materials and their heat treatments used in this work. All samples were polished mechanically on both sides in ethanol with silicon carbide
preparation. The samples were degreased with ethanol before attachment to the bottom of an acrylic cell by pressing against a teflon knife-edge O-ring to expose an area of 1 cm$^2$ for the foil penetration experiments.

4.2.2 Foil penetration method

The foil penetration method is a non-electrochemical method for the study of localized corrosion. The principle of this method is based on the fact that the penetration of localized corrosion sites (pits, crevice or intergranular attack) through a given thickness metal foil can be detected by an appropriate sensor system. Figure 4.2 schematically shows the electrochemical cell used for the foil penetration experiments. At the bottom of the acrylic cell, the polished sample was pressed against an O-ring. A piece of filter paper was sandwiched between the sample and a Cu foil, which were both supported by an acrylic cell backing plate. The penetration detection circuit used in the work, shown schematically in Figure 4.3, is similar to that developed by Hunkeler and Bohni$^8$, and has been reported previously$^2$. The filter paper is initially dry and its resistance is very large. Once the sample is penetrated, electrolyte from the corrosion site wets the paper and its resistance change is immediately sensed by the detection system, which then disconnects the cell power and shuts off a timer. By measuring the penetration time for different foil thicknesses, localized corrosion growth kinetics are determined. The relationship of penetration time as a function of foil thickness can be inverted to provide the relationship describing the penetration depth of the fastest
It should be pointed out that the foil penetration method only measures the time for the fastest-growing site of attack, be it a pit or IGC. Other sites will grow at slower rates varying over a range of values. However, the fastest growing localized corrosion site can be considered to be the most important from a practical point of view since it would first penetrate a structure or have the highest stress intensity. So measurement of localized corrosion propagation rates in Al alloys by the foil penetration method provides a basis for predicting the residual life of Al alloy components in service.

Figure 4.4 shows the experimental set up for the penetration experiment\textsuperscript{9}, which allows 8 samples to be tested simultaneously in eight different cells. A Gamry Instruments (Warminster, PA) PC3 potentiostat and multiplexer, along with Gamry Framework and custom-made programs were used to control the potential and acquire data.

Most of the penetration experiments were conducted in oxygen-bubbled 1.0 M NaCl solution, either at open circuit or under anodic potentiostatic conditions. For some open circuit penetration experiments, a small amount of persulfate was added to the chloride solutions to make the penetration measurement in a reasonable amount of time. The purpose of oxygen gas bubbling was to maintain a constant supply of cathodic reactant and to aid convection in the cell. For deaerated potentiostatic penetration experiments, Ar-bubbled 1.0 M NaCl solution was used, which lowers the open circuit potential (OCP) and allows testing penetration at low anodic potentials. In order to examine the influence of nitrate or sulfate on localized corrosion kinetics, nitrate or
Sulfate-containing 1.0 M NaCl stock solutions were prepared and added in a designed volume ratio into the 1.0 M NaCl solution after the penetration experiments were started for 2 to 4 min to eliminate their effects on the initiation of localized corrosion. For potentiostatically-controlled penetration experiments, a SCE reference electrode and Pt mesh counter electrode were used.

As mentioned earlier, the objective of the foil penetration experiment was to study localized corrosion kinetics at its growth stage, not its initiation stage. Therefore, the samples were first anodically polarized to -290 mV SCE (approximately 400 mV above the second breakdown potential of AA2024-T3 in 1.0 M NaCl) for 1 s to initiate pits, followed by an immediate change to the desired applied potential or release of potential control to open circuit. As shown in previous work, the setpoint of the detection circuit has little influence on the penetration time measurement, so the same 6.2 V was used for the setpoint voltage of the detection circuit.

4.2.3 Characterization techniques

Microfocal X-ray radiography

Microfocal X-ray radiography was used as a non-destructive evaluation method to characterize localized corrosion morphology of some penetrated AA2024 samples. Figure 4.5 schematically shows the microfocal X-ray radiographic set-up. A Feinfocus 225 kV X-ray unit with a 5 μm focal size was used as the x-ray source. The sample position was controlled by a computer-controlled 4 axis positioning system; three linear (2 μm resolution) and one rotating (0.01 degree resolution). Eastman Kodak AA film was
placed behind the sample. The final X-ray radiographic picture was digitized from the x-ray film using a data translation frame grabber (DT3155). More details about this technique, set-up and experimental procedure are reported elsewhere10. The microfocal x-ray radiographic analysis was performed by B. Zoofan in the department of Industrial Welding and Systems Engineering at OSU.

SEM and metallographic cross sections

SEM was also used to examine the penetrated areas on the unexposed surface of some penetrated samples. In addition, metallographic cross section and follow-up by optical microscopic observation were also performed to determine the localized corrosion growth paths and morphology through the penetrated foil thickness. The cross sections were examined in the as-polished condition and after etching.

4.3 Results and discussion

4.3.1 Localized corrosion growth at open circuit

The foil penetration technique provides an effective way to study pit growth at open circuit. In previous work, open circuit pit growth was investigated in 0.22 mm thick AA2024-T3 as-received sheet alloy2. The average penetration time was reported to be 50.6 ± 23.5 h for the 0.22 mm thick AA2024-T3 as-received sheet samples in oxygen-bubbled 1M NaCl under open circuit condition. It should be pointed out that the result was the average value of the five samples that penetrated through the thickness. Five other thin sheet samples remained unpenetrated after 168 h of exposure during the open circuit experiment. So the real average penetration time should be much longer than 50.6 h. The
Large scatter in the data was believed to be a result of the fact that AA2024-T3 is a wrought alloy. In other words, pits that grow intergranularly in a wrought structure may be deflected from penetrating through the foil thickness. They might finally grow in the longitudinal direction instead of through the foil thickness, and get "lost" in the microstructure (i.e. the sample is not penetrated for long time). However, the exact reason for this pit stifling phenomenon was not explored in detail. Furthermore, the previous work only measured pit growth rate in one direction (short transverse direction) because thin sheet foils were used. The pit growth rates are expected to be different in different orientations.

Since the data on pit growth under open circuit conditions are very useful for understanding localized corrosion kinetics of Al alloys in real service, open circuit penetration experiments were performed in both ST and L samples of 1.9 cm thick AA2024-T3. ST samples with thickness range from 0.1 to 0.21 mm were prepared from the sections near to the surface of the same 1.9 cm thick plate. The open circuit penetration results are summarized in Table 4.3. The results reported here are the average values of four to six different samples. It took $54.9 \pm 25.4$ h to penetrate about 0.12 mm thick ST samples taken from the 1.9 cm thick plate. None of the 0.21 mm thick ST samples penetrated even after 450 h exposure in 1 M NaCl at open circuit. Some of them should have penetrated after about 220 h based on the results of 0.12 mm thick samples if the pit growth follows a $t^{1/2}$ parabolic growth law as reported in the literature. The results suggest that either the exponent n is less than 0.5 at open circuit if growth follows the equation $d = at^n$, or the localized corrosion was stifled in the ST direction. In the literature, a cube root growth law was reported for Al at open circuit for some conditions.
was reported in the previous work to be about the same as for 0.12 mm ST samples taken from the 1.9 cm thick plate. This is a result of the difference in microstructure between the sheet and plate. Also the OCP of the plate was slightly lower than that for the sheet samples under the same conditions. There were no penetrated pits on the backside of these 0.21 mm thick samples when they were dissembled from the cell. Interestingly, lots of penetrated pits were found on the unexposed surface of these same unpenetrated samples after being left in laboratory air for several weeks. Localized corrosion apparently continued as a result of the aggressive environment trapped within occluded regions of the samples, which did not dry out quickly on removal from the bulk solution. This phenomenon is relevant to the real structures that go through cyclic exposure conditions, but was not studied further.

The localized corrosion morphologies of ST samples exposed at open circuit were examined by metallographic cross section. Figure 4.6 shows the different types of localized corrosion morphologies observed under these conditions. Hemispherical shaped pits (Figure 4.6(b)) or intergranular attack and exfoliation (Figure 4.6(a, c)) were observed. In the case of IG attack, only a few grain boundaries were attacked. If either pitting or intergranular corrosion occurs primarily in the longitudinal direction instead of through the thickness direction, it will take very long time to penetrate the foil. This may be the reason why some samples were not penetrated even after very long times.

The open circuit penetration rate on L samples taken from the 1.9 cm thick plate was considerably faster than both sheet and plate ST samples, Table 4.3. On average, it took only about 1 to 2 h to penetrate 0.1-0.2 mm thick L samples. But the penetration rate
267 h of exposure, which suggests that pit growth rate does not follow a $t^{1/2}$ growth law in the L direction, either. Figure 4.7 shows the open circuit foil penetration experiment results for 1.9 cm thick plate samples. The results for 0.22 mm thick as-received sheet samples are also shown for comparison. For samples from the same 1.9 cm thick plate, the penetration rate growth time for 0.12 mm thick L orientation samples was about 40-50 times shorter than for the same thickness ST orientation samples. For ST orientation samples, the growth rate was much faster in as-received thin sheet than for samples cut from the 1.9 cm thick plate.

Figure 4.8 shows localized corrosion morphologies in L samples exposed at open circuit for different times. The attack is neither hemispherical pitting nor focused intergranular corrosion. It may be considered to be either directional pitting or intergranular corrosion that has spread into the grain. Only a few grain boundaries were attacked on the cross sections, Figure 4.8.

In order to accelerate open circuit measurements, a small amount of oxidizing agent, persulfate, was added into chloride solution. The persulfate containing chloride solution was pumped in from a reservoir at 0.75 ml/h to keep the oxidant concentration constant. As above, both L and ST samples were prepared from the 1.9 cm thick AA2024-T3 plate. The results are also summarized in Table 4.3. Addition of a small amount of persulfate increased dramatically the localized corrosion growth rate (reduced the penetration time) on ST samples. It took $20 \pm 7.7$ h and $5.6 \pm 0.5$ h to penetrate 0.24 mm and 0.14 mm thick ST samples, respectively, in oxygen bubbled 1M NaCl + $5 \times 10^{-2}$ M
Na$_2$S$_2$O$_8$ solutions at open circuit, which is about 10-20 times shorter than in pure chloride solution. For ST orientated samples, the localized corrosion rate was still much faster in the as-received 0.2 mm sheet alloy than in the 1.9 cm thick plate alloy. While the penetration rate in the L direction increased with the addition of persulfate, the increase was not as great as for ST samples. Figure 4.9 shows the penetration results for these AA2024-T3 samples in 1 M NaCl + 5x10^{-2} M Na$_2$S$_2$O$_8$ solutions at open circuit. The results for 0.22 mm as-received sheet are also shown. The results reported here are the average values of four to six different samples, and the error bars represent the spread of the penetration time.

