ABSTRACT

ELSWICK, DANIELLE SHEA. Characterization of Corrosion Pit Initiation in Aluminum Using Advanced Electron Microscopy Techniques. (Under the direction of Dr. John J. Hren.)

The resistance to pitting corrosion in aluminum is due to the presence of a compact thin, approximately 5 nm, oxide. Certain conditions locally attack this protective oxide layer leading to its breakdown and resulting in the formation of corrosion pits. Numerous studies have investigated the growth and propagation stages of pitting corrosion yet the initiation stage remains not clearly defined nor well understood. The presence of aggressive chemical species, such as chloride, plays a critical role in the pitting phenomenon and is explored in this investigation.

This dissertation focuses on the localization of pitting corrosion in high purity aluminum in order to accurately predict where and when the pit initiation process will occur so that microstructural changes associated with pit initiation can be easily identified and characterized using electron microscopy. A comprehensive investigation into the corrosion initiation process was attempted utilizing advanced characterization techniques in the transmission electron microscope (TEM) coupled with high-resolution microanalysis. Localization of pitting was successful through use of different sample geometries that reduced the length scale for which pitting events occurred. Three geometries were investigated, each with unique features for pitting corrosion. Electropolished Al needles localized pitting to a sharp tip due to a geometric field enhancement effect, while other experiments employed an Al wire micro-electrode geometry. Both geometries minimized the area where corrosion pits initiated and were
electrochemically tested using a solution that contained the chloride species. A third geometry included electron beam evaporated Al films implanted with chloride, which induced pitting corrosion in an otherwise chloride-free environment.

Localization of pitting was successfully achieved using novel sample geometries that isolated the desired stages of pitting corrosion, i.e. metastable pitting, through controlled electrochemical tests. Potentiodynamic pitting experiments were performed on the different sample geometries and advanced TEM was utilized for characterization and microanalysis of the samples both prior to and following polarization. Automated eXpert Spectral Image Analysis (AXSIA) was one technique employed that allowed for spatial resolution of chloride in our material.

Preliminary experiments using the Al needle and micro-electrode geometries aided in defining electrochemical parameters and sample properties. Results from these geometries will be presented. A more in-depth study was performed using the Al thin films. TEM samples were made from the Al films in both cross-sectional and plan-view, which provided more information into the size and distribution of the chloride species. Oxide thickness increased locally prior to pitting when local areas high in chloride concentration were present. Results obtained from advanced TEM characterization and sophisticated microanalysis are presented in this dissertation and provide striking information into sample morphology and structural changes that resulted from electrochemically induced pitting corrosion.
CHARACTERIZATION OF CORROSION PIT INITIATION IN ALUMINUM USING ADVANCED ELECTRON MICROSCOPY TECHNIQUES

by

DANIELLE S. ELSWICK

A dissertation submitted to the Graduate Faculty of North Carolina State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy

MATERIALS SCIENCE AND ENGINEERING

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Nancy Missert                Peter Fedkiw
For
Mom and Dad,
Patrick
&
Sadie Sue.
For Love.
BIOGRAPHY

Danielle Elswick was born in Norfolk, Virginia and raised in Virginia Beach, Virginia. She graduated from Frank W. Cox High School in 1994 and then attended North Carolina State University to pursue a degree in Mechanical Engineering. During her undergraduate studies she was introduced to the field of Materials Science and Engineering, in which she changed her academic path and major field of study. The Department of Materials Science and Engineering graduated Danielle in the spring of 1999. Immediately following her undergraduate studies, Danielle began graduate school at North Carolina State University, which led her to this Ph.D. dissertation.

Her research efforts as a graduate student were in collaboration with a Basic Energy Science (BES) group at Sandia National Laboratories. The BES group consisted of many scientists from multiple disciplines working on a common research project. The project enabled Danielle to make several visits to the laboratory in Albuquerque, NM where she spent time working extensively with members from the BES corrosion group using advanced capabilities available at their facilities.

During her academic career, Danielle received a student scholarship and attended the high resolution electron microscopy school at Arizona State University in the winter of 2000. She also attended several conferences as a graduate student including the annual Microscopy and Microanalysis (M&M) meeting, where she presented her work at a poster platform in 2000 and 2002. She was awarded the Microbeam Analysis Society Distinguished Scholar Award in 2005 for M&M 2005 and presented in the Spectral Imaging: Advances and Applications platform session. The annual Electrochemical
Society Meeting, National Association of Corrosion Engineers and local Material Research Society Meetings also comprise conferences where her research work has been presented.

Danielle was involved in several teaching opportunities during her graduate career. She instructed undergraduate students at North Carolina State University in a laboratory course that taught the principles and fundamentals of material science. She also assisted in a graduate level transmission electron microscopy laboratory course where she trained graduate students in the alignment and operation of the microscope. Other teaching experience includes her participation as a counselor in a materials science summer camp for high school students at North Carolina State University.

Upon receiving her doctorate from North Carolina State University, Danielle hopes to pursue a post-doctoral position. She would like to continue and follow her interests in the field of electron microscopy through exploration of different materials systems and believes a post-doctoral position will provide her with the additional experience she seeks. She currently resides in Raleigh, North Carolina with her boyfriend, Patrick Long and her dog, Sadie Sue.
I would like to express my sincere thanks to my academic advisor, Dr. John Hren, for his dedication in the field and his compassion to explore new science. I also express my gratitude for his positive guidance and constant support. Many thanks are also extended to Dr. Gerd Duscher, Dr. Paul Kotula, Dr. Nancy Missert and Dr. Peter Fedkiw for serving on my committee and sharing their expertise on the project. This research was successful due to the support and collaborative efforts made by the Basic Energy Science program and corrosion group at Sandia National Laboratories. I’d like to especially thank Nancy Missert for her leadership with this group and for her extensive efforts made directly with me in my research; I found in you a great role model. A special thanks also to Paul Kotula for his expertise and contribution with work in microscopy.

I’d like to thank several scientists at Sandia National Laboratories including the entire BES Corrosion Group, with many thanks going to Doug Wall, Craig Johnson, Guild Copeland and Lysle Serna. I have an overwhelming appreciation for Michael Rye’s assistance and time with TEM sample preparation and for our incredible friendship. I also thank Chuck Hills for his guidance in different sample preparation techniques and Jerry Walraven for his support and friendship over the years.

An exclusive group whose support is undoubtedly appreciated and my heartfelt thanks go to my family. I’d like to thank my mom and dad, my brother Tyler, and my grandparents, for the love and support given during my journey. I could not have made it without you all. I would also like to recognize the love and support from my baby girl, Sadie Sue, the most beautiful, loyal and loving canine companion.
There are also several professors at North Carolina State University that deserve recognition and I’d like to express my sincere gratitude for their efforts in teaching and research. Thank you Dr. Scattergood, Dr. Benson, Dr. Russell, Dr. Hans-Joachim Lewerenz and Dr. Rigsbee. A huge appreciation is also given to Ms. Edna Deas, who every student finds dear for her hard work and friendly smile that helps everyone daily.

I’d also like to thank my huge pool of friends from every corner of my heart and soul for knowing and loving me throughout the years. I embrace my relationship with each of you uniquely and admire you each for different reasons. Thank you Dustin for being my best friend and an inspiration. Thank you Sharon for being a super cool and very true girlfriend. My dear friend Nicole, thanks for sharing in the soul searching. Becky and CC, I thank you for all the great moments and bringing many smiles to my heart. I would love to write a dissertation on why and how I love every one of my friends, because they truly embrace my spirit and remind me of the great perspectives of life, love and friendship, but that must wait for another transcript. SO, thanks are offered to many of my laid back, fun, supportive, creative and intelligent friends who always seem to love me and again I thank you for that; Courtney and Kimberly, Mama Judy, Dave McGregor, Richard, Ray, Chris Cross, Donovan, Andy, Pete and Brent.

I’ve saved the best for last. Patrick Long. You are the most amazing fellow and I thank you for standing by my side through many challenging years as a graduate student. Your fearless heart in questionable times taught me the true meaning of love. You are an incredibly smart and creative individual who I admire beyond words. Thanks for the inspiration and motivation. I love every day we share together and look forward to what crazy adventure we stumble upon next. Life and love is so amazing with you. Thanks!
# Table of Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>x</td>
</tr>
<tr>
<td>List of Figures</td>
<td>xi</td>
</tr>
<tr>
<td>1. Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Dissertation Overview</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Pitting Corrosion: Background and Motivation</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Role of Chloride</td>
<td>4</td>
</tr>
<tr>
<td>1.4 Scientific Approach</td>
<td>5</td>
</tr>
<tr>
<td>1.5 Summary</td>
<td>6</td>
</tr>
<tr>
<td>1.6 References</td>
<td>7</td>
</tr>
<tr>
<td>2. Sample Preparation</td>
<td>9</td>
</tr>
<tr>
<td>2.1 Introduction</td>
<td>9</td>
</tr>
<tr>
<td>2.2 Aluminum Needle Geometry</td>
<td>10</td>
</tr>
<tr>
<td>2.3 Bulk Aluminum Wires</td>
<td>13</td>
</tr>
<tr>
<td>2.4 Aluminum Thin Films</td>
<td>14</td>
</tr>
<tr>
<td>2.5 TEM sample preparation</td>
<td>15</td>
</tr>
<tr>
<td>2.5.1 Conventional Sample Preparation Techniques</td>
<td>15</td>
</tr>
<tr>
<td>2.5.2 Focused Ion Beam</td>
<td>17</td>
</tr>
<tr>
<td>2.6 Summary</td>
<td>20</td>
</tr>
<tr>
<td>2.7 References</td>
<td>22</td>
</tr>
</tbody>
</table>
### 3. Experimental Tests and Characterization Techniques

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Introduction</td>
<td>23</td>
</tr>
<tr>
<td>3.2 Electrochemical Testing</td>
<td>24</td>
</tr>
<tr>
<td>3.2.1 Aluminum Needle Experiments</td>
<td>25</td>
</tr>
<tr>
<td>3.2.2 Potentiodynamic Pitting Experiments</td>
<td>25</td>
</tr>
<tr>
<td>3.2.3 Induction Time Experiments</td>
<td>28</td>
</tr>
<tr>
<td>3.2.4 Summary of Experimental Tests</td>
<td>29</td>
</tr>
<tr>
<td>3.3 Scanning Electron Microscopy</td>
<td>30</td>
</tr>
<tr>
<td>3.4 Transmission Electron Microscopy</td>
<td>30</td>
</tr>
<tr>
<td>3.4.1 Conventional TEM techniques</td>
<td>32</td>
</tr>
<tr>
<td>3.4.2 Jump Ratio Imaging</td>
<td>32</td>
</tr>
<tr>
<td>3.4.3 Automated eXpert Spectral Image Analysis</td>
<td>34</td>
</tr>
<tr>
<td>3.4.4 Electron Energy Loss Spectroscopy</td>
<td>37</td>
</tr>
<tr>
<td>3.5 Summary of Characterization Techniques</td>
<td>38</td>
</tr>
<tr>
<td>3.6 References</td>
<td>39</td>
</tr>
</tbody>
</table>