It is interesting to note that the morphology of the localized corrosion on the penetrated surfaces tended to be aligned parallel to one direction (LT direction for L samples). Figure 4.10 shows an SEM picture of the unexposed surface of the L sample. The sample was penetrated after 2.4 h in 1 M NaCl + 5x10^{-2} M Na$_2$S$_2$O$_8$ solutions at open circuit. Several penetrated pits or pit clusters are evident. The sample was removed immediately from the solution after penetration. So either many sites reached the backside of the sample at about the same time or growth continued and more sites penetrated during the time between the removal of the sample and SEM analysis. The AA2024-T3 samples that were exposed to 1 M NaCl solution show similar attack morphologies on the unexposed surface. As discussed above, the attack may be intergranular in nature, not pitting. Metallographic cross section further confirmed that it was indeed intergranular attack, Figure 4.11. Obviously, the addition of persulfate increases the susceptibility of AA2024-T3 to IG attack. The IG growth rate is much faster in persulfate-containing solution than in pure chloride solution. The OCP was slightly higher in the persulfate-
containing solution. In addition, the pH of this solution (pH ~ 2.6) was lower than that of the 1 M chloride solution (pH ~ 5.8).

As discussed earlier, the pits that formed in AA2024-T3 alloy look very convoluted in shape under microfocal x-ray radiography, (Figure 2.30 in Chapter 2)^2. In contrast, the microradiographs of LT samples show the attack to be more concentrated, Figure 4.12. The dark spots in the microradiograph indicate the localized regions of least density or heaviest attack. The lateral spreading and branching observed in ST samples was not evident, which is in agreement with above metallographic cross section examination. Similar radiographs were found for L orientation samples.

The above open circuit foil penetration experiments have indicated that localized corrosion growth kinetics depend on sample orientation, alloy microstructure, and solution environment. The effects of sample orientation, alloy microstructure, and solution environments on the kinetics will be discussed in more detail below.

The measurement of localized corrosion kinetics at open circuit is time consuming, especially for ST orientation samples. The addition of a small amount of Na$_2$S$_2$O$_8$ reduced the open circuit measurement time by increasing the susceptibility of the alloy to IG attack and increasing the IG growth rate. However, it can be argued that persulfate addition may change the localized corrosion growth mechanism of AA2024-T3 in chloride containing environment. So persulfate was not added for the subsequent penetration experiments. Another way to accelerate localized corrosion is to apply anodic potential. The localized corrosion kinetics were studied further in 1 M NaCl under anodic potentiostatic conditions.
Various thickness ST, L, and LT samples were prepared from the 1.9 cm thick AA2024-T3 plate and tested in oxygen-stirred 1 M NaCl solution at different applied potentials. Figure 4.13 shows penetration results for these ST, L, and LT sections exposed to oxygen-bubbled 1.0 M NaCl at a potential of $-580$ mV SCE. As mentioned earlier, the experiment determines penetration time as a function of sample thickness, but the data are plotted as thickness (depth of the fastest growing localized corrosion site) as a function of time. The localized corrosion growth rate is much faster at $-580$ mV SCE than at open circuit ($-630$ mV SCE). The curves are fits to data in which the exponent was forced to be 0.5, i.e. $d=at^{1/2}$. In log-log plots, the data from each orientation almost form straight lines with slope ranging from 0.4 to 0.65, Figure 4.13 (b). By forcing the fits to have an exponent of $1/2$, comparison of the various rates can be made using only the multiplicative factor, $a$. For the 1.9 cm thick T3 plate in oxygenated 1 M NaCl at $-580$ mV SCE, the values of $a$, determined from the curve fitting, are 0.076 ($R^2 = 0.98$), 0.273 ($R^2 = 0.96$), and 0.324 ($R^2 = 0.97$), for the ST, LT, and L sections, respectively.

It is clear that the growth of localized corrosion in the 1.9 cm thick AA2024-T3 plate exhibits a strong anisotropy under these conditions. Growth in the longitudinal (L) direction was found to be slightly faster than that in the long transverse (LT) direction, and much faster than that in the short transverse (ST) direction. This is in contrast to the pitting potentials, which were almost identical for the different orientations, as discussed earlier in chapter 3. The anisotropic growth behavior can be attributed to the pancake-shaped grain structure (Figure 3.1 in chapter 3), and is indirect evidence that the path of
attack in this material under these conditions is intergranular in nature. Direct evidence
for the association of localized corrosion growth paths with grain boundaries was
obtained by metallographic cross sections. Figures 4.14-4.16 show some typical
metallographic cross sections of AA2024-T3 ST, L and LT samples penetrated in
oxygenated 1.0 M NaCl at -580 mV SCE. Unlike the growth at open circuit, sharp IG
attack took place under these conditions. The path of IGC through ST sections is
circuitous and relatively long, whereas it is short and relatively straight in L and LT
sections. It should be pointed out that there is no reason to expect that the local rate of
IGC propagation is different in the different alloy orientations, since the material is
identical and only the nominal growth direction is different. The nominal growth rate is a
function of orientation only because the aspect ratios of the grains result in a difference in
IG path length for the different orientations.

It has been reported that pit growth kinetics take the following form:

\[ d_p = a t^n \]  \hspace{1cm} (4.1)

where \( d_p \) is the pit depth, \( t \) is time, and \( a \) and \( n \) are constants dependent on the metal and
environment\textsuperscript{8,11,12}. The value of \( n \) has been found to be close to 0.5 for pits in pure
Al\textsuperscript{8,11,12}. The \( t^{1/2} \) dependence of pit growth was proposed and confirmed by several
authors\textsuperscript{15-17}. Interestingly, the data obtained at a high potential such as -580 mV SCE,
which primarily describe IGC kinetics as indicated by metallographic cross section, can
also be well fitted to a \( d = a t^{1/2} \) parabolic growth law, where \( a \) is dependent on sample
orientation. The kinetics of localized corrosion depend on not only sample orientation,
but also alloy microstructure including grain size and grain aspect ratios. Therefore, the
anisotropy of growth is expected to change for different AA2024-T3 plate and sheet starting materials having different microstructures. Penetration results obtained from 8.9 cm thick AA2024-T3 plate confirm this prediction. Figure 4.17 shows foil penetration results for ST, L, and LT sections prepared from the 8.9 cm thick AA2024-T3 plate exposed to the same oxygenated 1.0 M NaCl solution at the same controlled potential of -580 mV SCE. The lines in the figure are also fits to \( d = a t^{1/2} \). The values of \( a \) determined from the fits are 0.123 (\( R^2 = 0.92 \)), 0.209 (\( R^2 = 0.89 \)), and 0.271 (\( R^2 = 0.97 \)), for the ST, LT, and L sections, respectively. Clearly, both 1.9 cm and 8.9 cm thick plates show similar anisotropic growth of localized corrosion in AA2024-T3, but the thinner one (1.9 cm thick plate) exhibits much stronger anisotropy. The microstructure is the only reason for the difference because both alloys have same nominal composition and they are in the same temper. The results suggest that grain structure (both grain size and aspect ratio) may influence localized corrosion growth kinetics, mainly IGC growth under these conditions.

In order to further demonstrate the effect of microstructure on IGC growth kinetics, experiments were performed on the ST sections of AA2024-T3 materials with three different original thicknesses: 0.2 mm sheet, 1.9 cm, and 8.9 cm thick plates. Since the microstructure in the mid-plane of a thick plate can be different than that at the surface, ST sections of the 1.9 cm thick plate were taken from both close to the surface of the alloy plate and from the mid-plane (T/2 section). ST samples from the 8.9 cm thick plate were prepared only from close to the surface of the plate. Figure 4.18 shows foil penetration results for these AA2024-T3 ST samples in oxygenated 1.0 M NaCl at -580
mV SCE. The penetration rate in the ST samples from the 8.9 cm thick plate was found
to be the fastest. The penetration rate in the 0.2 mm thick sheet is between that of the 9.8
cm thick and 1.9 cm thick plate. Mid-plane ST samples from the 1.9 cm plate show a
much slower penetration rate than those from the regions close to the surface. These
differences in penetration rates result from differences in the grain structure (grain size
and aspect ratio) among these alloys. Figures 4.19-21 show some metallographic cross
sections of these penetrated ST samples. Both the 0.2 mm thick sheet and the 8.9 cm
thick plate (close to the surface) have equiaxed grain structure (sub-grain structure) with
fine grains (Figures 4.19-20), which is probably due to recrystallization during alloy
metallurgical processing. In contrast, the 1.9 cm thick plate sample shows a strongly
elongated grain structure. Severe exfoliation occurred on the mid-section ST as a result of
more elongated grain structure in this plane (Figure 4.21). This result further supports the
notion that both grain size and aspect ratio affect IGC kinetics and attack morphology.
Qualitatively, it appears that the fine and equiaxed grain structure reduces the anisotropy
of IGC growth, while elongated grain structure increases anisotropic IGC growth because
of the difference in IG path length through the foils. A statistical model developed to
establish the quantitative relationships between IGC kinetics and microstructure
including grain size and aspect ratio will be discussed in Chapter 5.

4.3.3 Effect of potential

The effect of applied potential on localized corrosion kinetics is of interest
because, in real service environments, high strength aluminum alloys could experience a
range of potentials. An increase in potential could result from galvanic coupling. For instance, steel fasters have been used in aircraft lap joints. Also, the environment can pose a range of oxidizing power as a result of the presence of different pollutants.

As discussed in Chapter 3, potential was found to influence localized corrosion morphology of AA2024-T3 alloys. Localized corrosion occurs mainly in form of pitting corrosion at low potential (below $E_c$), and as IG attack and pitting at high potential (above $E_c$). The influence of potential on localized corrosion kinetics was also studied using the foil penetration technique in an attempt to better understand the localized corrosion growth mechanism. Figure 4.22 shows penetration results for L sections of AA2024-T3 at anodic potentials ranging from -675 to +500 mV SCE. The penetration time was plotted in a logarithmic scale to highlight the differences. The penetration rate was found to be almost independent of potential over a range of potential from -610 to +500 mV SCE. The attack is intergranular in nature in this potential range, and the data reflect the IGC rate.

The potential-independent dissolution rate suggests that intergranular dissolution might be under mass transport control. Electrochemical kinetics are often reported to be potential-independent at high anodic potentials as a result of transport limited dissolution. However, mass-transport limited dissolution is typically associated with the formation of a salt film on the metal surface and electropolishing of the metal, which smooths the surface leading to isotropic growth. As seen from the cross sections of the samples penetrated at -580 mV SCE (Figures 4.14-4.16), the growth morphology is highly localized; the surface is roughened and not smoothed. Clearly, at -580 mV SCE, the
attack is limited to a narrow region near the grain boundaries so that the grains are immune to attack. The tortuous path from the active IGC tip to the bulk would present a transport barrier that promotes transport-limited dissolution. However, this phenomenon is only possible if there are critical conditions in the IGC crack that allow dissolution of the grain boundary regions, but prevent dissolution of the grains.