### 4. Al Needles

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>40</td>
</tr>
<tr>
<td>4.2 Experimental</td>
<td>41</td>
</tr>
<tr>
<td>4.3 Results.</td>
<td>42</td>
</tr>
<tr>
<td>4.4 Discussion and Summary</td>
<td>56</td>
</tr>
<tr>
<td>4.5 References</td>
<td>59</td>
</tr>
</tbody>
</table>

### 5. Bulk Al Wire

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>60</td>
</tr>
</tbody>
</table>
5.2 Experimental .............................................. 60
5.3 Results .................................................. 62
5.4 Discussion and Summary ................................. 80
5.5 References .............................................. 83

6. Chloride Implanted Aluminum Thin Films ........... 84
   6.1 Introduction .......................................... 84
   6.2 Experimental ......................................... 87
   6.3 Results: Al Thin Films ............................... 89
       6.3.1 AFM Results .................................... 90
       6.3.2 Unpolarized Thin Film Samples in TEM cross-section .................................. 92
       6.3.3 Unpolarized Thin Film Samples in TEM plan-view .................................. 100
       6.3.4 Summary of Unpolarized Al Films ............ 120
       6.3.5 Polarized Thin Films in TEM cross-section ........................................ 121
       6.3.6 Polarized Thin Films in TEM plan-view ........................................ 127
       6.3.7 Summary of Polarized Al Films .................. 140
   6.4 Discussion and Summary ............................... 140
   6.5 References ............................................ 145

7. Summary, Conclusions and Future Work ............... 146
   7.1 Summary of Results .................................... 146
   7.2 Conclusions & Discussions ............................. 151
   7.3 Suggested Future Work ................................. 153

Appendix A .................................................. 158
Appendix B .................................................. 160
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-1</td>
<td>Resulting pitting potentials from anodic polarization in 0.05 M NaCl&lt;sub&gt;aq&lt;/sub&gt; solution</td>
<td>58</td>
</tr>
<tr>
<td>6-1</td>
<td>Lattice (d) spacings for given hkl in pure aluminum and AlCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>118</td>
</tr>
</tbody>
</table>
## List of Figures

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Schematic of electropolishing set up for Al wires</td>
<td>11</td>
</tr>
<tr>
<td>2-2</td>
<td>Flow chart summarizing Al needle preparation for TEM samples</td>
<td>11</td>
</tr>
<tr>
<td>2-3</td>
<td>Schematic of bulk aluminum wires, flat samples. Top surface is electropolished and treated to HNO₃ for one minute. a.) Array of Al wires embedded in epoxy. b.) Single Al wire embedded in epoxy. Both showing the wire extended out the back side of the epoxy for electrical contact</td>
<td>13</td>
</tr>
<tr>
<td>2-4</td>
<td>FEI DB-235 dual-beam FIB/SEM, located at Sandia National Laboratories, used for TEM sample preparation</td>
<td>17</td>
</tr>
<tr>
<td>2-5</td>
<td>a.) Schematic showing the use of FIB for TEM sample preparation. The red rectangle (20μ x 2μ) is the area of interest for the TEM sample. The grid regions adjacent to this area are milled away using an ion beam. The sample is further thinned by milling toward the center of the area of interest until the sample is electron transparent. b.) Representative TEM cross section of sample after the sample is placed on a carbon film TEM grid demonstrating the various layers present</td>
<td>19</td>
</tr>
<tr>
<td>2-6</td>
<td>SEM image top down of an area thinned using the FIB. The TEM foil is labeled and considered electron transparent when contrast is lost in secondary electron image from an angle</td>
<td>20</td>
</tr>
<tr>
<td>3-1</td>
<td>Current-potential data from a potentiodynamic pitting experiment with important regions labeled. A constant potential scan rate (ex. 0.2 mV/s) is applied to the sample while being exposed to 0.05 M NaClₐq solution</td>
<td>26</td>
</tr>
<tr>
<td>3-2</td>
<td>Representative data from an induction time experiment. A constant potential is applied and held for a given time. Peak in current represents the initiation of a pit</td>
<td>28</td>
</tr>
<tr>
<td>3-3</td>
<td>a.) Schematic of EELS spectrum for oxygen K-edge demonstrating the energy windows used for constructing an elemental jump ratio image. Two energy filtered images are collected pre (blue) and post (red) edge. b.) EELS jump ratio image formed on Al cross-section. Division of two energy filtered TEM images (pre-edge by post-edge) results in a jump ratio image for a particular element, in this example, oxygen</td>
<td>33</td>
</tr>
<tr>
<td>3-4</td>
<td>a.) Schematic of focused electron beam interaction with TEM specimen where data for AXSIA can be collected from either EDS or EELS. b.) AXSIA resulting spectrum image formed from pure individual components and spectra</td>
<td>35</td>
</tr>
<tr>
<td>4-1</td>
<td>a.) Electropolished Al needle. b.) High magnification image showing smooth surface with 4-5 nm uniform oxide layer on tip approximately 50 nm in radius. c.) High magnification jump ratio image using O K-edge</td>
<td>43</td>
</tr>
</tbody>
</table>
Al needle at three different magnifications increasing respectively in a., b.) and c.) to show the oxide. d.) Oxygen jump ratio image. The black line in this image represents a small correlation shift (misalignment) between the oxygen pre and post edge images.

TEM of Al needle approximately one micron from the tip a.) Bright field image of oxide and contaminant cluster. b.) oxygen K-edge jump ratio image. c.) carbon K-edge jump ratio image.

Al needle after exposure to 0.05 M NaCl\textsubscript{aq} solution for 30 minutes. a.) Low magnification b.) and c.) High magnification showing initial oxide underlying the exposure layer.

Al needle exposed to 0.05M NaCl\textsubscript{aq} solution for 1 hour.

Al needle before exposure demonstrating uniform oxide. b.) and c.) After exposure to H\textsubscript{2}O for three hours.

Al needle after exposure to HNO\textsubscript{3} for one hour.

Schematic and photographs of electrochemical set up for polarizing Al needles using VMP multi-channel potentiostat.

Current-potential plots for sharp electropolished needles subjected to potentiodynamic pitting experiments and pitted at the potentials given at right. OC potentials were within 80 mV for all eight samples.

SEM of needles polarized in Figure 4-9 with corrosion product blooms on and/or near tip apex.

Current-potential plots for dull electropolished wires subjected to potentiodynamic pitting experiments and pitted with the exception to channel 4. Corresponding pitting potentials also given at right. OC potentials were within 100 mV for all eight samples.

SEM images of dull electropolished wires subjected to experiment in Figure 4-11. Pitting potentials were a.) -555mV in Channel 8 and b.) -574mV in Channel 3. Both samples feature similar corrosion pitting sites along the shank of the wire.

Current-potential plots for sharp electropolished needles treated to 1 minute nitric etch and subjected to potentiodynamic pitting experiments and pitted at potentials given at right. OC potentials were within 70 mV for all eight samples.

Current-potential plots for dull electropolished wires treated to a 1 minute nitric etch and then subjected to potentiodynamic pitting experiments. Signs of pitting were not indicated in the data. OC potentials were within 10 mV for all eight samples.

Distribution of pitting potentials for needles and dull wires.

Current-time plot from an induction time test for a wire polarized at -450 mV in 0.05 M NaCl\textsubscript{aq}. Multiple current peaks correspond to pit initiations.

SEM of mechanically polished surface demonstrating both polishing damage and corrosion events. b.) SEM of damage resulting from mechanical polish. c.) SEM of area resulting from pitting corrosion.
5-3 a.) TEM bright field of pitted region of mechanically polished surface.  
b.) BF of corrosion pit. .......................................................... 64

5-4 a.) TEM BF of electropolished Al wire with smooth, uniform 5nm surface oxide.  
b.) High resolution image of surface oxide.  
c.) High resolution image of oxide across boundary showing no thickness change across different grains. .............. 65

5-5 a.) TEM BF image of surface oxide of electropolished wire with jump ratio images obtained using  
b.) oxygen K-edge  
c.) carbon K-edge  
d.) aluminum L-edge. ........... 66

5-6 a.) SEM image of electropolished wire subjected to potentiodynamic pitting experiment.  
b.) Single pit formed which was site for TEM cross-sectional sample prepared using FIB. .................................................. 67

5-7 a.) STEM ADF image of pit in cross-section with red square encompassing a 50 nm by 50 nm area scanned for AXSIA, results in Figure 5-9.  
b.) High magnification of pit in cross-section, approximately 2 μm in width and formed at grain boundary. ....... 68

5-8 a.) and b.) TEM BF images of oxide captured from surface approximately 2 μm away from pit. Images are taken at different tilts to show oxide thickness which has increased from 5 nm to 30 nm  
c.) aluminum jump ratio image  
d.) oxygen jump ratio image .......................................................... 70

5-9 Individual component spectra taken from area in Figure 5-7.  
a.) Spectrum image of Al wire  
b.) Spectrum image of surface oxide layer with small Cl signal. ............. 71

5-10 SEM images of a corroded Al bulk wire with an initial electropolished surface.  
Images show different areas of attack as a result of polarization in NaClaq. ........... 72

5-11 a.) SEM of corroded Al wire demonstrating crevice corrosion.  
b.) High magnification of pitted area adjacent to epoxy wall. .................................................. 72

5-12 a.) SEM top down view of corroded wire.  
b.) and c.) Large pit formed at Al wire-epoxy contact area. .......................................................... 73

5-13 a.) SEM of corroded electropolished wire.  
b.) Outer edge of wire in contact with epoxy wall.  
c.) Cross-sectional FIB cut of Al wire-epoxy interface demonstrating the crevice formed (circled) from the electropolish and/or polarization. .............. 74

5-14 TEM bright field images of exposed but not pitted Al wire. .................. 75

5-15 a.) Energy filtered bright field TEM Image. Jump ratio image using  
b.) C K-edge  
c.) O K-edge. .......................................................... 75

5-16 TEM bright field images showing surface oxide.  
a.) Low magnification image of TEM cross-section, with layers labeled: Al, oxide, carbon (deposited for contrast in TEM), Pt (deposited to make FIB cut).  
b.) Mechanically polished surface. Oxide distinct and approximately 5-7 nm thick.  
c.) High magnification image; edge-on showing oxide. .......................................................... 76

5-17 a.) STEM ADF image with red box of dimensions 100 nm by 100 nm scanned for AXSIA. Individual component spectrum images (0.78 nm/pixel) identifying 3 phases;  
b.) Al bulk wire  
c.) Cl-rich Al with Ga  
d.) Al oxide w/Cl. .................. 77
ADF STEM image with red box of dimensions 125 nm by 500 nm scanned for AXSIA. Individual component spectrum images (0.977 nm/pixel) identifying 3 phases; b) Al bulk wire c) Al oxide d) Cl-rich Al with Ga. 