An alternative explanation for the observation of highly localized IG attack combined with only slight dependence of rate on applied potential is that most of the anodic current generated by the local dissolution was consumed by cathodic reactions within the grain boundary (GB) crevice, so that little came out for collection by the potentiostat. The potential applied to the exposed surface by the potentiostat would only affect reactions for which the current exited to the bulk solution. The applied potential would have no effect on reactions that are essentially isolated from the bulk solution. It has been reported that about 15% of the anodic current generated in 2-D thin film pits is consumed by local cathodic reactions\textsuperscript{18}. A similar value was reported for Al artificial crevice electrodes\textsuperscript{19}. Recent work by Ramgopal et al.\textsuperscript{20} provides an explanation for the sharp IG attack and the lack of potential dependence. The solute depleted zones (SDZ) near the grain boundary (GB) are considered to be the site for local attack, but Cu-rich S phase particles at the GB are also attacked. These particles have been shown to release Cu\textsuperscript{21}. Deposition of Cu on the grain faces lining the GB crevice would protect those faces from attack. Also, they provide a corrosive site that would consume current generated by IGC at the attack front. Since most of the current would not escape from the GB crevice, the dissolution rate of the front would not be strongly dependent on external
applied potential. This explains the localized nature of the attack and the apparent potential independence.

Figure 4.23 shows metallographic cross sections of two L samples penetrated at +500 mV SCE. The attack looks more isotropic, particularly near the exposed surface. At the bottom, where the attack is penetrating the sample, sharp IG corrosion can be seen. However, the grain walls are no longer totally protected and the attack penetrates into the grains at +500 mV SCE as it deepens by IGC. The cross section of an ST sample penetrated at +500 mV SCE provides more evidence for this conclusion, Figure 4.24. This ST sample had a thickness of about 0.6 mm, but was penetrated in oxygenated 1 M NaCl solution after only 3.2 h at +500 mV, which is much faster than predicted by parabolic growth kinetics for ST samples, and similar to what would be predicted for an L section of this thickness. The attack front can be seen to be advancing by IGC, but the grains are consumed behind the attack front. Matrix dissolution at +500 mV SCE was also confirmed by X-ray microradiographic analysis. Figure 4.25 is a microradiograph of an AA2024-T3 L sample penetrated at +500 mV SCE, showing a lot of concentrated dark spots. This indicates that the lost material is not an artifact of polishing.

It should be pointed out that visual observation indicated that a huge amount of H₂ was generated during the penetration experiments at +500 mV SCE, apparently more than at lower potentials. The bulk solution pH became as high as 9.2 after the penetration at +500 mV SCE. Figure 4.26 shows an SEM image of the unexposed surface of a penetrated sample at +500 mV, showing the presence of both penetrated pits and IG cracks. It is not clear whether the presence of the IG cracks is related to H₂ embrittlement.
However, a large amount of local hydrogen evolution could have an influence on the IGC growth kinetics in the presence of stress. It is possible that a residual stress exists in the samples during the experiments. The penetration rate was found to increase significantly in stressed L samples, in which hydrogen embrittlement may play a role.

At lower potentials, the penetration rates were clearly dependent on potential, Figure 4.22. The penetration rate decreased when the potential was decreased only 20 mV from −610 mV SCE to the OCP in oxygen-bubbled 1.0 M NaCl, which is about −630 mV SCE for AA2024-T3. The penetration rate was almost the same at −630 mV SCE in both oxygen aerated solution at open circuit and under potentiostatic control in argon deaerated solution. Deaerated solutions were used for experiments at low potentials to avoid cathodic polarization, which would result in local pH changes associated with the net cathodic current at the surface. The penetration rates were found to decrease with decreasing potential below about −610 mV SCE, Figure 4.22.

The localized corrosion morphology also changed as the applied potential decreased. Figure 4.27 shows metallographic cross sections of L samples exposed at different low potentials. First, the localized corrosion density or number of sites per unit cross section area decreased with decreasing potential. As discussed earlier, at a relatively high potential such as −580 mV SCE, the attack was sharp IGC. At −630 mV, which is about the open circuit potential in the O₂ bubbled 1 M NaCl solution, the attack morphology became directional pitting or IGC that has spread into the grains, Figure 4.27(a). The localized corrosion morphology was more pit-like attack with decreasing potential, such as for the samples exposed at −650 and −675 mV SCE, Figure 4.27(b, c).
This result is consistent with the potentiostatic polarization observations discussed in Chapter 3.

Figure 4.28 shows penetration results for ST samples in the potential range from −580 to −520 mV SCE. The data look more scattered than those of L samples, but, in general, the penetration rate for ST samples is almost independent of potential in the studied potential range. Experiments on ST samples at lower potentials were also performed in Ar-deaerated 1 M NaCl solutions. The result is summarized in Table 4.4. As discussed earlier, the penetration rates are very slow on ST samples at open circuit in oxygen bubbled 1 M NaCl. Table 4.4 shows that the penetration rates are much slower at −645 and −660 mV SCE than at open circuit in the oxygenated solution (−640 mV SCE). None of three ST samples with thickness about 0.1 mm penetrated after 260 h of exposure at −660 mV SCE. At −645 mV SCE, it took about 150 h to penetrate one 0.12 mm thick ST sample while other two ST samples did not penetrate after 260 h of exposure. Figure 4.28 shows the cross sections of those samples. No sharp IGC occurred under these conditions. The attack was more like pitting.

4.3.3 Effect of artificial aging

It is generally accepted that intergranular corrosion in high strength Al-Cu and Al-Cu-Mg alloys is associated with precipitates in grain boundaries. The idea of the existence of a preferential anodic path as a result of solute enrichment in grain boundary regions has been well known for a while. However, it is not clear what makes the grain boundary so susceptible in AA2024-T3 under these conditions, i.e. whether it is the
fractionation of intermetallic particles in the grain boundary, the copper-depleted zone along the grain boundary, a combination of the two, or the grain boundary structure. To address this issue, AA2024-T3 was artificially aged at 190°C for various times before testing by the foil penetration method.

Artificial aging is an important factor that has been shown to influence the IGC susceptibility and growth in high strength Al alloys. It has been reported that artificial overaging had a beneficial effect on the susceptibility of an alloy to IGC by reducing IGC growth rate. Others reported that AA2024-T6 and T8 tempers improved resistance to IGC as compared to the T3 temper. As discussed in Chapter 3, artificial aging was found to lower the breakdown potential of AA2024, and change the localized corrosion morphology. Selected granular attack dissolution was found to be the dominant form of localized corrosion near the breakdown potential of AA2024-T8 as a result of the artificial aging at 190°C. The effect of artificial aging on localized corrosion growth kinetics is discussed presently.

Figure 4.30 shows localized corrosion growth at open circuit and at various applied potentials for L sections of AA2024-T8 in oxygenated 1 M NaCl solution. The OCP for T8 samples in this solution was about -740 mV SCE, which is considerably lower than for T3 samples, consistent with the decrease in breakdown potential, as discussed in Chapter 3. As in the case of the T3 temper, the penetration rate was found to be much slower at the OCP than that at high anodic potentials. Also like T3, the penetration rate was not much affected by the value of applied potential in the range from -610 to -490 mV SCE. Figure 4.31 shows a metallographic cross section of a T8 sample.
penetrated at open circuit (about −740 mV SCE). As discussed in Chapter 3, the attack morphology is selected grain dissolution, not sharp IG attack as observed in the case of T3 sample. The number of grains attacked increased with increasing anodic potential, as shown in Figure 4.32 for a T8 sample penetrated at −580 mV SCE.

Figure 4.33 shows penetration results for the different tempers of AA2024 alloys at −580 mV SCE. It is surprising that artificial aging did not produce a significant effect on the penetration rate even though it had a large effect on localized corrosion morphology. The T8 and T3+ tempers had a slightly slower penetration rate than T3, but there is no clear trend. The data also indicate that AA2024-SHT (water quenched) had almost the same penetration rate as the aged samples. The penetration rates at open circuit for the aged samples exhibited considerable scatter, Figure 4.34. However, it is seen that artificial aging had no clear effect on penetration rate at open circuit either.

The attack morphology changed with temper. Figure 4.35 shows some cross sections of T3+ and T8+ samples. The T3+ temper exhibited sharp IGC morphology at −580 mV SCE, and directional grain boundary attack at open circuit, both of which, in general, are very similar to those of T3 under the same conditions. However, localized corrosion morphology for T8+ is more like selected grain dissolution as in the case of T8 at −580 mV SCE. The selective grain attack seen on the T8 and T8+ tempers is consistent with the observation of decreased susceptibility to IGC with artificial aging\(^\text{26}\). The change in the form of attack can be explained by a decrease in Cu content of matrix phase with aging, which makes the grain more susceptible to breakdown than the grain boundary or SDZ. However, it is interesting that the attack stays within single grains and

168
does not spread to adjoining grains to become isotropic. It is possible that the less susceptible grain boundary is protected by Cu deposition in the same fashion as was suggested above for the grain face during sharp IGC of T3 temper. This also explains the lack of potential dependence because the Cu-rich walls would similarly act as local cathodic sites.

4.3.5 Effect of nitrate or sulfate addition

The effect of nitrate or sulfate addition to the chloride solution on the potentiodynamic polarization behavior of AA2024-T3 was discussed in Chapter 3. It was found that addition of nitrate raised the breakdown potential and repassivation potential. However, addition of sulfate did not have a significant effect on polarization of AA2024-T3. In this section, the effect of these additions on localized corrosion kinetics is discussed.

Figure 4.36 shows penetration results for L sections of AA2024-T3 in 1 M NaCl solutions containing 0.2 M nitrate or 0.5 M sulfate. A small amount of nitrate or sulfate was added into the chloride solutions during the growth stage (about 2-3 min after starting the experiments) to exclude a possible inhibition effect on initiation of localized corrosion. The measured current suddenly decreased upon addition of nitrate to chloride solution during the experiments. However, the localized corrosion (IGC) kinetics were found to be unchanged at −520 mV SCE in 1 M NaCl + 0.2 M NaNO₃. It should be noted that the penetration curve for AA2024-T3 in 1.0 M NaCl at −520 mV SCE is essentially identical to that at −580 mV SCE, which is shown in Figure 4.22. However, the IG attack

169
density (number of grain boundaries attacked per unit cross section area) seems to decrease in nitrate containing solution, as shown in Figure 4.38. One explanation is that nitrate addition raises the breakdown potentials for IGC, which makes it more difficult for IGC to initiate and grow. The penetration rate in 1 M NaCl + 0.2 M NaNO₃ is slower for thicker samples at −580 mV compared to that in 1 M NaCl at −580 mV SCE although it was still IGC attack in nature. The reason may be due to the fact that the OCP was raised to about −580 mV SCE after addition of the nitrate as discussed in Chapter 3 (Figure 3.32). So growth kinetics at −580 mV SCE in 1 M NaCl + 0.2 M NaNO₃ are similar to those at open circuit in 1 M NaCl. This also may be why the data were very scattered.

It has been reported that addition of sulfate increases the localized corrosion kinetics by increasing the conductivity of the solution. However, our anodic potentiostatic penetration experiments show that the addition of sulfate up to 0.5 M did not change localized corrosion kinetics at potentials of −520 and −580 mV SCE, respectively. The localized corrosion morphology was still IG attack in nature in sulfate-containing chloride solutions, Figure 4.39. But IG attack density (number of grain boundaries attacked per unit cross section area) seemed to decrease in sulfate-containing chloride solution as well.

4.4 Summary

The influence of foil orientation, microstructure, temper, and anodic potential on localized corrosion growth and morphology in AA2024 alloys was studied using the foil
penetration technique, metallography, and microfocal X-ray radiography. This work has found:

1. The growth kinetics of localized corrosion in AA2024-T3 exhibited a strong anisotropy. Growth in the short transverse direction (through-thickness direction of a rolled plate) was found to be much slower than that in either the longitudinal or long transverse direction. The difference was a result of the microstructural anisotropy of the material.

2. Alloy microstructure affects localized corrosion morphology as well as growth kinetics. Both grain size and aspect ratio are important factors in controlling the localized corrosion growth kinetics and morphologies.

3. Localized corrosion kinetics and morphology depend on potential. Above open circuit potential, it is primarily IG attack that governs localized corrosion growth kinetics of AA2024-T3 in oxygenated 1 M chloride solution. The IGC growth is almost potential-independent at high potential. Pitting dominates only at very low potentials, where pit growth is largely dependent on potential.

4. Localized corrosion growth kinetics are slightly dependent on potential from -490 to +500 mV SCE, which suggests that only small amount of anodic current escapes from active tip of isolated IG cracks at very high potential.

5. Artificial aging was found to decrease the breakdown potential of AA2024, resulting in different forms of localized corrosion, but had a small effect on the localized corrosion growth kinetics.
The addition of nitrate decreased localized corrosion kinetics at $-580 \text{ mV SCE}$, but had no significant effect on kinetics at $-580 \text{ mV SCE}$. On the other hand, the sulfate addition did not produce significant influence on kinetics at $-580 \text{ mV SCE}$ and $-520 \text{ mV SCE}$.

REFERENCES


## TABLES AND FIGURES

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallographic</td>
<td>Section and polish through selected pits followed by microscopic measurement</td>
<td>Time consuming, results inaccurate</td>
</tr>
<tr>
<td>Machining</td>
<td>Measure depth until no evidence of pits</td>
<td>Sample destroyed and regular shape required</td>
</tr>
<tr>
<td>Micrometer Depth</td>
<td>Compare reading between surface and pit bottoms with needle probe (such as AFM probe)</td>
<td>Pit bottom may not be seen easily for undercutting or convoluted pits</td>
</tr>
<tr>
<td>Microscopic</td>
<td>Use calibrated fine focus to determine depth difference between surface and pit bottoms</td>
<td>Difficult for undercut or convoluted pits</td>
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Table 4.1 Methods for pit depth measurements.

174
<table>
<thead>
<tr>
<th>Temper</th>
<th>Heat treatments</th>
<th>Notes</th>
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<tbody>
<tr>
<td>0.2 mm thick sheet (T3)</td>
<td>None</td>
<td>As-received</td>
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<td>1.9 cm thick plate (T3)</td>
<td>None</td>
<td>As-received</td>
</tr>
<tr>
<td>8.9 cm thick plate (T3)</td>
<td>None</td>
<td>As-received</td>
</tr>
<tr>
<td>T3+</td>
<td>2.5 h –190 °C</td>
<td>Using 1.9 cm thick T3 plate as starting material</td>
</tr>
<tr>
<td>T8</td>
<td>12 h –190 °C</td>
<td>Using 1.9 cm thick T3 plate as starting material</td>
</tr>
<tr>
<td>T8+</td>
<td>36 h –190 °C</td>
<td>Using 1.9 cm thick T3 plate as starting material</td>
</tr>
<tr>
<td>SHT</td>
<td>1 h –490 °C</td>
<td>Using 1.9 cm thick T3 plate as starting material</td>
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Table 4.2 AA2024 materials and their heat treatments used in this work.
<table>
<thead>
<tr>
<th>Thickness (mm)</th>
<th>Applied potentials (mV SCE)</th>
<th>Penetration time (h)</th>
<th>Notes</th>
</tr>
</thead>
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<tr>
<td>0.08</td>
<td>-645</td>
<td>Unpenetrated, &gt; 260</td>
<td>Average penetration time is about 55 ± 25 h at open circuit (~ - 640 mV SCE)</td>
</tr>
<tr>
<td>0.12</td>
<td>-645</td>
<td>~ 150</td>
<td></td>
</tr>
<tr>
<td>0.14</td>
<td>-645</td>
<td>Unpenetrated &gt; 260</td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>-660</td>
<td>Unpenetrated &gt; 260</td>
<td></td>
</tr>
<tr>
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<td>-660</td>
<td>Unpenetrated &gt; 260</td>
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Table 4.4 Penetration experiment results for AA2024-T3 ST samples at low potentials in Ar-deaerated 1 M NaCl.
Figure 4.1. Metallographic sections of AA2024-T3. Also given is the terminology used for the different sections.

Figure 4.2 Schematic of the electrochemical cell for the penetration experiment.
Figure 4.3 Schematic of detection circuit diagram.

Figure 4.4 Schematic of foil penetration experimental set-up.

178
Figure 4.5 Schematic of microfocal X-ray radiography system.\(^\text{10}\)
Figure 4.6 Localized corrosion morphologies for 1.9 cm thick AA2024-T3 (ST) at open circuit. (a) after 89 h exposure, (b) after 332 h exposure, (c) after 450 h exposure.
Figure 4.7 Penetration time for 1.9 cm thick plate and 0.21 mm as-received sheet alloys in oxygen-bubbled 1 M NaCl at open circuit.
Figure 4.8 Localized corrosion morphologies for 1.9 cm thick AA2024-T3 (L) samples at open circuit.
Figure 4.9 Penetration time for plate and as-received sheet alloys in 1 M NaCl + 5x10^{-2} M Na_{2}S_{2}O_{3} solution at open circuit.
Figure 4.10 SEM picture showing unexposed surface of AA2024-T3 L (1.9 cm thick plate) penetrated in 1 M NaCl + 5 x 10^-2 M Na_2S_2O_3 solution at open circuit.

Figure 4.11 Metallographic cross section of AA2024-T3 ST (1.9 cm thick plate) penetrated for 11.1 h in 1 M NaCl + 5 x 10^-2 M Na_2S_2O_3 solution at open circuit (~ -610 mV SCE).
Figure 4.12 X-ray microradiographs for AA2024-T3 (LT) penetrated at OCP for 2.4 h.
Figure 4.13 Penetration rates for AA2024-T3 plate (1.9 cm thick plate) in oxygenated 1M NaCl at -580 mV SCE.

186
Figure 4.14 Optical micrographs of penetrated AA2024-T3 (ST) cross section showing IG attack through ST sample thickness.
Figure 4.15 Optical micrographs of penetrated AA2024-T3 (L) cross-section showing sharp IG attack along the grain boundaries.
Figure 4.16 Optical micrograph of penetrated AA2024-T3 (LT) cross-section showing IG attack along the grain boundaries.

Figure 4.17 Penetration rates for AA2024-T3 (8.9 cm thick plate) in oxygenated 1 M NaCl at -580 mV SCE.

189
Figure 4.18 Penetration rates for various ST samples of AA2024-T3 in oxygenated 1M NaCl at $-580 \text{ mV SCE}$. 
Figure 4.19 Metallographic cross section of AA2024-T3 (ST) penetrated at -580 mV SCE showing pitting and IG attack. (a) ST sample prepared from close to the surface of 8.9 cm thick T3 plate, (b) Large magnification.
Figure 4.20 Metallographic cross section of as-received 0.22 mm thick AA2024-T3 (ST) penetrated at -580 mV SCE showing pitting and IG attack. (a) as-polished, (b) etched.
Figure 4.21 Metallographic cross section of 1.9 cm thick AA2024-T3 (ST from midsection) penetrated at -580 mV SCE, (a) showing heavy exfoliation, (b) showing IGC.
Figure 4.22 Penetration time for L sections of 1.9 cm thick AA2024-T3 in oxygen/Ar bubbled 1 M NaCl at potential range from −675 mV to +500 mV SCE.

(a) +500 mV SCE for 1.0 h  (b) +500 mV SCE for 3.4 h

Figure 4.23 (a), (b) Metallographic cross sections of AA2024-T3 L samples penetrated at +500 mV in oxygen bubbled 1 M NaCl solution.
Figure 4.24 Metallographic cross section of AA2024-T3 (ST) sample penetrated at +500 for 3.3 h in Ar-deaerated 1 M NaCl solution.

Figure 4.25 X-ray microradiographs for AA2024-T3 (L) penetrated at +500 mV SCE for 1.1 h in oxygen-bubbled 1 M NaCl.
Figure 4.26 SEM picture showing unexposed surface of AA2024-T3 L sample penetrated at +500 mV SCE in oxygen bubbled 1 M NaCl solution.
Figure 4.27 Cross sections of AA2024-T3 (L) penetrated, (a) 10.3 h at OCP (~-630 mV SCE), (b) 16.5 h at -650 mV SCE, (c) 267 h at -675 mV SCE.
Figure 4.28 Penetration rates for AA2024-T3 (ST) at different potentials.

Figure 4.29 Cross sections of AA2024-T3 (ST) exposed in Ar-deaerated 1 M NaCl, (a) 260 h at -645 mV SCE, (b) 260 hr at -660 mV SCE.
Figure 4.30 Penetration rates of AA2024-T8 (L) samples at different potentials in O₂ bubbled 1 M NaCl solution.

Figure 4.31 Metallographic cross section of AA2024-T8 (L) penetrated at OCP (~ -740 mV SCE) showing selected granular attack.
Figure 4.32 Metallographic cross section of AA2024-T8 (L) penetrated at -580 mV SCE showing heavy selected granular attack along the elongated grain direction.

Figure 4.33 Penetration rates for various tempered AA2024 (L) samples at -580 mV SCE in O₂ bubbled 1.0 M NaCl.
Figure 4.34 Penetration rates for various tempered AA2024 (L) samples in O₂ bubbled 1 M NaCl at open circuit potential (OCP). Open circuit potential is about -630 mV for T3 temper, -670 mV for T3+ temper, -740 mV SCE for T8 and T8+ tempers in oxygenated 1 M NaCl solutions.
Figure 4.35 Metallographic cross sections of AA2024-T3+, T8+ L samples. (a) T3+ penetrated at OCP (~665 mV SCE) for 72 h, (b) T3+ penetrated at -580 mV SCE for 2.2 h, (c) T8+ penetrated at -580 mV SCE for 1.8 h.
**Figure 4.36** Penetration rates for AA2024-T3 (L) samples in nitrate and sulfate containing 1 M NaCl solutions.

**Figure 4.37** Cross section for AA2024-T3 (L) penetrated at -520 mV SCE in oxygenated 0.2 M NaNO₃ + 1.0 M NaCl solution.
Figure 4.38 Cross section for AA2024-T3 (L) sample penetrated at -580 mV SCE in oxygenated 0.25 M Na₂SO₄ + 1.0 M NaCl solution.
CHAPTER 5

STATISTICAL MODELING FOR IGC GROWTH

5.1 Introduction

As discussed in Chapter 4, the growth kinetics of IGC in AA2024-T3 are strongly anisotropic as a result of the anisotropic microstructure. The growth rate in the ST direction (short transverse) is much slower than growth in either the L (longitudinal) or (long transverse) direction. Since samples with all three orientations were prepared from the same plate alloy, they are identical in grain boundary composition and structure, so there is no reason to expect that the local intergranular growth rate is different in the different orientations. The nominal growth rate is a function of orientation only because the aspect ratios of the grains result in a difference in intergranular path length for the different orientations. The foil penetration technique measures the penetration time for the fastest growing localized corrosion sites through the thickness direction. In case of intergranular corrosion growth, the measured fastest growing intergranular corrosion site might be regarded as the one taking the shortest intergranular corrosion path through the thickness direction providing that local intergranular growth rate is independent of the
a statistical model for IGC growth that explains the observed anisotropic growth rates, which are mainly controlled by the grain size and aspect ratio of Al alloys, and to forecast the nominal localized corrosion growth rate that may be expected to occur in other Al alloy systems on the basis of the microstructure if the local intergranular growth rate is known. These models were developed in collaboration with Prof. Doug Wolfe in the OSU Department of Statistics and his graduate students, in particular, Ms. Shiling Ruan.