Cl depth profile obtained from integrating over spectrum image in Figure 5-18. 

Cl depth profiles for three different implantation energies at constant, 3 x 10^{16} Cl/cm², ion fluence. a) depth profile for bulk film. b) depth profile of oxide layer, 0-4 nm. 

Cl depth profile using 35 keV Cl ions for four different implantation fluences. 

Three electrode cell set up for thin films. b) 1 mm capillary used for exposure. 

AFM images of Al thin films. Area is 1.5µm by 1.5µm showing morphology changes with implantation fluence. a) no implant b) 1 x 10^{16} Cl/cm² c) 3 x 10^{16} Cl/cm² d) 5 x 10^{16} Cl/cm² e) 7 x 10^{16} Cl/cm². 

STEM ADF image of film implanted 1 x 10^{16} Cl/cm². The red area (labeled 1) is a 400 by 800 nm region used for AXSIA. 

EDS component spectra overlay from AXSIA and corresponding RGB overlay image (3.1 nm/pixel) showing the output components from area in Figure 6-5. 

TEM BF image, 390kX showing 4-5 nm surface oxide. b) STEM ADF image of film implanted 5 x 10^{16} Cl/cm². The red area (labeled 1) is a 400 by 800 nm region used for AXSIA. 

EDS component spectra overlay from AXSIA and corresponding RGB overlay image (3.1 nm/pixel) showing the output components from area in Figure 6-7. 

TEM bright field images of film implanted 7 x 10^{16} Cl/cm² showing a) implanted region b) implantation damage across low angle boundary c) and d) near surface region & uniform 4-5 nm oxide. e) and f) STEM ADF images showing density changes (arrows) correlated to implantation damage & Cl ppts. 

HRTEM images, 7 x 10^{16} Cl/cm², near surface showing oxide and crystalline regions. 

STEM ADF image of film implanted 7 x 10^{16} Cl/cm². The red area (labeled 1) is a 400 by 800 nm region used for AXSIA. 

EDS component spectra overlay from AXSIA and corresponding RGB overlay image (3.1 nm/pixel) showing the output components from area in Figure 6-11. 

STEM ADF image of film implanted 5 x 10^{16} Cl/cm². The red area (labeled 1) is a 400 by 400 nm region used for AXSIA. b) Spectral component image for Cl-rich Al phase (3.125 nm/pixel). c) Individual component spectra, color coded, and overlay of spectra. d) RGB overlay spectrum image; green=Cl-rich Al phase and blue=Al matrix. 

STEM ADF image of film implanted 5 x 10^{16} Cl/cm². The red area (labeled 1) is a 300 by 300 nm region used for AXSIA. b) Spectrum component image (2.34 nm/pixel) for Cl-rich Al phase. c) and d) TEM BF images of area scanned for AXSIA at different tilts showing the alignment of Cl component with grain boundaries. e) Z-contrast image of blue region in a.
6-15  a.) STEM ADF image of film implanted $5 \times 10^{16}$ Cl/cm$^2$. The red area (labeled 1) is a 500 by 500 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (3.9 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase and red=Al matrix.

6-16  a.) STEM ADF image of film implanted $5 \times 10^{16}$ Cl/cm$^2$. The red area (labeled 1) is a 500 by 500 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (3.9 nm/pixel). c.) Corresponding individual component spectra of Cl-rich Al component.

6-17  a.) STEM ADF image of film implanted $1 \times 10^{16}$ Cl/cm$^2$. The red area (labeled 1) is a 200 by 200 nm region used for AXSIA. b.) Individual component spectra, color coded. c.) RGB overlay spectrum image; red=Al matrix with Cl and blue=Al oxide component (1.56 nm/pixel).

6-18  a.) STEM ADF image of film implanted $7 \times 10^{16}$ Cl/cm$^2$. The red area (labeled 1) is a 200 by 200 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (1.56 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase, red=Al matrix and blue=Al oxide.

6-19  a.) STEM ADF image of film implanted $7 \times 10^{16}$ Cl/cm$^2$. The red area (labeled 1) is a 500 by 500 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (3.9 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase and red=Al matrix with circled regions are indicative of adjoining clusters.

6-20  Z-contrast image of film implanted $5 \times 10^{16}$ Cl/cm$^2$ and EELS spectra collected using aperture over entire area. Black line shows the Cl edge background subtracted from spectrum.

6-21  a.) DF Z-contrast image (sample implanted $7 \times 10^{16}$ Cl/cm$^2$) with arrow pointing to triple boundary point where EELS spectrum was taken using electron beam in spot mode in STEM. b.) Corresponding bright field image.

6-22  a.) BF image (sample implanted $7 \times 10^{16}$ Cl/cm$^2$) and corresponding b.) DF image with two arrows indicating areas where EELS spectra were collected in STEM spot mode. c.) EELS spectra from regions indicated in b showing higher Cl concentration at boundary triple point (Spectrum 1) compared to within the grain (Spectrum 2).

6-23  a.) DF image (sample implanted $7 \times 10^{16}$ Cl/cm$^2$) showing points where EELS spectra were collected in STEM spot mode across the boundary. b.) Corresponding BF image. c.) EELS spectra from regions $a$ and $c$ showing higher Cl concentration within the grain (spectrum $a$) than at the boundary (spectrum $c$).

6-24  a.) DF image from the same region as in Figure 6-23, only with a series of EELS spectra collected in STEM spot mode from different areas. b.) EELS spectra from some of the different points. Spectra $b$ and $d$ both along boundary with one showing significantly more Cl than the other. Spectra $a$ and $f$, one at boundary triple point and one within the grain indicating more Cl at triple point.
6-25  a.) and b.) BF and DF images, respectively, from sample implanted 7 \times 10^{16} \text{Cl/cm}^2 showing types of diffraction contrast and Z-contrast. c.) and d.) High magnification BF and DF pair from triple point indicated with red arrows in left side of images in a and b. ................................................................. 117

6-26  a.) SAD from sample implanted 7 \times 10^{16} \text{Cl/cm}^2 with weak reflections from AlCl$_3$ phase. b.) DF image captured using reflection from the 222 AlCl$_3$ reflection. .............. 119

6-27  BF and DF image pairs a.) & b.) and c.) & d.) from sample implanted 7 \times 10^{16} \text{Cl/cm}^2. Precipitates are easily observed in the DF image with many showing strain contrast. ................................................................. 120

6-28  a.) STEM ADF image in cross-section of unimplanted sample that was polarized in 50 mM NaCl with a 200 by 200 nm area labeled 1, selected for AXSIA analysis. b.) Three components computed using AXSIA, Al=red, Al oxide with Ga=blue, and Al oxide plus surface contaminants=cyan. c.) RGB overlay image of components (1.56 nm/pixel). ................................................................. 122

6-29  Hypothetical polarization curve demonstrating experimental data (blue) and experiment termination at a potential below what is anticipated for pitting (red). .... 123

6-30  Current-potential data for sample implanted with 5 \times 10^{16} \text{Cl/cm}^2 and polarized to 60 mV below the pitting potential. ................................................................. 124

6-31  a.) STEM ADF image in cross-section of sample implanted 5 \times 10^{16} \text{Cl/cm}^2 that was polarized in 50 mM K$_2$SO$_4$ with a 200 by 200 nm area labeled 1, selected for AXSIA analysis. b.) Three components computed using AXSIA, Al=red, Cl-rich Al=green and an Al oxide w/Cl=blue. c.) RGB overlay image of components (1.56 nm/pixel). ................................................................. 125

6-32  Individual component spectrum images from AXSIA results in Figure 6-31. a.) Cl-rich Al component b.) Al-oxide containing Cl and c.) Al matrix. Each pixel is the equivalent of 1.56 nm. ................................................................. 126

6-33  a.) STEM ADF image of film implanted 1 \times 10^{16} \text{Cl/cm}^2 and polarized in 50 mM K$_2$SO$_4$ in plan-view made via FIB. Region labeled 1 is a 300 by 300 nm area selected for AXSIA. b.) Spectrum image (RGB overlay) showing two components, Al and Al w/Ga and no chlorine components. Each pixel is 3.125 nm. .................. 128

6-34  a.) STEM ADF image of film implanted 5 \times 10^{16} \text{Cl/cm}^2 and made in plan-view using FIB. The red area (labeled 1) is a 300 by 300 nm region used for AXSIA. b.) Individual spectrum component images for component spectra, red=Al, green=Cl-rich Al, blue=Al and aqua=Ga. c.) RGB overlay spectrum image (2.34 nm/pixel). d.) Spectrum image for Cl-rich Al component showing larger clusters away from boundaries. ................................................................. 130

6-35  a.) STEM ADF image of film implanted 5 \times 10^{16} \text{Cl/cm}^2 and made in plan-view using FIB. The red area (labeled 1) is a 300 by 300 nm region used for AXSIA. b.) Individual spectrum component images for component spectra, red=Al, green=Cl-rich Al, blue=Ga and aqua=Al-Si contaminant particle. c.) RGB overlay spectrum image (2.34 nm/pixel). d.) Spectrum image for Cl-rich Al component showing larger clusters away from boundaries. ................................................................. 132
Spectrum images for individual components from AXSIA results in Figure 6-34. 

a.) Al with some Ga from FIB  
b.) Ga from FIB decorating the grain boundaries and  
c.) Cl-rich Al showing up as larger clusters and segregated away from boundaries. .................................................................

6-37  
a.) STEM ADF image of film implanted 5 x 10^{16} Cl/cm^2 and polarized in 50 mM K_2SO_4. Sample was prepared via conventional sample preparation in contrast to the plan-view polarized samples seen in Figures 6-34 and 6-35. The red area (labeled 1) is a 300 by 300 nm region used for AXSIA.  
b.) Spectrum component image for Cl-rich Al phase (3.125 nm/pixel).  
c.) Individual component spectra, color coded, and overlay of spectra.  
d.) RGB overlay spectrum image; green=Cl-rich Al phase and red=Al matrix. .................................................................