5.2 Statistical Modeling for IGC Growth

Grain size and distribution

In order to accurately model the effects of microstructural anisotropy, it is necessary to quantitatively characterize the microstructure. Grain size measurements were performed on metallographically prepared sections of 1.9 cm thick AA2024-T3, which were polished to 1 micron, and etched with Keller's agent to reveal the grain structure. Grains are three-dimensional, but they are viewed and measured on a two-dimensional cross section that is polished and etched. Because of this, the measured grain sizes are termed planar dimensions rather than spatial dimensions of the three-dimensional grains. Figure 5.1 shows some typical optical micrographs showing the grain microstructure of the 1.9 cm thick AA2024-T3 plate in ST and L etched sections. The grains of this wrought plate are flattened in the thickness and elongated in the rolling direction. The etching did not reveal sub-grain structure. While there are a number of methods for measuring planar grain sizes\(^1\), the most frequently used measured methods are Jeffries planimetric...
the elongated grain structure in 1.9 cm thick AA2024-T3 plate, the intercept method was used for the planar grain dimension measurement. Both lengths and widths of approximately 150 grains, selected randomly in the region from the surface to \( \frac{1}{4} \) T thickness plane of the plate, were measured individually with an optical micrometer on polished and etched L and LT sections. The ST section for grain size measurement was cut at the \( \frac{1}{4} \) T thickness plane of the plate. The average grain sizes and standard deviations were calculated, and the results are given in Table 5.1. The grains exhibit the largest anisotropy index on the LT section. Microstructural anisotropy is determined from the ratios of \( c/a \), \( a/b \) and \( c/b \) in ST, L and LT sections, respectively. Each of the grain planar dimensions can be determined independently from 2 different sections. The values measured for average grain thickness, \( b \), and grain length, \( c \), were quite similar for the different sections. However, a significant difference in grain width, \( a \), was found from measurements made on ST and L sections. The exact reason for this difference is unknown, but it may be due to the fact that the elongated grain sizes are dependent on the location of the cross sections. Figures 5.2-5.3 show the histograms for grain width and thickness distributions. Both grain planar dimensions are slightly positive skewed toward the right, with a long tail at high values. However, if a logarithmic transformation is employed, the resulting grain dimensions are well approximated by normal distributions, Figures 5.2(b), 5.3(b).
Suppose that an ST sample is composed of $N$ layers of elongated grains with grain width $a$, and thickness $b$. Each grain is piled up along the same elongated direction to create a brick wall structure as shown in Figure 5.4. The total foil thickness, $d$, is equal to $N b$. Both $a$ and $b$ can have probability distributions in size, but for the simple case, $b$ is assumed to be the same for all grains. Suppose that there is a fixed number of localized corrosion sites, $m$, which are initiated on the surface and grow into the microstructure along different intergranular paths $i$, and we assume that they make a turn at every junction, where $i = 1, 2, ... m$. Using an ST sample with grain dimensions of $0.3 \times 2.0$ (mm) and assuming each grain produces about 4 initial corrosion sites for IGC growth along the $L$ direction, the value of $m$ is estimated to be on the order of 1000 for a 1 cm$^2$ area, which is the exposed area for the foil penetration experiments. Let $W_{i,D}$ denote the total distance that the $i^{th}$ corrosion site travels to get through $k$ ($k < N$) layers to a depth of $D = kb$. The total distance $W_{i,D}$ can be expressed as follows:

$$W_{i,D} = kb + \sum_{j=1}^{k} X_{i}(j) = kb + W_{i,D,H} \quad (5.1)$$

where $X_{i}(j)$ is the horizontal distance that the $i^{th}$ intergranular corrosion site will travel on the $j^{th}$ layer, $j = 1, 2, ... k$. $W_{i,D,H}$ is the total horizontal distance that the $i^{th}$ intergranular site travels. As discussed earlier, the foil penetration technique measures the rate of the fastest growing corrosion site, which is assumed to take the shortest path length through the foil thickness. Assuming that all $m$ corrosion sites have a common probability distribution, it is of interest to know the probability distribution for the...
minimum total distance (denoted as \( W_{(1),D} \)) traveled by a corrosion site to reach a depth equal to a specified thickness of the ST sample. In other words, we want to find the cumulative distribution function for \( W_{(1),D} \), the minimum sum of \( k \) (\( k \) is the number of layers) independently and identically distributed \( X_i(j) \) for a given thickness \( D=kb \) of the ST sample under the assumption that the grain thickness \( b \) is constant for all layers. (As we will see later, this is not a very good assumption). As mentioned above, the grain dimensions were measured for our samples, so the probability distribution for the minimum sum of \( k \) \( X_i(j) \) can be estimated under certain assumptions.

**Uniform distribution model**

First, consider a very simple case where all grains have the same width \( a \) and thickness \( b \). Assume that the horizontal distances \( X_i(j) \) have a common uniform distribution over the interval \([0, a]\). This means that a vertical segment has a uniform probability of landing at any intersection point along the length of the underlying grain and that the path of localized corrosion could then go either way between the levels, Figure 5.5. The case of localized corrosion proceeding in both directions at an intersection leads to an increase in the number of sites \( m \), with time. This case of increasing numbers of sites is a good deal more complicated and will not be considered here. Let \( W_{i,D,H} \) denote the sum of \( k \) independent random variables each having the same distribution on \([0, a]\), and let \( F_{D,H}(at) \) denote the cumulative distribution function (c.d.f.) for \( W_{i,D,H} \); that is:

\[
F_{D,H}(at) = P\{W_{i,D,H} \leq at\} \quad (5.2a)
\]
is the cumulative probability that $W_{i,D,H}$ is less than or equal to the value "at", where $a$ is the grain width and $t$ is any real number.

For the case of a common uniform distribution on $[0, a]$ for the $X_i(j)$, this c.d.f. for $W_{i,D,H}$ is given by$^3$:

$$F_{D,H}(at) = \sum_{j=1}^{\#} (-1)^j \left( \frac{t - j}{k} \right)^k, \quad 0 \leq t \leq k, \quad (5.2b)$$

$$= 0, \quad t < 0,$$

$$= 1, \quad t > k,$$

where $\langle t \rangle$ denotes the greatest integer strictly less than $t$; and "at" is the total distance traveled in the horizontal direction by a corrosion site.

Considering that there are $m$ intergranular corrosion sites, the first one to penetrate will be the one that travels the shortest horizontal distance, denoted as $W_{\min,D,H}$. The cumulative distribution function for the minimum horizontal distance traveled among $m$ sites is given by $P\{W_{\min,D,H} \leq at\}$. Note that if the minimum horizontal distance is larger than a value "at", then all $m$ of the horizontal distances must be larger than "at". Thus the c.d.f. for the minimum horizontal distance traveled among $m$ corrosion sites can be expressed as:

$$P\{W_{\min,D,H} \leq at\} = 1 - P\{W_{\min,D,H} > at\}$$

$$= 1 - P\{\text{the horizontal distance for each corrosion site is} \geq at\} \quad (5.3a)$$

From equation (5.2), we find that the probability for the single $i^{th}$ corrosion site to travel a distance larger than a value "at" is given by:

$$P\{W_{i,D,H} > at\} = 1 - P\{W_{i,D,H} \leq at\} = 1 - F_{D,H}(at)$$

210
that each of the corrosion sites travels a total horizontal distance larger than a value of "at" is given by:

\[ P\{ \text{the horizontal distance for each corrosion site is } > \text{at} \} = \]

\[ [1 - F_{D,H}(\text{at})] \times [1 - F_{D,H}(\text{at})] \times \cdots \times [1 - F_{D,H}(\text{at})] = [1 - F_{D,H}(\text{at})]^m \]  

(5.3b)

Substituting (5.3b) into equation (5.3a), we obtain the cumulative distribution function (c.d.f.) for the minimum total horizontal distance traveled among m corrosion sites:

\[ P\{W_{\text{min,}D,H} \leq \text{at}\} = 1 - [1 - F_{D,H}(\text{at})]^m \]  

(5.3c)

From equations (5.1), (5.2) and (5.3), the c.d.f. for the minimum total distance among the m corrosion sites can be determined as a function of the grain planar dimensions a and b, and the number of intergranular corrosion sites m. With our assumed uniform distribution on [0, a], Figure 5.6 shows the influence of m on the cumulative distribution function (c.d.f.) for the minimum total distance normalized by the foil thickness. The c.d.f. shifts to the left with increasing values of m, which suggests that there is a higher likelihood for shorter IGC pathways through a foil as the number of corrosion sites increases. This indicates that penetration time should decrease as the exposed area of the sample increases, assuming a uniform area density of initiation sites.

This predicted decrease in minimum IG path length and resulting decrease in penetration time for a given thickness as the exposure area increases is similar in nature to empirical relationships discussed by Fontana in his textbook\textsuperscript{5}. It was suggested that the distribution of pit depths would shift to higher values as the exposed area increased because of the
increased probability of exposing more susceptible sites. These viewpoints suggest that care should be taken when predicting the behavior of a large plant based on experiments performed on small samples. However, the dependency of the c.d.f. on m is not strong. An increase in the number on sites by a factor of $10^4$ only decreases the median (0.50 probability) of the distribution by a factor of about 2, Figure 5.6(b).

Figure 5.7 shows the influence of the grain width, a, on the cumulative distribution function (c.d.f.) for the minimum total distance normalized by the foil thickness. The c.d.f. for the minimum total distance shifts to the right with increasing grain width as expected. The dependence of the median minimum total distance normalized by the foil thickness on grain width, a, is much stronger than that on m, the number of corrosion sites, Figures 5.6 (b), and 5.7(b).

Since our foil penetration experiments measured only one penetration time at each thickness, we would expect that the penetration time for the observed fastest-growing corrosion site, having minimum total distance, should be somewhere around a probability of 0.5 in the c.d.f. for the minimum IGC distance if the model fits the data well, since our single data point should represent a typical minimum value. If we tested replicate samples at each foil thickness, then the observed minimums should exhibit an empirical cumulative distribution curve like that in Figure 5.6.

From the foil penetration data for the 1.9 cm thick plate of AA202-T3, the nominal depths of the fastest growing sites as a function of time for the L and ST directions are given by:
These equations are fits to the data in which the exponent was forced to be \( \frac{1}{2} \). Power fits to the data, allowing the exponent to vary to obtain the best fit, resulted in values of 0.65 and 0.41 for penetration in the L and ST directions, respectively, both of which are close to 0.5. We can assume that the local dissolution rate is given by the rate in the L direction since the IG attack is almost straight in that L direction. At any time during penetration in the ST direction, the total distance traveled, \( d_{\text{TOT}}(t) \), is given by \( d_L(t) \), so the ratio of the total distance traveled divided by the nominal penetration rate in the ST direction is given by:

\[
\frac{d_{\text{TOT}}}{d_{\text{ST}}} = \frac{d_L}{d_{\text{ST}}} = \frac{0.3244t^{1/2}}{0.0756t^{1/2}} = 4.29
\]

As mentioned earlier, the average grain dimension, \( a \), of the 1.9 cm thick AA2024-T3 plate is 0.48 mm (determined from the L section) or 0.3 mm (determined from the ST section). The average grain dimension, \( b \), is 0.05 mm (determined from either the L or LT sections) in the ST direction. Figure 5.7 shows the cumulative distribution functions for the minimum total distance normalized by the foil thickness for different grain dimensions, \( a \), under the simple uniform distribution model, and assuming \( b=0.05 \) mm. The simple uniform distribution model predicts a value for the median ratio of minimum total distance normalized by the foil thickness of about 2.3 to 3.0. This value is smaller than 4.3, which is determined from the real penetration data. In order to force the median...
value to be 4.3, the grain width must be assumed to be much wider, on the order of 0.8 mm rather than 0.3-0.5 mm.

There are several possible reasons for this discrepancy. First, in a real microstructure of Al alloy, grains have a distribution of sizes, so there is a certain probability for the grain width to be greater than the average grain width. Second, IGC might not necessarily take the shortest intergranular corrosion pathway by turning down at each intersection because not all grain boundaries have the same susceptibility to IGC. Also, it is possible that the horizontal distances $X_i(j)$ could follow another type of distribution rather than a uniform distribution. This latter possibility led to consideration of a normal distribution in an attempt to improve the fit to the IGC growth data.

**Normal distribution model**

Here we assume that $X_i(j)$ follows a normal distribution on the interval $[0,a]$, with mean $\mu$ and variance $\sigma^2$ chosen to match with observed mean and variance of the sample grain widths. For the simple case, the grain dimensions $a$ and $b$ are still assumed to be the same for all grains. Based on the normal distribution properties, $W_{i,D,H}$, the sum of $k$ independent identically distributed normal distributions, is also distributed normally with mean $k\mu$ and variance $k\sigma^2$.

With such a simple normal distribution assumption, the range of $W_{i,D,H}$ is from negative infinity to positive infinity. However, the average grain width is $a$ and there are a total of $k$ grain layers that an intergranular corrosion site can travel to reach a depth $D$. Therefore, $W_{i,D,H}$ is constrained to fall between 0 and approximately $ka$, represented by
the notation $W_{i,D,H} \in [0, ka]$. To satisfy this constraint, we take $W_{i,D,H}$ to have a doubly truncated normal distribution with truncation points 0 and $ka$.

The truncated probability distribution function (p.d.f.) for $W_{i,D,H}$ is given by:

$$f(x) = \frac{1}{\sqrt{2\pi k\sigma^2}} e^{-\frac{(x-k\mu)^2}{2k\sigma^2}} \left[\frac{1}{\sqrt{2\pi k\sigma^2}} \int_{ka}^{0} e^{-\frac{(t-k\mu)^2}{2k\sigma^2}} dt\right]^{-1}$$

$$= \frac{1}{\sqrt{2\pi k\sigma^2}} e^{-\frac{(x-k\mu)^2}{2k\sigma^2}} \left[\Phi\left(\frac{ka - k\mu}{\sqrt{k\sigma^2}}\right) - \Phi\left(\frac{0 - k\mu}{\sqrt{k\sigma^2}}\right)\right]^{-1}$$

$$= \frac{1}{\sqrt{2\pi k\sigma^2}} e^{-\frac{(x-k\mu)^2}{2k\sigma^2}} B^{-1} \quad (5.7)$$

where $\Phi(\cdot)$ is the cumulative distribution function of the standard normal distribution (mean = 0, and standard deviation = 1), and the normalizing constant

$$B = \left[\Phi\left(\frac{ka - k\mu}{\sqrt{k\sigma^2}}\right) - \Phi\left(\frac{0 - k\mu}{\sqrt{k\sigma^2}}\right)\right]$$

is a function of $k, a, \mu, \sigma$. The cumulative distribution function (c.d.f.) for $W_{i,D,H}$ under this model given by:
\[
F_{D,H}(at) = P(W_{i,D,H} \leq at) = \frac{1}{\sqrt{2\pi k\sigma^2}} \int_{0}^{at} e^{-\frac{(x-t)^2}{2k\sigma^2}} \, dx
\]

\[
= B^{-1} \int_{0}^{at} \frac{1}{\sqrt{2\pi k\sigma^2}} e^{-\frac{(x-t)^2}{2k\sigma^2}} \, dx
\]

\[
=[\Phi\left(\frac{ka-k\mu}{\sqrt{k\sigma^2}}\right) - \Phi\left(\frac{0-k\mu}{\sqrt{k\sigma^2}}\right)]^{-1} \times [\Phi\left(\frac{at-k\mu}{\sqrt{k\sigma^2}}\right) - \Phi\left(\frac{0-k\mu}{\sqrt{k\sigma^2}}\right)]
\]

(5.8)

where \(0 \leq t \leq k\).

As before, let \(W_{\text{min},D,H}\) be the minimum order statistic of \(m\) independent identically distributed truncated normal random variables with common mean \(k\mu\), variance \(k\sigma^2\), and truncation points 0 and \(ka\). The c.d.f. for \(W_{\text{min},D,H}\) is then given by:

\[
P\{W_{\text{min},D,H} \leq at\} = 1 - [1 - F_{D,H}(at)]^m
\]

\[
= 1 - [1 - \Phi\left(\frac{ka-k\mu}{\sqrt{k\sigma^2}}\right) - \Phi\left(\frac{0-k\mu}{\sqrt{k\sigma^2}}\right)]^{-1} \times [\Phi\left(\frac{at-k\mu}{\sqrt{k\sigma^2}}\right) - \Phi\left(\frac{0-k\mu}{\sqrt{k\sigma^2}}\right)]^m
\]

(5.9)

The effect of the grain dimensions \(a\) and \(b\), and the number of intergranular corrosion sites \(m\) on c.d.f. for the minimum horizontal distance can be determined from equation 5.9 for the truncated normal distribution assumption. Figure 5.8 shows the cumulative distribution function (c.d.f.) for the minimum total distance normalized by the foil thickness with different values of \(m\), the number of intergranular corrosion sites. As expected, the cumulative probability distribution for the minimum total distance shifts to the left as the number of corrosion sites increases, which again suggests a higher likelihood for shorter IGC pathways through a foil as the exposed area increases.

Figure 5.9 shows cumulative distribution functions for minimum total distance for IG path length normalized by the foil thickness assuming a truncated normal distribution.
The two curves in the figure were plotted using the grain dimension distributions measured on ST and L sections of 1.9 cm thick AA2024-T3 plate, respectively. In principle, if the model fits the real data, the cumulative probability should be around 0.50 at the ratio of 4.3. The grain dimension distributions measured from the ST section results in a value of the ratio about 4.5 at the median value for 1000 sites, which is quite close to the prediction from the penetration results. However, the grain dimension distribution measured from the L section yields a value about 7.0, which is much larger than the predicted value. The reason for this discrepancy from the truncated normal distribution model is that the horizontal distance $X_i(j)$ is assumed to have the same distribution as the grain width. In the microstructure, the horizontal distance may have the same type of distribution, but the mean of the horizontal distribution should be smaller than the mean of the grain width distribution. In addition, as with the uniform distribution model, the normal distribution model does not take into account the grain size distribution, which needs to be considered in order to improve the fit of the statistical model. So a gamma distribution model was explored.

**Gamma distribution model**

As shown in Figures 5.2 and 5.3, the grain dimensions have long tails in the right direction. Such right-skewed distributions are better described by gamma distributions than either uniform or truncated normal distribution. The gamma distribution has two parameters $\alpha$ and $\beta$, with a mean (the average grain dimension) of $\alpha \beta$, and a variance of $\alpha \beta^3$. Based on the measured grain dimensions, we can calculate values of $\alpha$ and $\beta$ for the gamma distribution that best fit the data. The results are shown in Table 5.2. Taking $\alpha$
values of $\beta$ accordingly. The resulting integer $\alpha$ and its corresponding $\beta$ are listed in the last column of Table 5.2.

As with the uniform distribution model, let $X_i(j)$ represent the horizontal distance that the $i$th corrosion site travels on the $j$th layer of the brick wall, for $j=1, 2, \ldots, k$. The horizontal distance $X_i(j)$ is assumed to be uniformly distributed over $[0,a]$, where $a$ is no longer a constant, but is now governed by a gamma distribution with parameters $\alpha$ and $\beta$. The associated probability distribution function for $a$ is given by:

$$f(a) = \frac{1}{\Gamma(\alpha)\beta^\alpha} a^{\alpha-1} e^{-\frac{a}{\beta}}, \quad 0 < a < \infty \quad (5.10)$$

The conditional distribution of $X_i(j)$ for a given value of $a$ is uniform on $[0, a]$, so that the unconditional probability distribution function for $X_i(j)$ is given by:

$$h(x) = \int f(a) f(x | a) da = \int_x^\infty \frac{1}{\Gamma(\alpha)\beta^\alpha} a^{\alpha-1} e^{-\frac{a}{\beta}} da$$

$$= \frac{1}{(\alpha-1)\beta} \int_x^\infty \frac{1}{\Gamma(\alpha-1)\beta^{\alpha-1}} a^{\alpha-2} e^{-\frac{a}{\beta}} da$$

$$= \frac{1}{(\alpha-1)\beta} \sum_{t=0}^{\alpha-2} \frac{\left(\frac{x}{\beta}\right)^t}{t!} e^{-\frac{x}{\beta}} \quad (\text{if } \alpha \text{ is an integer}) \quad (0 < x < \infty) \quad (5.11)$$

The c.d.f. for $X_i(j)$ is given by:

$$F_D(x) = \int_0^x f(a) da = \int_0^x \frac{1}{\Gamma(\alpha)\beta^\alpha} a^{\alpha-1} e^{-\frac{a}{\beta}} da$$

$$= \frac{1}{\Gamma(\alpha)} \sum_{t=0}^{\alpha-2} \frac{w^t}{\beta^t t!}$$

$$= \frac{1}{(\alpha-1)} \sum_{t=0}^{\alpha-2} \frac{w^t}{\beta^t t!} \frac{1}{\Gamma(t+1)}$$

218
where $Y$ has a poisson distribution with parameter $\lambda=x/\beta$, so that

$$P(Y=t) = \frac{x^t e^{-x}}{\beta^t t!}, \quad t=1,2,3,\ldots$$

(5.12)