6-38  
Three BF images from the sample implanted 5 x 10^{16} Cl/cm^2 and polarized in 50 mM K_2SO_4 and made using FIB. Moiré fringes and precipitates present with possible effect of amorphization from FIB preparation. .................................................................

6-39  
BF images from polarized sample implanted 5 x 10^{16} Cl/cm^2 showing various types of diffraction contrast observed. .................................................................

6-40  
SAD patterns from FIB plan view of Al film implanted 5 x 10^{16} Cl/cm^2 and polarized showing weak reflections of Cl. .................................................................

6-41  
Series of DF images captured by rotating aperture around central spot. Several precipitates appear at different tilts which denote the value of AXSIA technique and the ability to “see” all precipitates with one data collection. .................................................................

6-42  
a.) BF TEM image of polarized and implanted sample.  
b.) – e.) DF images at different rotational tilts showing various precipitates for comparison to diffraction contrast observed in BF image. .................................................................

6-43  
Schematic showing possible imaging depths because precipitates are seen both along boundaries, yet also depleting boundaries in AXSIA results. Schematic demonstrates the dependence of region being characterized and sensitive depth profile. The orange, green and red arrows in a.) when translated to a particular depth profile in b.) show that Cl concentrations can vary from 2-10 at% over a 20 nm thickness difference. .................................................................

6-44  
a.) AXSIA results from sample implanted 5 x 10^{16} Cl/cm^2 with Cl-rich spectral image showing depletion of Cl along the grain boundaries  
b.) AXSIA results from sample implanted 5 x 10^{16} Cl/cm^2 with Cl-rich spectral image showing precipitates of Cl along the grain boundaries. Proposed phenomenon in Figure 6-43 is an effect of imaged areas differing in thickness. .................................................................

7-1  
RGB spectrum image overlays of aluminum film implanted with 5 x 10^{16} Cl/cm^2 at 35 keV. Red = Al, Green = Al-Cl for both.  
a.) As-received, before anodic polarization, with image enlarged to equate with scale in 7-1b, blue = Al-oxide.  
b.) After anodic polarization to 60 mV below pitting potential, blue = Al-oxide w/chlorine. .................................................................

A-1  
STEM ADF image (top left) and resulting spectrum image (top right) with component spectra for sample implanted 5 x 10^{16} Cl/cm^2. .................................................................
A-2 STEM ADF image (top left) and resulting spectrum image (top right) with component spectra for sample implanted 7 x10^{16} Cl/cm^2. Arrows point to clustered regions of chlorine observed with the higher fluence and not with Al implanted 5 x10^{16} Cl/cm^2. ................................................................. 159

B-1 TEM BF of 3 mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV as-received (unpolarized). Diffraction contrast from boundary. ......................... 161

B-2 TEM BF of 3 mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV as-received (unpolarized). Diffraction contrast from different regions along boundary. Top right image near area scanned for AXSIA in Figure B-3. ......................... 162

B-3 a.) STEM ADF of 3 mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV as-received (unpolarized) with 300 by 300 nm area selected (labeled 1) for AXSIA. Arrows pointing to voids. b.) Spectrum image (2.34 nm/pixel) from boundary (green) resultant component. c.) AXSIA results, individual component spectra and RGB overlay spectrum image. ................................................................. 163

B-4 TEM BF images of 3mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV and polarized below pitting potential. Rectangular inclusions observed along boundaries. ................................................................. 164

B-5 a.) STEM ADF of 3 mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV and polarized with 400 by 400 nm area selected (labeled 1) for AXSIA. b.) Spectrum image (3.125 nm/pixel) and component spectra from boundary (green) resultant component. c.) AXSIA results, component spectra overlay and RGB overlay spectrum image. ................................................................. 165

B-6 a.) STEM ADF of 3 mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV and polarized with 400 by 200 nm area selected (labeled 1) for AXSIA. b.) Individual component spectra and spectrum image (1.56 nm/pixel) from boundary (green) resultant component. c.) AXSIA results, component spectra overlay and RGB overlay spectrum image. ................................................................. 166
CHAPTER 1

INTRODUCTION

1.1 DISSERTATION OVERVIEW

The emphasis of this dissertation is pitting corrosion, which is a complex process that occurs in many metals. Aluminum is model system for these metals and forms an especially strong protective layer of Al₂O₃. While numerous parameters must be considered, the exact mechanism behind the initiation of pitting corrosion is not very well understood. It is known that the presence of the compact, thin oxide (10-100 Å) is responsible for the corrosion resistance in passive metals [1-3]. Pitting corrosion is characterized by a local destruction of this protective surface oxide layer allowing metal dissolution and pit formation. Chloride is a well known aggressive species that causes pitting in aluminum and is commonly used to induce breakdown of the passive oxide [3-11]. During the initiation stages of pitting corrosion, many processes that lead to this breakdown are dependent on composition and structure of the oxide [1]. The focus of this study is thereby to gain an understanding in the process of corrosion pit initiation in aluminum by investigating with advanced techniques employed in the transmission electron microscope (TEM).

Since the fundamentals behind pitting corrosion initiation are unclear, they are the basis for funding a Basic Energy Science (BES) program at Sandia National Laboratories in Albuquerque, NM. This dissertation is a part of that program and includes work
performed in collaboration with a group of researchers with varying backgrounds at Sandia, in efforts to collectively learn more about the initiation process in pitting corrosion. The emphasis of the work presented here will concentrate on transmission electron microscopic applications to characterize pitting corrosion in high purity aluminum. Our ultimate goal is to couple TEM with other analytical techniques employed within the BES group (electrical measurements, polarization curves, atomic force microscopy and secondary ion mass spectrometry) to characterize pitting corrosion during its initiation stage in high purity aluminum.

The motivation for utilizing transmission electron microscopy lies with its ability to characterize nanostructures at the atomic level and thereby providing important details that are otherwise neglected. Localization of pitting corrosion is required in order to capture the initiation stage and characterize it using transmission electron microscopy. This was achieved by using methods that reduced the size scale needed for corrosion. Samples were used in this study that confined corrosion to a smaller lateral area which permitted better location and characterization using TEM. Our efforts were also directed towards utilizing sophisticated microanalysis tools at the nanometer scale with these samples.

1.2 Pitting Corrosion: Background and Motivation

Aggressive anions like chloride, present in many environments, are the driving force behind the attack of passivating thin oxide layers present on metals such as aluminum. Such an attack of the surface leads to intense localized metal dissolution and
is the preeminent feature of pitting corrosion [14], but the process of pitting corrosion is very complex and can be divided into four different stages:

1. processes occurring on the surface of the passive film and/or at the boundary of the passive film and solution;
2. processes occurring within the passive film;
3. the initiation of metastable pits and their growth;
4. stable pit growth above a critical pitting potential [1].

Our interest lie with the first two processes which define the initiation stages of pitting corrosion.

The growth and propagation stages of pitting corrosion are widely studied [12, 13], but the initiation stages of pitting appear to be both unpredictable and unpreventable. This unpredictability shows the lack of understanding of the processes involved. The emphasis on the initiation stage has been limited by the length scale of the underlying processes of pitting corrosion occur is much smaller than the length scales investigated for pit initiation.

The significance in understanding the initiation stage of corrosion pitting comes from the realization that pitting corrosion is a dominant factor in the life limiting degradation process in many materials and systems. For example, pitting corrosion leads to the failure of many components in microelectronic and micromechanical devices. Interests also lie within the airline industries due to the significant aging of Al-alloys used in aircraft and similar Al alloys are also being reintroduced into many automotive applications [1]. Impacts made on understanding pit initiation will lead to an increased accuracy in lifetime predictions and reliability. Such an understanding could lead to new
corrosion monitoring schemes as well as corrosion inhibition schemes, including new alloy chemistries with microstructures resistant to pitting corrosion. Overall, an understanding of the pit initiation process will make an impact on many of the existing efforts in Al corrosion studies.

1.3 **ROLE OF CHLORIDE**

The critical event that occurs in the oxide that leads to the onset of pitting is dependent on the presence of chloride (Cl\(^-\)). Several models exist for the breakdown of passivity. These include a penetration mechanism [5], a film breaking mechanism [15, 16] and an adsorption at the oxide surface mechanism [17, 18]. Many models consider the adsorption of chloride ions on the surface of the oxide, followed by penetration of Cl\(^-\) through the oxide film and localized Cl\(^-\) assisted dissolution of aluminum at the metal-oxide interface [19]. Other considerations include adsorption of Cl\(^-\) which facilitates oxide breakdown and prevents the repair process of the oxide thereby resulting in pitting [9].

The exact role of interactions between Cl\(^-\) and the oxide in pitting corrosion remain unclear [15, 20, 21]. Many theories stand reason for pit initiation but have not been analyzed or confirmed because the current tools available for characterization do not meet the required nanometer length scale for which pits initiate. Therefore, understanding the role of chloride in pitting is a primary goal in this dissertation, with an emphasis to characterize Cl\(^-\) with new and innovative microanalysis tools.
1.4 Scientific Approach

Past analytical tools used in pitting corrosion investigations are not capable of quantifying the presence of Cl\textsuperscript{−} with the required spatial resolution. The localized sites for pit initiation occur on a much smaller spatial scale than observable with current spectroscopy techniques [22-25]. One approach involved in this dissertation uses specimens with greatly reduced length scales to confine pit initiation events to specific sites that can be reliably observed then characterized with transmission electron microscopy. The capability to characterize aluminum at different stages of polarizations by means of manipulating sample geometry offers a new emphasis in pitting corrosion initiation studies.

Aluminum samples typically undergo anodic polarizations in media containing chloride and as a result pitting corrosion occurs. Changes most likely occur within the passive oxide that allows Cl\textsuperscript{−} contributions in the process that breaks down the oxide film. Concentrations of Cl\textsuperscript{−} incorporated into the oxide through adsorption or penetration mechanisms is also very low and thereby contributes to the difficulty for quantification and characterization with the different analytical techniques. Another means to better analyze chloride in such investigations is achieved by introducing Cl\textsuperscript{−} into the specimen, with well controlled and defined concentrations, e.g. by ion implantation.

The expectations from using the two approaches, both unique sample geometry and chloride ion implantation, is that in combination with more sophisticated microscopic and spectroscopic techniques, the role of Cl\textsuperscript{−} in pitting corrosion should be better understood. The work presented in this dissertation is based on an experimental approach to develop novel methods to investigate pitting corrosion and will thus provide a
description of different trials and results from three samples geometries, each of which provided striking and promising new results.

1.5 SUMMARY

Due to the complexity of pitting corrosion processes and the difficulties in recording such events, research efforts are focused here on learning more about the initiation process of pitting corrosion. The efforts made in this dissertation incorporate various analytical features of electron microscopy to characterize and determine the effects of oxide chemistry/structure on the initiation of pitting. TEM characterization at the surface of the oxide, within the oxide and at the metal-oxide interface coupled with electrochemical observations offers new microstructural information. Changes that occur in the oxide with thickness and morphology may also depend upon the applied potential, chemical environment (Cl\textsuperscript{−} incorporation, state of hydration) and/or on metal crystallographic orientations. Advanced imaging techniques and chemical analysis performed in the TEM are powerful tools to characterize these changes in pitting corrosion.

The incorporation of advanced electron microscopy techniques is also expected to further enhance other ongoing research efforts in pitting corrosion. Optical microscopy, secondary electron microscopy (SEM), and secondary ion mass spectrometry (SIMS) are just a few characterization techniques currently used. These techniques are available for surface studies and chemical depth profiling, however they do not have sufficient spatial resolution to observe and analyze individual pit initiation sites. The characterization techniques employed here all have near atomic spatial resolution and higher sensitivity
for exploring localized corrosion pit initiation. These include Automated eXpert Spectrum Image Analysis (AXSIA), a newly developed and novel technique that utilizes X-rays from energy dispersive spectroscopy (EDS) to perform chemical and phase identification at the nanometer spatial scale. Such advanced “nano”analysis offers much additional information in characterizing the surface oxide, that when successfully employed, can provide new insights otherwise not observed.

1.6 REFERENCES


CHAPTER 2

SAMPLE PREPARATION

2.1 INTRODUCTION

Three sample configurations have evolved throughout this study of corrosion pit initiation in high purity aluminum. In the pursuit to understand the science behind the initiation stages of pitting, the length scale at which pitting corrosion is investigated must be reduced. Aluminum needle geometry was thereby first explored, which resembled the shape and dimensions of a sharp field emitter tip. Another approach to reduce the dimensionality of the problem was achieved with aluminum flat samples that consisted of cross-sectional bulk Al wires embedded in epoxy. The final sample geometry analyzed in this study was Al thin films grown on Si/SiO₂.

Sample geometry resulting from these three configurations, each unique in their own way, contribute to reducing the length scale and allowed the initiation stages of corrosion to be examined. The use of Al needles, with an applied field concentrated at a sharp tip, localized corrosion to that particular reduced area as a result of a geometric field enhancement effect demonstrated in Chapter 4. The needles are also initially electron transparent, which allows the specimen to be imaged in the microscope both before and following corrosion experiments. The bulk Al wires (flat geometry) initiates pitting corrosion on individual wires at a reduced scale based on their small diameters. Advanced sample preparation using focused ion beam technology (FIB) allowed TEM cross-sections to be made at specific sites such as corrosion pits. Al thin films further
advanced the study of corrosion pit initiation by utilizing a microcapillary test cell that limited pitting corrosion to a confined surface area.

This chapter will discuss sample preparation techniques for the different geometries. Sample preparation for the TEM, including conventional and focused ion beam techniques, will also be explained.

2.2 **Aluminum Needle Geometry**

Sharp needles with tip radii below 100nm can be produced by electrochemically etching metal wires [1]. Samples were fabricated by electropolishing high purity (99.995%) Al wire. The initial diameter of the wire was 200 μm. A solution of 20% perchloric acid, 80% methanol was prepared and maintained at a constant temperature (approximately -30°C) using a dry ice/methanol bath. An electrical cell is created by connecting a platinum electrode in the perchloric/methanol solution and an Al wire to be polished to an external AC voltage supply. A schematic for the polishing set up is given in Figure 2-1. A potential between 14-18 V AC was applied to the aluminum wire of initially uniform diameter. The sample was slowly dipped in and out of solution while the metal etching rapidly progressed. The wire continuously thinned during the dipping process until it eventually broke off. It was immediately rinsed in methanol so that any remaining etching solution on the needle would be rinsed off. The final geometry consisted of an Al needle with a smooth surface and a radius that ranged between 40-150 nm. The resulting needle was also typically single crystalline at the tip.

The electropolished needles were exposed to 50% HNO₃ solution for one minute after preparation to strip away the oxide grown in solution and rebuild a new, uniform
5nm native oxide. This step was necessary to maintain consistency. A summary of the needle preparation process is given in Figure 2-2.

**Figure 2-1:** Schematic of electropolishing set up for Al wires.

**Figure 2-2:** Flow chart summarizing Al needle preparation for TEM samples.
The time required to fabricate an Al needle is very short, 2-3 minutes, which enabled multiple samples to be made. After being electropolished, an Al needle is electron transparent and ready to be characterized in the TEM. A specialized TEM holder was machined to support the base of the Al needle which required no additional TEM preparation steps. The holder fits both the Philips CM30 and FEI Tecnai microscopes. The major advantage for this type of sample geometry is the flexibility to examine a sample in the TEM prior to any electrochemical tests and/or after any tests without destruction or damage to the sample. The Al needles were made with the intent that a single sample could be prepared fast, subjected to a corrosive environment, and still have the ability to be viewed in the microscope at any desired time. As a result, multiple samples were characterized and a consistent comparison amongst samples was possible.

It is extremely difficult to reproduce two identical Al needles and therefore the preparation of this sample geometry was often considered an “art” and not a science. Much complexity is attached to the electrochemical etching of metal to form sharp needles. Numerous variables such as dipping technique, temperature, solution concentration and mixing, all affect reproducibility. Inconsistency in sample size was the major disadvantage with the needle geometry. Radii ranged from 50-250 nm and were classified as sharp to blunt respectively. Size discrepancies also aided in variable electrochemical behavior. Pitting potentials proved to be dependent on the radius of the needle and it was assumed that exposed surface area also influenced pitting potential. As both parameters are important and contribute to the determined pitting potential, the variability in the results ultimately directed the study toward the flat geometry attained with high purity aluminum wires.
2.3 **BULK ALUMINUM WIRES**

Aluminum wires, with an initial diameter of 125 μm, were embedded in an epoxy matrix and became the next approach for pit localization in this study. Either a single Al wire or an array of wires was embedded in epoxy. A schematic of this sample geometry is given in Figure 2-3. The wires were first prepared by applying a mechanical, 1 μm diamond polish, to the surface before subjecting the surface to any corrosion experiments. Damage resulting from the mechanical polish made it difficult to distinguish between pitting sites and surface irregularities, which led to an additional preparation step for this geometry. One end of the wire was cut flush with the epoxy surface and then electropolished in a similar manner as the needles. The other end of the wire was left extended from the backside of the epoxy and was available for the required electrical connections needed to perform the corrosion experiments. The electropolish made to the Al surfaces used a 20% perchloric acid, 5% glycerol and 75% methanol solution at -30°C.

![Figure 2-3: Schematic of bulk aluminum wires, flat samples. Top surface is electropolished and treated to HNO₃ for one minute. a.) Array of Al wires embedded in epoxy. b.) Single Al wire embedded in epoxy. Both showing the wire extended out the back side of the epoxy for electrical contact.](image-url)
followed by a methanol rinse and treatment to 50% HNO₃ solution for the formation of the initial oxide. A voltage of 20 V AC was used for electropolishing the aluminum wires. The additional surface electropolish resulted in an initial smooth surface and uniform oxide for reproducible corrosion experiments.

The samples could then be subjected to various corrosive environments and/or electrochemical experiments before further TEM preparation. Unfortunately, the sample must be destroyed in order to prepare a successful TEM cross-section with this geometry. This is a disadvantage in comparison to the Al needles which remained in tact for microscopy. TEM cross sections for the flat geometry were made using a dual-beam scanning electron (SEM)/focused ion beam (FIB) microscope. The FIB is considered a unique tool for TEM sample preparation, in particular for this geometry, because it permits site-specific samples to be made. Many cross-sectional TEM samples were made where the FIB sectioned through a pitted area of the surface.

2.4 Aluminum Thin Films

High purity aluminum films were deposited on SiO₂/Si substrate by electron-beam evaporation. The films were grown at room temperature at a rate of 1 Å per second until approximately 2000 Å thick. A uniform 4-5 nm surface oxide was formed by exposing the film to ultra high purity oxygen after growth. The resulting films were polycrystalline with columnar grains ranging in size from 50 to 150 nm.

The initial microstructure of the thin films is consistent. Chloride was incorporated into the thin films by ion implantation as discussed in greater detail in Chapter 6 and corrosion localization was achieved by polarizing a reduced area using a
microcapillary test cell approximately 1 mm in diameter. TEM samples were prepared from the implanted thin films through conventional techniques and also with the FIB in both cross-sectional and plan-view.

2.5 TEM Sample Preparation

The ultimate goal of this project is to gain further insight into the initiation stages of pitting corrosion by means of advanced characterization techniques in the electron microscope. Therefore, thin TEM samples are needed from all three geometries discussed. The Al needles are electron transparent and because a special TEM holder was available for the microscopes, no additional preparation steps were needed. TEM samples were made from the Al wires and the Al thin films both in cross-sectional and in plan-view. Samples were made from traditional methods, referred to as conventional TEM sample preparation or from new techniques utilizing a SEM equipped with a liquid metal gallium ion gun, referred to as a focused ion beam (FIB) microscope. Both preparation techniques will be briefly covered in the following sections. The FIB offers site-specific sample preparation for TEM, which is often unattainable through conventional techniques.

2.5.1 Conventional Sample Preparation Techniques

Conventional TEM sample preparation techniques were employed for the Al thin films. Cross-sectional samples were made by bonding two film surfaces together with epoxy and then slicing into individual samples that could further be thinned [2]. The cross-sections were mechanically thinned and then dimpled. Final thinning was
performed used a precision ion polishing system (PIPS) [3]. Unfortunately, the nature of the metal film’s thickness being relatively small in comparison to the SiO₂/Si substrate, did not allow for successful preparation. The thick substrate thinned at a rate relatively faster than the metallic thin film, even when low inclination angles (<5°) were used. Ion milling could therefore not be successfully manipulated to thin the sample for TEM. TEM results demonstrated that the Al film peeled away from the substrate with very little thin area existing, especially of the surface oxide.