Thus we have

$$F_D(x) = 1 - \frac{e^{-x} x^t}{\beta^t t!} \left[ (\alpha - 1 - X) \sum_{i=0}^{\alpha-2} \frac{(\frac{x}{\beta})^i}{i!} + \frac{(\frac{x}{\beta})^{\alpha-1}}{(\alpha-2)!} \right] \quad 0 < X < \infty$$

(5.13)

Using equation (5.13), for given values of $\alpha$ and $\beta$, we can generate a number of random values of $X_i(j)$ by numerical inversion of the c.d.f. to represent possible horizontal distances that corrosion sites could travel in the different layers of the microstructure. Randomly choosing $k$ values ($k$ is the number of layers that one corrosion site travels in the microstructure) and calculating the probability distribution for the sum of $k$ random values $\sum X_i(j) = W_{nD,H}$ using a computer program (MATLAB), we get $m$ values, which are representatives of all possible distances that $m$ corrosion sites travel individually in the microstructure. The minimum total distance is obtained from those $m$ values. Once again, we generate a second group of random values of $X_i(j)$, and follow the same above process, and finally find the second minimum total distance. The above process is repeated until a specified number of the minimum total distances are collected. The cumulative probability distribution for these minimum total distances can
then be plotted. Figure 5.10 shows the cumulative distribution functions for the minimum total distance normalized by the foil thickness for penetration in the ST direction for two different sets of $\alpha$ and $\beta$, which were estimated from the measured grain dimension distribution for grain width $a$. Both gamma distributions predict smaller median ratios than 4.3, as determined by the real penetration data. It was expected that the gamma distribution model would provide an improved data fit. However, with the assumption of a common grain thickness, $b$, the number of layers, $k$, is underestimated. In the case where the grain thickness $b$ has a size distribution, the number of the layers that corrosion sites travel should be larger than the average number of grains in the thickness direction. Such an increase in the value of $k$ will shift the cumulative distribution curves in Figure 5.10 to the right, which would improve the model fit.

As shown in Figure 5.3, the grain thickness has also a size distribution. Assuming that the grain thickness also has a gamma distribution, and using the same approach as described above for the case where only the grain width is assumed to have a gamma distribution, we finally obtain two new cumulative distribution functions for the minimum total distance normalized by the foil thickness for penetration in the ST direction, Figures 5.11-12. The simulated results are much better, but there is still a discrepancy from the predicted value from the penetration data using the grain dimension measured from an ST or L section. One explanation is that the mean of $X_i(j)$ is still underestimated because the mean of $X_i(j)$ is assumed to be half of the measured average grain dimension under the gamma distribution assumption. The increase in the mean of $X_i(j)$ will also improve the simulation results. Other factors could be that corrosion sites
may not necessarily make a turn at each junction of the microstructure during their growth, which will lead to an increase in the mean of the horizontal distances. It is also possible the local IG rate depends on the geometry, rather than being independent of the orientation as assumed in this work. More work is needed to understand these factors.

Application of the statistical model

The measured localized corrosion kinetics under a variety of conditions, as discussed in Chapter 4, have clearly demonstrated the dependence of the IGC kinetics on the grain size and aspect ratio. The anisotropy of the IGC kinetics was a result of a large difference in intergranular path length per nominal thickness for different orientations. IGC kinetics were also found to be the same for various tempers of AA2024. In addition, recent penetration work on AA7178 alloys has shown that an equiaxed grain structure in AA7178 resulted in isotropic localized corrosion kinetics\(^6\), which further supports the dependence of the IGC kinetics on grain size and aspect ratio. The above statistical model provides a quantitative relationship between the grain size, grain aspect ratio, and IGC kinetics provided that the susceptibility to IGC is independent of the grain boundary orientation, and that the fastest growing IGC takes the shortest IG pathway. Based on the above model, it is expected that the more elongated grain structure will be more resistant to IGC penetration in the ST direction. The foil penetration experimental results showed that the penetration rate was much slower for ST samples from the T/2 location than ST samples from the surface of the plate. This could only have resulted from the difference in the grain aspect ratio since both ST sections were prepared from the same plate, which supports above prediction from the statistical model.
The above model can also be used to predict the relative exfoliation rate of wrought Al alloys if the alloys are susceptible to exfoliation as well as IGC. For wrought Al alloys where grains are elongated and flattened, the severity of the exfoliation is related to the rate of IGC growing into the microstructure. According to the above statistical model, the rate of exfoliation is expected to be slower for the alloys with more elongated grain structure. It was reported that AA2024-T3 exfoliated faster than AA2014-T6. One of the reasons for the slower exfoliation in AA2014-T6 was thought to be the fact that the AA2014-T6 had a more elongated grain structure than that of the AA2024-T3. The average grain dimension was 360 μm in the LT direction on the T/2 section of AA2014-6 compared with 220 μm for AA2024-T3.

However, the growth kinetics of exfoliation may not be directly proportional to the IGC kinetics because the susceptibility to exfoliation is also directly related to the grain aspect ratio. Our model assumes that the local IGC susceptibility is independent of grain aspect ratio as well as GB orientation. For example, it was reported that the exfoliation depths were almost independent of grain aspect ratio in Al-Li-Cu alloys, which cannot be explained by the above model. It is possible that the exfoliation rate may also depend on the wedging force generated during the exfoliation. In order to extend the application of the statistical model, it is necessary to introduce other parameters in the model. The most important one should describe the susceptibility of a GB to localized corrosion, such as a distribution of GB susceptibility with respect to grain orientations. As shown in the early chapter, not all grain boundaries were attacked during foil penetration experiments, which suggests that not all grain boundaries have the same
susceptibility to IGC. However, it is difficult to define the susceptibility of GB to localized corrosion. One possible way to define the GB susceptibility to IGC is to use the concept of coincidence site lattice (CSL) interface theory\cite{8,9}. As discussed in Chapter 2, this model assumes that both the misorientation angle and GB structure (characterized by CSL) determine whether it is intrinsically susceptible or immune to IGC\cite{10,11}. Orientation image microscopy will be needed to obtain the CSL orientation of GB in Al alloys. The development of the model is expected once a better understanding of the distribution of the GB susceptibility is available.

The statistical model only considers geometrical aspects of the microstructure. The influence of other parameter on IGC such as potential or bulk environment can be accounted for by determining their effect on the local IGC rate using L oriented samples in foil penetration experiments. Penetration kinetics in the ST direction can then be predicted using the statistical model.

It should also be mentioned that this statistical model is 2-dimensional. Penetration in the third direction was ignored because the grain size in the longitudinal or rolling direction was so much larger than the other grain dimensions for the 1.9 cm thick plate. Penetration in the third dimension would become more important for a more equiaxed microstructure.

5.3 Summary

Different statistical models were developed under different distribution assumptions. The cumulative distribution functions for the minimum total intergranular
Corrosion path length through the thickness of the ST samples were calculated on the basis of the different distribution models. The simulated results indicate that both intergranular corrosion sites and grain dimension distribution have marked effects on the cumulative probability distribution of minimum total distance. The anisotropic kinetics of IGC growth observed in AA2024-T3 are explained by the statistical distribution models. These statistical models provide a quantitative way to predict the possible IGC growth kinetics based on the microstructure and local IGC rate. More work is needed to understand the criterion for the GB susceptibility to IGC, and improve the statistical models.

REFERENCES:


TABLES AND FIGURES

<table>
<thead>
<tr>
<th>Sections</th>
<th>Grain dimensions (μm)</th>
<th>Anisotropy index</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST (a x c)</td>
<td>a = 304 ±155, c = 2017 ±830</td>
<td>6.6</td>
</tr>
<tr>
<td>L (a x b)</td>
<td>a = 480 ± 180, b = 52 ± 32</td>
<td>9.2</td>
</tr>
<tr>
<td>LT (b x c)</td>
<td>b = 55 ± 37, c = 2000</td>
<td>36.4</td>
</tr>
</tbody>
</table>

Table 5.1 Average grain dimensions determined from ST, L and LT sections of AA2024-T3 plate. Anisotropy is the ratio of c/a, a/b, and c/b in ST, L and LT sections, respectively.

<table>
<thead>
<tr>
<th>Grain dimension, a</th>
<th>Mean (mm)</th>
<th>Standard Dev. (mm)</th>
<th>Median (mm)</th>
<th>α</th>
<th>β</th>
<th>Notes*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST</td>
<td>0.304</td>
<td>0.155</td>
<td>0.277</td>
<td>3.85</td>
<td>0.079</td>
<td>α =4, β =0.075</td>
</tr>
<tr>
<td>L</td>
<td>0.480</td>
<td>0.180</td>
<td>0.460</td>
<td>7.11</td>
<td>0.0675</td>
<td>α =7, β =0.069</td>
</tr>
</tbody>
</table>

Table 5.2 α and β values of the gamma distributions estimated from the measured grain dimensions from both ST and L sections.

*Note: α is assumed to be an integer close to the estimated values from the measured grain dimensions.
Figure 5.1 Optical micrographs for L and ST sections of 1.9 cm thick AA2024-T3 plate.

(a) L section of 1.9 cm thick AA2024-T3 plate (etched)

(b) ST (¼ T plane) of 1.9 cm thick AA2024-T3 plate (etched)
Figure 5.2 Histograms for grain width measured from an ST section of 1.9 cm thick plate, (a) the original data distribution, (b) the distribution after a logarithm transformation.
Figure 5.3 Histograms for grain thickness, b, measured from a L section 1.9 cm thick plate; (a) the original data distribution, (b) the distribution after a logarithm transformation.
Figure 5.4 Schematic of brick wall model for IGC growth.

Figure 5.5 The uniform distribution of the horizontal distance $X_i(j)$ that corrosion site $i$ could travel in the $j^{th}$ layer of the microstructure over the interval $[0, a]$ where $a$ is the grain width.
Figure 5.6 (a) Cumulative distribution functions for minimum total path length for IGC normalized by the foil thickness for different values of $m$, the number of corrosion sites. (b) Median minimum total distance/foil thickness for different numbers of corrosion sites; the grain width and thickness are assumed to be 0.3 and 0.05 mm.
Figure 5.7 (a) Cumulative distribution functions for the minimum total IG path length normalized by the foil thickness for different grain widths. (b) Median minimum total distance/foil thickness for different grain widths \(a\); the grain thickness is assumed to be 0.05 mm, and the number of corrosion sites is assumed to be 1000.
Figure 5.8 Cumulative distribution functions for minimum total path length for IGC normalized by the foil thickness for different values of $m$, the number of corrosion sites. The grain width is assumed to have a normal distribution with mean 0.3 mm and standard deviation 0.15 mm. Grain thickness $b$ is assumed to be 0.05 mm.

Figure 5.9 Cumulative distribution functions for minimum total path length for IGC normalized by the foil thickness for different normal distributions of grain width, $a$. The grain thickness is assumed to be 0.05 mm and the number of corrosion sites is assumed to be 1000.
Figure 5.10 Cumulative distributions for the minimum total IG path length for penetration in the ST direction normalized by the foil thickness for two gamma distributions: (a) alpha = 7 and beta = 0.0675; (b) alpha = 4 and beta = 0.075.