Conventional plan-view samples were however successfully made. An area 3 mm in diameter was cut using an ultrasonic diamond cutter. The sample was then attached face down to a stage so that it could be mechanically polished from the backside. The top surface of the aluminum film is placed face down in efforts to preserve the top surface, the area of interest for characterization in the TEM. The sample was mechanically thinned to 100 μm. It was then placed on a stage and dimpled to approximately 10 μm. The final step performed included ion milling from the backside using a single ion gun so that the top surface of the plan-view sample was not thinned and was also protected in the PIPS by its holder. The sample was carefully monitored while it was being thinned in the PIPS. Ion milling was carried out at low angles so the material was removed relatively slowly [2, 3]. Fringes were eventually observed and corresponded to the final thinning of the substrate material. Following the appearance of a second set of fringes, a small hole developed and the ion milling was stopped with the sample ready for characterization in the microscope.
Several conventional plan-view samples were made from the different Al thin film samples. There were no site specific requirements for the unpolarized material, however FIB plan-view samples were first attempted for the polarized material because the reduced area of interest would be difficult to center for TEM preparation. Undesired effects from the Ga occurred during the process of FIB TEM sample preparation in plan-view. These will be discussed in detail in Chapter 6, yet careful precautions were taken to make conventional TEM plan-view samples from the polarized aluminum thin films.

2.5.2 Focused Ion Beam

A FEI DB-235 dual-beam FIB/SEM available at Sandia National Laboratories (Figure 2-4) was used to prepare many samples for the TEM. Prior to loading the sample into the FIB, the sample is first coated with a thin layer of carbon in order to gain contrast in the TEM against the oxide layer. For the Al wires embedded in epoxy, a thin layer of gold-palladium was also deposited to avoid charging problems that occurred from the

![FEI DB-235 dual-beam FIB/SEM](image-url)
epoxy. The sample was then placed in the FIB and imaged in SEM mode. After the surface was examined in SEM mode, an area of the Al surface was selected for TEM sample preparation.

The area of interest in a polarized sample included corrosion pits and adjacent areas. For samples not subjected to any polarization scans, this area may be arbitrarily chosen. Once a desired area is selected for TEM preparation, electron beam platinum is deposited followed by deposition of ion-beam platinum onto the particular area of interest. This step of the preparation process protects the surface from any damage during ion milling with the Ga beam.

A thin area typically 12-20 μm long by 2 μm wide is chosen for the TEM sample. Areas adjacent to the sides of this election are milled away using the ion beam. Further specimen thinning is then carried out using a successively finer (i.e. lower current) ion beam, until the sample is electron transparent [4]. Indication of the sample’s electron transparency is made when contrast of the FIB TEM slice is lost in the secondary electron image. The sample is then detached from the bulk material using the ion beam. The bulk material with the TEM sample is removed from the SEM/FIB and the TEM sample is pulled away from the bulk material and placed onto a TEM carbon coated grid.

Figure 2-5a is a schematic representing the process. The area of interest in this figure is represented by the red rectangle. The cross-hatched areas are regions milled away using the ion beam. Further thinning is then performed once this area is removed and milling continues inward toward the center of the red rectangle until the sample is electron transparent. An SEM top down image of a thinned area is also presented in Figure 2-6.
Figure 2-5: a.) Schematic showing the use of FIB for TEM sample preparation. The red rectangle (20μm x 2μm) is the area of interest for the TEM sample. The grid regions adjacent to this area are milled away using an ion beam. The sample is further thinned by milling toward the center of the area of interest until the sample is electron transparent. b.) Representative TEM cross section of sample after the sample is placed on a carbon film TEM grid demonstrating the various layers present.

Figure 2-5b is a schematic of a typical TEM sample in cross-section prepared using FIB. FIB cross-sections were successfully made for both the Al wire and thin film geometry. Site-specific samples were made and deemed to be the greatest advantage of FIB sample preparation. The FIB is destructive to the sample prohibiting it from future use or experimentation. For example, a TEM sample and analysis could be made from the material, but as a result of the FIB processing for TEM, would not be available for polarization and further TEM sample preparation from the same material.
Although sample preparation is more tedious and time consuming, plan-view samples can also be made using the FIB [5]. A novel technique was developed to thin a plan-view sample in the FIB while preserving the top surface. A larger area, the desired area of interest for plan-view microscopy, is first coated with platinum in the FIB. Two trenches are then cut at a large angle along each side of this area. The sample is then spot welded onto a microprobe using electron beam deposited Pt. It is lifted away from the bulk material and placed onto a TEM sample grid, via spot welding, using the FIB. The TEM grid and sample are then rotated 90° onto its side and thinned from the back side using the ion beam. The sample is thinned until contrast again disappears. The TEM sample is then assumed to be electron transparent and removed from the FIB, ready for characterization in the TEM.

2.6 SUMMARY

This study resulted in the evolution of three sample geometries. Initial studies focused on the Al needles because they could be examined in the TEM prior to testing and examined again afterward. The needles also provided a small surface area with a
sharp tip that localized pitting corrosion to that area. The needles presented many problems discussed in Chapter 4, including inconsistency in electrochemical behavior, and imaging concerns such as contamination and radiation damage that could not be resolved in the available microscope.

Further studies then investigated Al flat samples from bulk wires for pitting corrosion. Sample preparation could be site-specific with this geometry; unfortunately preparation time is longer and destructive, allowing each sample to be examined only once, typically after any electrochemical testing. A reference from the same sample prior to testing was not available when using FIB for sample preparation, except for any information gained from the SEM before FIB preparation.

It was found that the area subjected to polarization for the Al wires was too large to predict where initiation sites would occur. It was also observed that the microstructure varied among wires, so the Al thin film geometry was developed. This final geometry provided a consistent initial microstructure and allowed localization of corrosion pitting sites by using a well designed microcapillary test cell.

The three sample geometries were implemented into various electrochemical experiments with the intent to localize the pitting site so it could be characterized in the TEM. Each geometry offered unique features to aid in this type of investigation. Conventional sample preparation techniques and also FIB sample preparations were used to prepare TEM samples from the different geometries. The following chapters will review the analytical and characterization techniques employed in the TEM and will also present data from each of the sample geometries.
2.7 References


CHAPTER 3

EXPERIMENTAL TESTS AND CHARACTERIZATION TECHNIQUES

3.1 INTRODUCTION

Experimental tests were performed to electrochemically induce pitting corrosion in the aluminum samples. Electrochemical tests that used a chloride-containing electrolyte such as NaCl$_{aq}$ served as a medium to introduce Cl$^-$ into the samples, while electrolytes free of Cl$^-$ were used during experimental tests for the thin films implanted with Cl$^-$. Anodic polarization scans comprise the experimental tests employed on the different aluminum sample geometries and will be discussed in this chapter.

Transmission electron microscopy is the tool predominately used in this work to investigate changes in microstructure and chemical content that accompany the early stages of pitting corrosion in high purity aluminum. A few studies did include characterization or microanalysis in the electron microscope [1-3], but they did not focus on changes to the oxide layer upon polarization and the role of Cl$^-$ in pit initiation. The research efforts of this project tie several goals to microanalysis in an attempt to answer questions concerning corrosion pit initiation:

- What is the structure of the oxide and how thick is it?
- What changes in the oxide occur as a result of polarization?
- What is the chemistry in, near and away from a pit?
- How is the Cl$^-$ distributed?
- Does the presence of Cl$^-$ in the oxide enhance pitting susceptibility?
To answer these questions, investigations with high spatial resolution have to be made.

The available techniques with such a high spatial resolution include:

- bright field/ dark field image pairs (BF/DF),
- energy filtered jump ratio imaging,
- electron energy loss spectroscopy,
- spectrum imaging using energy dispersive spectroscopy

For a successful interpretation, the automated expert spectral image analysis (AXSIA) technique was an important tool for microanalysis.

Transmission electron microscopy was used to examine the Al substrate, Al-oxide interface and oxide structure. Basic techniques along with advanced techniques including microanalysis at the nanometer-scale using EDS were employed to investigate the pit initiation process in aluminum. Discussion of these techniques will be presented following information about the experimental electrochemical tests used in this research.

### 3.2 ELECTROCHEMICAL TESTING

Two types of electrochemical tests were performed on the Al flat samples to initiate corrosion. These tests are defined as potentiodynamic pitting experiments and induction time experiments. Both tests were considered in determining the pitting potentials for pit initiation in the different geometries presented. A distribution of pitting potentials existed which may be a result of local variations in the properties of the oxide or underlying metal microstructure. Specific defect structures and variations in thickness are minimized by reducing the sample area available to initiate corrosion. The electrochemical tests discussed in this section measure current-voltage relationships that
may, combined with microanalysis, correlate pitting potential to other important parameters, such as defects within the oxide, near the metal-oxide interface or within the underlying metal.

3.2.1 **Al Needle Experiments**

The Al needles, chosen for their unique geometry, were the first samples investigated in this work. They were characterized in the TEM prior to any electrolytic exposures in order to learn the initial structures associated with this sample geometry. They were then immersed in different electrolytes, including NaCl$_{aq}$, without polarization for specified periods of time. The needles were then subjected to potentiodynamic polarizations to determine the field enhancement effect associated with this geometry. These experiments were performed on both sharp Al needles (radii < 150 nm) and also on blunt, dull electropolished wires exhibiting no sharp edges.

3.2.2 **Potentiodynamic Pitting Experiments**

Experiments conducted where a potential is applied to the sample and increased at a constant rate while exposed to an electrolytic solution are referred to as potentiodynamic pitting experiments. The sample is allowed to sit at open circuit potential, where no current flow is measured to or from the reference electrode. After one minute of exposure, the open circuit potential is determined, and a bias is then applied and increased at a constant scan rate. The sample’s anodic potential increases, becoming more positive, from the initial open circuit potential as a result of current flow effects at or near the anode surface [4]. The potential difference between the anode and a
reference electrode is measured along with the resultant current flow. This current, measured at a platinum counter electrode, is recorded and then plotted versus potential.

Current-potential data from a typical potentiodynamic pitting experiment is represented in Figure 3-1, where the corrosion current is plotted against applied potential. For this example, the sample was electropolished and exposed in 0.05 M NaCl solution at 25°C, open to ambient air, for 3600 seconds. The open circuit potential was

![Figure 3-1: Current-potential data from a potentiodynamic pitting experiment with important regions labeled. A constant potential scan rate (ex. 0.2 mV/s) is applied to the sample while being exposed to 0.05 M NaCl solution.](image-url)
determined, (e.g. approximately -1.25 V versus the Ag/AgCl reference electrode), and a
potential scan was then run at a constant scan rate of 0.1667 mV/sec until the current
reached a set current limit of 1 μA, at which the applied potential was removed. Specific
regions of differing behavior can be identified from the data. At low potential and current
the oxide is present in a passive regime where the current density is extremely low.
Current and potential both increase above this region and eventually transient increases in
the current are observed. These transients have been noted as evidence of metastable pit
initiation [5]. The pitting potential is quickly reached above this potential, from which
stable pit growth occurs in the sample, indicated by a persistent high current density. The
pitting potential is defined as the potential where the stable, high current density first
initiates.

This type of potentiodynamic scan provides information regarding the state of the
sample throughout the various stages leading to stable pitting. The current can be closely
monitored while the test is in progress, permitting the test to be stopped at any desired
time enabling the samples to be examined at various stages of pitting corrosion.
Attempts were made to remove the applied potential just before a sample reached the
“anticipated” (predicted based on previous results) pitting potential. Attempts were also
made to remove the applied potential during the metastable pit initiation regime, while
for other experiments, the applied potential was removed after stable pit growth had
begun. The ability to prepare and analyze the samples at each of these different stages
allowed for the development of a more comprehensive picture of the entire pitting
process.
3.2.3  **INDUCTION TIME EXPERIMENTS**

A second type of electrochemical test briefly employed on the Al flat samples was the induction time test, which is demonstrated in Figure 3-2. This test is much simpler to perform yet more difficult in isolating a particular corrosion event. The test applies a constant potential to the sample for a given length of time (1 hour for test in Figure 3-2) while submerged in 0.05 M NaCl\(_{aq}\) solution at room temperature. Current is measured as a function of time for the applied potential. Current transients observed as random peaks correspond to the formation of metastable pits in the sample. Often, multiple peaks were observed, representing multiple pitting sites or repeated metastable initiation at a single site [6].

This type of electrochemical test was only employed for a few samples because considerably less data was available to accurately predict the induction time for pitting. The working aluminum electrodes were also polarized at potentials above the average pitting potentials for this type of experiment. The potentiodynamic pitting test changed
the potential at a constant rate up to pitting, which allowed characterization in regions prior to pitting and served as a valuable technique for controlling the pit initiation process.

3.2.4 SUMMARY OF EXPERIMENTAL TESTS

Al needles, Al flat samples from bulk wires and Al thin films were each electrochemically tested by the techniques described above. Induction times were also measured for several of the mechanically polished samples subjected to 50 mM NaCl\textsubscript{aq} at potentials near and above the recorded pitting potentials. Many samples were subjected to induction time experiments yet localization of pitting corrosion was less predictable with this type of experiment and often resulted in stable pit growth. Potentiodynamic pitting experiments consequently proved to be a better designed experiment and a well controlled test to electrochemically induce pitting. The applied potential could be ramped to a desired value and then removed prior to the expectation of pitting or just after pitting begins. This technique was therefore chosen as the primary means to initiate pitting in the work presented in this dissertation.

The well defined and controlled electrochemical tests described in this section combined with a reduced lateral area exposed to the electrolyte allowed distinct regions to be identified for microanalysis. The majority of efforts presented in the chapters to follow will primarily use the potentiodynamic pitting experiment in attempts to induce pitting corrosion and spatially confine it for characterization in the microscope.
3.3 **Scanning Electron Microscopy**

Higher spatial resolution and cross-sectional information from the sample is achieved with TEM compared to morphology and surface information available with scanning electron microscopy (SEM). While the majority of characterization was performed in the TEM, SEM was utilized for surface analysis and to obtain fast and local information about the samples.

The population of needles fabricated was large and easily fabricated due to the quick nature of the sample preparation process. SEM was employed to obtain an initial characterization of the needles prior to exposure to the electrolyte. The needles were then subjected to electrolyte exposures and potentiodynamic pitting experiments. Basic imaging using secondary electrons was sufficient to identify approximate tip radii and surface products/reactions resulting from any exposures or tests. SEM was useful for quick analysis with the needles and will be presented in many of the preliminary experiments and results.

3.4 **Transmission Electron Microscopy**

The central focus of this dissertation used advanced characterization techniques in the transmission electron microscope to elucidate structural and chemical changes in the passive oxide that accompanies pitting corrosion in high purity aluminum. Advanced techniques demonstrated in the following sections will include jump ratio imaging, automated expert spectrum image analysis (AXSIA) and electron energy loss spectroscopy (EELS), along with complementary conventional imaging techniques performed in the TEM. The ability to isolate the pitting process at controlled locations...
and then characterize the resulting changes through use of different image and analysis techniques is the major innovative efforts of this research project.

X-ray microanalysis in the electron microscope coupled with other analytical techniques (secondary ion mass spectrometry (SIMS), electrochemical data, atomic force microscopy, optical microscopy, electrical measurements) has proven to be a powerful tool in understanding what changes, both structurally and chemically, are occurring in the sample as a result of polarization. The techniques discussed in this chapter provide a means for determining the effects of the oxide chemistry and structure at the surface of the oxide, within the oxide and at the metal-oxide interface. Characterization of the oxide thickness and morphology contributes to understanding the dependence of applied potential, chemical environment (Cl⁻ incorporation, state of hydration) and metal crystallographic orientation in the role of corrosion initiation.

Three transmission electron microscopes were used in this study along with a dual beam SEM/FIB for sample preparation. A Philips CM30 using a LaB₆ source and equipped with a Gatan Imaging Filter (GIF) system was available for characterizing many of the needle samples. This microscope, stationed at Sandia National Laboratories, operates at 300 keV. The FEI Tecnai TEM/STEM also at Sandia later became available in the study for characterizing many of the Al wires and thin films. This microscope is equipped with EDS capabilities and is capable of operating at accelerating voltages of 100, 200 and 300 keV in both transmission and scanning mode. The Tecnai has a field emission source allowing more brightness (signal) during analysis. A JEOL 2010F field emission TEM/STEM equipped with the GIF system was also used at North Carolina State University operating at 200 keV. The GIF system is a powerful tool for TEM
filtered imaging and EELS collection, which was needed for many of the techniques used in this study.

3.4.1 CONVENTIONAL TEM TECHNIQUES

Basic imaging techniques were also employed in the TEM and when combined with additional advanced techniques, more information may be extracted from the material being sampled. Many conventional TEM imaging techniques were employed in this work to acquire information about the sample’s chemistry and crystallography [5]. High resolution TEM is used to identify the oxide and measure thickness. Selected area diffraction was used to confirm the presence of AlCl₃ precipitates, although difficult to identify possible reflections from Cl⁻ due to the low concentrations present and size of the precipitates being a few nanometers. TEM bright field and dark field image pairs will also be presented which help identify the presence of chloride precipitates. While a complementary technique, the dark field image pairs do not give detailed chemical information, which is obtained by using AXSIA.

3.4.2 JUMP RATIO IMAGING

Jump ratio imaging is one technique that utilized the GIF system and coupled with bright field images has the ability to show a 2 dimensional distribution of elements present. Jump ratio imaging is a form of elemental mapping achieved using a narrow energy selecting slit (15-20 eV) in the spectrometer. It is produced by collecting two filtered images in this energy bandwidth at energy loss just before and after an ionization
edge of a particular element of interest. This form of imaging is demonstrated schematically in Figure 3-2.

The procedure for obtaining a jump ratio map involves collecting images with the energy filter set above and below a given ionization edge. The division of these two images and hence the ratio of these intensities, results in a jump-ratio image, or elemental map, where intensity present in the image directly corresponds to the element of that particular ionization edge [7]. Variations in specimen thickness and diffraction conditions do not affect the resulting jump ratio image. This method for mapping elements can be very beneficial. In most bright field TEM images, diffraction contrast can limit the amount of information available. Recording filtered bright field images and forming jump-ratio images assists in distinguishing many elements and/or phases present.

**Figure 3-3:**

a.) Schematic of EELS spectrum for oxygen K-edge demonstrating the energy windows used for constructing an elemental jump ratio image. Two energy filtered images are collected pre (blue) and post (red) edge.

b.) EELS jump ratio image formed on Al cross-section. Division of two energy filtered TEM images (pre-edge by post-edge) results in a jump ratio image for a particular element, in this example, oxygen.
in the form of a spatial elemental map. A spatial resolution of 1 nm can be achieved when performing jump ratio images, which permits detailed analysis of interfaces or thin film structures. This technique was used for several of the Al samples using the O K-edge, Al L-edge and Cl L-edge in both the Philips CM30 and the FEI Tecnai microscopes.

3.4.3 **AUTOMATED EXPERT SPECTRAL IMAGE ANALYSIS (AXSIA)**

A second technique used to characterize the Al and oxide structures in this study is spectrum imaging. Automated expert spectral image analysis (AXSIA) is a recently emerged new tool that analyzes data obtained from microanalysis. This technique is employed in this work for chemical phase identification with excellent spatial and spectral resolution [8-10]. Spectrum imaging, like jump-ratio imaging, uses either parallel EELS detection or EDS collection. Spectrum images formed with the samples explored in this dissertation used X-ray signals for the analyses of data collected in scanning transmission electron microscopy (STEM).

With X-ray collection in STEM, the incident beam is focused to a small probe and scanned across an area of interest in the specimen (Figure 3-4a). Within this area, a matrix of pixels is created where each pixel serves as a spectral data cube and has three coordinates; x and y spatial coordinates and a 1024 channel X-ray spectrum [8]. Conditions are then specified, such as number of pixels and dwell time at each pixel, for the selected area and the scan is started. An EDS spectrum is recorded at each point in the scan; for example, a 256 x 256 pixel scan would record 65,536 full X-ray spectra.
The data can later be processed with advanced software that uses multivariate statistical analysis and principal component analysis [8-11]. This computational process statistically distinguishes the various phases present from the acquired spectra and ultimately transforms the raw data into important and relevant chemical components that are spatially resolved. Figure 3-4b [8] is an example that demonstrates resulting data from an analysis where a summation of the pure component and spectra are presented from a 3-dimensional data cube. Each x and y spatial coordinate is represented by an individual output component. A spectrum image is produced by summing all x and y components with spectral similarities. An elemental map of distinct chemical phases that uniquely identifies the different components based on spectral features is produced. The analysis is processed for the entire X-ray spectrum at each 2-dimensional pixel so that all spectral similarities are accounted for at each x, y coordinate.

Figure 3-4: a.) Schematic of focused electron beam interaction with TEM specimen where data for AXSIA can be collected from either EDS or EELS. b.) AXSIA resulting spectrum image formed from pure individual components and spectra.
In STEM mode, the spatial resolution is not limited by the spectrometer but by the incident probe diameter, which can be 1 nm or less using a field emission source. The advantage of spectrum imaging is that more information provided by the electron/specimen interaction is recorded and any information that may have been lost is now collected, stored and can be later processed. The number of intensity values involved with spectrum imaging is however large and acquisition times may be very long. For a 512 x 512 image using a 1024 channel spectrum, the image size may be 250 MB requiring nearly 2 hours for collection time. Although sampling time is very short at each pixel, some sample drift may occur. The Tecnai microscope can correct for drift during the data acquisition. The major advantage offered with AXSIA is the capability to achieve high spatial resolution (1 nm) along with the ability to detect trace elements and produce very detailed elemental maps from X-ray information. The statistical approach behind AXSIA allows identification of elemental spectral features with lower limits for detection as compared with traditional EDS. It is also capable of discerning between elemental components.