Figure 5.11 Cumulative distribution for the minimum total IG path length for penetration in the ST direction normalized by the foil thickness for the gamma distribution (4, 0.075) after the grain thickness b is also assumed to have a gamma distribution.
Figure 5.12 Cumulative distributions for the minimum total IG path length for penetration in the ST direction normalized by the foil thickness for the gamma distribution (7, 0.0675) after the grain thickness is also assumed to have a gamma distribution.
6.1 Conclusions

The objective of this work was to provide quantitative information on localized corrosion kinetics in AA2024 alloys by studying some critical factors such as alloy microstructure, sample orientation, aging, potential and solution environment. Both electrochemical and non-electrochemical approaches were taken to study the susceptibility of localized corrosion and growth kinetics in high strength AA2024 under a variety of experimental conditions. The following conclusions were made from this work:

1. The anodic polarization curves of AA2024 in the solution heat treated and water quenched condition, T3, and T3+ tempers exhibited two breakdown potentials, whereas AA2024-T8, and T8+ exhibited only one breakdown potential. The polarization curves were independent of sample orientation in all tempers. The breakdown potential decreased with increasing aging time at 190 °C, and only one breakdown potential appeared for T8 and T8+ tempers. When two breakdown
potentials were observed, the more active one was found to be related to the transient dissolution of S-phase Al$_2$CuMg particles leading to pitting while the noble one was a result of initiation and growth of IGC. In the case of one breakdown potential, selected grain dissolution was believed to be the cause for the localized corrosion in T8 and T8+ tempers.

2. The growth kinetics of localized corrosion in AA2024-T3 exhibited a strong anisotropy. Growth in the short transverse direction (through-thickness direction of a rolled plate) was found to be much slower than that in either the longitudinal or long transverse direction. The anisotropy occurred because pits that initiated on the surface often developed into IGC as they grew into the microstructure. Metallographic cross sections confirmed that the growth rate anisotropy was a result of microstructural anisotropy and a large difference in intergranular path length per nominal thickness for various orientations. The anisotropy of growth kinetics was found to be different for various forms of T3 temper having different microstructures. Both grain size and aspect ratio were found to be important factors controlling IGC kinetics.

3. A corrosion morphology transition between pitting and intergranular attack was found at critical potentials on upward or reverse scans in T3 temper. IGC only initiated and grew at high potentials, where IGC growth kinetics were found to be almost potential-independent over a large potential range. At very high potentials such as +500 mV SVE, matrix phase dissolution occurs in addition to IGC. IGC growth kinetics were found to increase slightly with potential from −490 to +500 mV SCE, which suggests that only small amount of anodic current may escape from active tip of the isolated
IG cracks at a very high potential. Pitting dominated at low potentials, where pit growth is dependent on potential. Like pitting, there may exist an induction stage for IGC to initiate. Once initiated, IGC repassivated at a much higher potential than pits.

4. TEM observations did not provide much evidence that Cu-depleted zones were present at the grain boundaries of AA2023-T3, but the Cu-depleted zones were observed in T8 temper. Artificial aging resulted in more precipitation of intermetallic particles and formation of copper depleted matrix, which greatly changed the polarization behavior and localized corrosion morphology of AA2024. However, artificial aging was found to have little effect on the localized corrosion kinetics at \(-580 \text{ mV SCE}\) and open circuit.

5. Nitrate was found to increase the breakdown potential for S phase dissolution and changed the repassivation behavior of AA2024-T3. The nitrate decreased IGC kinetics at \(-580 \text{ mV SCE}\), but had little effect at \(-520 \text{ mV SCE}\). Sulfate appeared to have little influence on polarization and localized corrosion growth kinetics.

6. Open circuit penetration experiments showed that localized corrosion kinetics were still dependent on sample orientation, but were much slower than at high potentials. The localized corrosion on ST samples grew preferentially along longitudinal direction rather than through the sample thickness. Persulfate addition greatly enhanced the IGC kinetics at open circuit.

7. AA2024-T3 plate and sheet alloys exhibited different grain structures. Both had similar anodic polarization behavior, but exhibited different growth kinetics.

8. A statistical model was developed for IGC growth kinetics. The statistical modeling
6.2 Relevance of this work

This work focused on one of the most critical aspects of aging aircraft corrosion problems: understanding of the susceptibility to localized corrosion and quantitative determination of localized corrosion morphology and propagation rate under a variety of conditions. Although much is already known about localized corrosion of Al alloys, there are still currently no appropriate tools to quantify localized corrosion damage. Electrochemical techniques are widely used for the study of metal dissolution kinetics by measuring anodic current transients. In order to translate the measured current into the anodic dissolution current density, the active dissolved areas must be accurately determined. However, active dissolved areas during localized corrosion are typically unknown, and difficult to measure. They often are assumed to be regular in shape. However, localized corrosion can take in more than one form of attack morphologies. Furthermore, the measured current is only net current, not true anodic current. For the case of Al, the local hydrogen evolution within the attacked regions can consume a reasonable fraction of the anodic dissolution current density\(^1\). As shown in this work, the measured net current can be negative under some conditions because of extremely high local cathodic reaction. Furthermore, electrochemical measurement alone cannot provide quantitative information on growth kinetics under open circuit condition, which are more relevant to those of situations in real service.
developed in early 80's for the study of pit growth\(^2\). As discussed in this work, the foil penetration method also provides a direct way to study IGC kinetics under some conditions, which has never been quantitatively studied in Al alloys. The anisotropy of IGC kinetics, resulted from the anisotropic microstructure, was first demonstrated quantitatively in this work. Furthermore, the grain dimension and grain aspect were identified and confirmed as one of important factors controlling IGC kinetics. The grain boundary precipitates and composition were found to strongly affect the initiation of both pitting and IG, but had no significant effect on the fastest growing IGC kinetics at \(-580\) mV SCE, which provided a fresh understanding of the susceptibility to localized corrosion. The quantitative data of localized corrosion kinetics also make it possible to evaluate the susceptibility of an Al alloy to localized corrosion on the basis of the Al alloy microstructure, since the use of breakdown potential is not a very satisfactory criterion for the measurement of the susceptibility of materials to localized corrosion. As shown in this work, the breakdown potentials were almost independent of sample orientation in AA2024, but localized corrosion kinetics were strongly dependent on the orientation. The quantitative data of localized corrosion kinetics also provided valuable input in developing the predictive model for localized corrosion in aging aircrafts.

Although the foil penetration method measures only the fastest growing localized corrosion site, this information is more important than the average pit depth or IGC rate from a practical point of view since it would first penetrate a structure or have the highest stress intensity. The foil penetration method also makes it possible to quantitatively study
the localized corrosion kinetics at open circuit. The results from the foil penetration experiments at open circuit indicated that localized corrosion grew at a much slower rate than that at high potentials, but the growth mechanism was very similar to those at high potentials. A small amount of persulfate ions was found to greatly enhance the IGC kinetics at open circuit. Nitrate and sulfate ions are expected to influence the IGC kinetics at open circuit although they did not affect the IGC kinetics at -580 mV SCE. In summary, the quantitative information about growth kinetics at open circuit is critical for lifetime prediction of Al alloy components in real service.

This work also showed that localized corrosion could continue to grow as a result of the aggressive species trapped within occluded regions in the microstructure. This phenomenon is relevant to the real structures that go through cyclic exposure conditions. A detailed understanding of this phenomenon was not developed in this work, but it provided new direction for future work regarding localized corrosion kinetics. The results from this work have motivated the initiation of another project that will study the effects of stress on the kinetics using a modified version of the foil penetration technique. This work has also opened up several new issues, which are of interest regarding kinetics, as summarized below.

Finally, this thesis explored the possibility of statistical modeling for IGC growth kinetics. The model developed so far is still rather simple, and some new parameters such as a distribution grain boundary susceptibility to IGC need to be included, but it explained well the anisotropic IGC kinetics found in this work on the basis of the Al microstructure.
6.3 Suggestions for future work

This thesis work focused on only a few critical factors controlling the localized corrosion kinetics in AA2024, and some of them are still not fully understood. The work has also opened up several new issues that are of interest in the future. Following are a list of suggestions for the future work regarding kinetics.

1. As shown in this work, potential is an important factor determining the localized corrosion transition between pitting (S phase particle-induced) and IGC in T3 temper, but a detailed understanding of this transition process was not developed in this work. It is impossible to use metallographic cross sections to understand IGC initiation and measure its depth on the order of micron size, or to study local environments inside the sharp IG attack regions, but focused ion beam (FIB) cross sectioning allows for an exact determination of IGC depth. FIB technique can also be used to determine the exact nature of corrosion product along the propagated IGC path regions. In addition, in-situ microfocal X-ray radiography is also expected to contribute to the understanding of localized corrosion morphology transition.

2. It was found that the dissolution of the S phase particles on the surface occurred prior to the initiation and growth of IGC in AA2024-T3. However, in the case of over aged AA2024, large constituent S phase intermetallic particles are not responsible for localized corrosion. There is a lot of literature work about S phase particle dissolution in AA2024-T3, but no work about the S phase particle behavior in overaged AA2024. It may gain some useful information regarding the influence of S phase particle on localized corrosion of AA2024.
3. It is generally accepted that S phase particle dissolution generates a copper-rich layer deposited on the surface. It is expected that this Cu-rich layer might greatly affect the later stage of localized corrosion growth. However, it is unclear that how the S phase particle dissolution finally leads to later initiation and growth of IGC. It might be worthwhile to compare the current foil penetration results with the thin and pretreated AA2024-T3 samples where S phase particles are completely removed on the surfaces. The comparison will provide information whether initial S phase particle dissolution changes localized corrosion kinetics.

4. As shown in this work, there exists an induction stage for the initiation of IGC. At high potentials, the time for IGC initiation may be negligible, but it needs to be taken into account at low potentials. In order to accurately determine IGC kinetics at low potentials, it is important to separate the IGC initiation from its growth.

5. It was found that, in addition to penetrated pits, IG cracks also appeared on the backside of the penetrated samples under some conditions. It is believed that both residual stress and hydrogen produced during the penetration experiments may be responsible for the formation and development of the cracks, but the effects of the stress and H₂ have not been explored in this work. Under stressed condition, IGC is expected to develop into IGSCC, controlled by hydrogen embrittlement or anodic dissolution. One way to elucidate the relative role of hydrogen embrittlement and anodic dissolution on IGC and IGSCC is to understand the local environments such as pH, potential, and chemistry at the propagating IG tips or IG cracks.
6. The effects of nitrate and sulfate ions on polarization behavior and kinetics were studied, but more work is necessary to fully understand their effects. Other environmental factors, such as solution pH, solution temperature, and chloride concentration are also important for future work.

7. More open circuit penetration should be performed since the data on localized corrosion at OCP are more relevant for the lifetime prediction of Al alloys in real service. Another way to accelerate open circuit measurement is to use large surface area samples. The statistical model developed in this work has indicated that the total minimum IC path length depends on both grain dimension and corrosion site. This will also provide another way to verify the statistical model since localized corrosion sites are expected to be proportional to the exposed surface areas.

8. As shown in this work, localized corrosion can continue to grow because of the aggressive species trapped within the occluded regions in the microstructure. More work is expected to understand the kinetics under those conditions.

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249


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