The results from automated expert spectral image analysis can be presented in multiple formats. In this dissertation the data will be presented typically with an annular dark field (ADF) STEM image showing the selected area for analysis. A second area in the image may also be acknowledged which corresponds to an area used for drift correction. The output data from this analysis is given in individual component spectra and corresponding component spectrum images, assigned different RGB values. An RGB composite image of all the individual components may also be given. Individual component spectrum images can also be presented in a format where the pure component
is presented on an intensity scale from dark blue to red, increasing in spectral intensity respectively, for that particular spectrum component. The intensity of this scale is usually normalized with respect to the mean spectrum from the analysis. Throughout the results presented in this dissertation, individual output components are recognized as “phases” or “components”.

A typical area selected for interest and analysis in the aluminum specimens was usually a few hundred nanometers by a few hundred nanometers and included the oxide-Al substrate interface and near surface region. These areas were of particular interest because evidence for pit initiation sites is likely to be found within this region. AXSIA was used to map the distribution of the different chemical constituents (e.g. Al, O, and Cl) and was successful in distinguishing between the aluminum chloride and aluminum oxide components as well as the pure aluminum matrix phase.

### 3.4.4 Electron Energy Loss Spectroscopy

Electron energy loss spectroscopy was also employed briefly in this study. EELS measures the loss of energy from electrons transmitted after interactions with the specimen with the spectrum recorded in either TEM or STEM mode [12, 13]. EELS was used to confirm the presence of Cl⁻ in our samples and an attempt was also made to correlate the EELS signal with contrast observed in STEM Z-contrast images. A Z-contrast image is formed from electron scattering at larger angles that are collected on an annular detector in STEM mode. The component represents Rutherford scattering and has a strong Z-dependence so intensity differences observed comes from Z-contrast not diffraction contrast [5].
The electron beam in STEM mode was focused in spot mode for EELS acquisition. The spot could be translated to a particular area of interest for EELS. For example, the beam may be set on a boundary which is observed in the Z-contrast image showing more intensity. This technique was performed on the implanted aluminum films to spatially correlate intensity with different atomic species (Z).

3.5 **Summary of Characterization Techniques**

Transmission electron microscopy offers opportunities for characterization and microanalysis that can aid in better understanding microstructural changes associated with pit initiation in aluminum. Careful electrochemical testing in combination with microanalysis allowed specific changes in structure and chemical composition to be correlated to electrochemical polarizations. Samples made from the various geometries were subjected to different electrochemical environments and examined using the variety of techniques described above. Jump ratio imaging and spectrum imaging have been very valuable for spatially mapping the oxide and interpreting the oxide structure, while TEM bright field has been beneficial at studying the morphology of the oxide. Dark field images and EELS also provided complementary information about the presence and role of chloride, in particular spatial distribution for both the flat samples and aluminum thin films. These techniques are powerful tools capable of characterizing at the length scale needed for the initiation of pitting corrosion. The techniques discussed in this chapter were successfully employed in this corrosion study. The information provided from TEM demonstrated the role of the chloride species coupled with changes observed in oxide structure for the initiation of pitting corrosion in aluminum.
3.6 REFERENCES


CHAPTER 4

ALUMINUM NEEDLES

4.1 INTRODUCTION

Sharp aluminum needles with radii between 50-250 nm were fabricated and offered differing crystallographic directions. The greatest advantage with the Al needles is that their unique geometry localized the onset of pitting corrosion by defining the area at which pitting events occurred. This was accomplished using an applied potential to the tip which produced a resultant electric field that is, due to geometry, concentrated at the tip radius. The resultant field strength from the applied bias is inversely proportional to the radius thereby enhancing the field strength for needles with sharper radii [1-5]. This field enhancement is the driving force behind the use of the needle geometry in this corrosion study. If correctly manipulated, it is believed that the field strength at the tip could induce pitting confined solely at the tip radius.

Another advantage of the needle tip is that it is electron transparent for TEM studies. Therefore, the desired outcome from using Al needles is to characterize a needle in the TEM, perform an electrochemical polarization to initiate pitting at the tip, followed by further characterization in the TEM. The ability to characterize the same sample throughout a corrosion experiment without destroying it for microscopy is most beneficial. Although the initial investigations of the Al needles were unsuccessful, preliminary results proved the needle geometry is viable for future work. The
microscope available for examining the needles during the beginning stages of this project was the Philips CM30 TEM which operated at 300 keV.

4.2 Experimental

The needle geometry, new and unique to the corrosion study, opened many doors for variations in electrochemical testing and behavior. Initial characterizations of the samples were needed to determine the starting conditions of our material. An aluminum needle is the anode in a corrosion experiment and since it will play a critical role in the pitting process, it is desired to know the shape and surface area of this geometry. The importance of surface area exposed in pit initiation experiments was questioned for the needles, while the assumption made was that a concentrated field at the tip served as a means for localizing corrosion to that area. Therefore, any remaining surfaces exposed to the electrolyte, including areas along the shank of the needle, could be neglected.

It was important to first learn about the needle’s initial microstructure, such as grain size, oxide thickness and morphology, which was done by examining the needles in the TEM. As described in Chapter 2, the needles experienced a one minute nitric etch after being made in order to remove the initial oxide and form a controlled passive oxide. Experimental conditions of this preparation technique were also investigated and will be presented. Corrosion experiments involved subjecting the samples to 50 mM NaCl$_{aq}$ electrolyte and experimenting with various electrochemical tests discussed in chapter 3.

Results will be demonstrated in this chapter for the various experiments described here which further evaluate the needle geometry for employment in this study. Many microscopy problems occurred during the initial investigation attempts and will also be
presented. Independent of the TEM difficulties and other problems associated with the needle geometry, potentiodynamic pitting experiments were also pursued and will be presented. A distribution of pitting potentials was collected in order to characterize the variation in corrosion susceptibility among the needles prior to further characterization in the TEM.

The needle geometry was a novel approach to addressing corrosion pit initiation. Although this geometry ultimately proved problematic for TEM characterization, this approach offered a unique opportunity to investigate certain aspects of corrosion pit initiation. The aluminum needle experiments are included here for completeness, but the results obtained suggested that more traditional flat specimens would be better suited for microscopy investigations.

4.3 RESULTS

Prior to any exposures, the Al needles were smooth, with a uniform surface oxide, 4-5 nm thick for all orientation accessible, and with a radius ranging between 40 and 150 nm as demonstrated in Figure 4-1. TEM of a typical Al needle is represented in this figure where the radius for this particular needle would be defined as approximately 50 nm. A jump ratio image using the O K-edge was made to map the oxide on the needle shown in Figure 4-1c. Taken at higher magnification, the oxygen jump ratio image confirms the uniformity of the surface oxide present on the Al needle. A needle larger in radius and exhibiting similar oxide characteristics is given in Figure 4-2. Smaller needles are generally more electron transparent, yet are more susceptible to beam damage. Larger needles are more substantial in material and take longer for contamination to build
up yet they are not as easily imaged in the TEM. Therefore, compensation in size must be optimized in order to be successfully imaged in the TEM and also remain sharp enough to accommodate field enhancement for pitting polarizations. Regardless, the oxide is uniform and remains the same thickness on needles of both sizes and for all orientations.

The surface oxide present on the Al needle in Figure 4-2 is identified using TEM and jump ratio imaging. A common artifact that can exist in a jump ratio image is demonstrated in Figure 4-2d. The black line at the surface of the needle is an artifact that occurs from a misalignment in the GIF system. This misalignment most likely occurs from a correlation shift between the pre and post-edge images of the element under
investigation, i.e. oxygen for this case. Specimen drift in the microscope contributes to this effect while collection times for the pre and post-edge images can be long enough for sample drift to occur. This allows the two images in the GIF system to become slightly misaligned resulting in the artifact seen here.

Figure 4-2: Al needle at three different magnifications increasing respectively in a.), b.) and c.) to show the oxide. d.) Oxygen jump ratio image. The black line in this image represents a small correlation shift (misalignment) between the oxygen pre and post edge images.

Initial examination of the Al needles in the TEM showed that they were subjected to electron beam damage. A needle that remained in the microscope for a long period of time, with the beam on the specimen, would gradually experience changes in diffraction contrast. These changes were observed for several of the Al needles. Severe radiation damage did result from the electron beam, while localized heating was unavoidable. The needles also exhibited signs of contamination during the initial TEM investigations. Beam damage was unavoidable since the microscope operated at 300 keV and the
displacement threshold of Al is approximately 160 keV [6, 7]. Needles with smaller radii experienced larger amounts of radiation damage compared to needles with larger radii. Contamination problems could have arisen from several sources, including sample preparation, from the microscope itself (column contamination), and possibly from sample storage conditions. The samples were cleaned after being prepared by using a quick methanol rinse; however no additional cleaning steps were taken prior to loading the samples into the TEM. It is possible that an oxygen plasma clean could have remedied this problem.

Carbon contamination is demonstrated in Figure 4-3. This feature was observed a few microns away from the needle tip. Contamination was often observed to migrate along the shank of the needles and build up near or at the tip apex. Several attempts were made to clean the microscope environment including bake outs and replacement of the o-rings on the microscope holder with clean new o-rings. Unfortunately, contamination problems persisted throughout the initial needle studies.

![Figure 4-3: TEM of Al needle approximately one micron from the tip a.) Bright field image of oxide and contaminant cluster. b.) oxygen K-edge jump ratio image. c.) carbon K-edge jump ratio image.](image)
Investigations into the aluminum needles continued in spite of the observed imaging problems in the TEM. The thickness and morphology of the oxide when exposed to an electrolyte and for various times were the focus of the first set of tests. The majority of electrochemical tests done on previous sample geometries used a 0.05 M NaCl\text{aq} solution. Therefore, Al needles were individually exposed to 0.05 M NaCl\text{aq} solution for different periods of time. The exposure times were 30 minutes and one hour.

The Al needle exposed for 30 minutes is shown in Figure 4-4. The needle became too thick to perform jump ratio images as seen in the low magnification image, Figure 4-4a. By close examination of the high magnification image, as in 4-4b and 4-4c, the initial oxide layer is still present underlying the exposure layer. The thick layer that prevented the opportunity for microscopy is hypothesized to consist of either the chloride precipitates from the electrolyte solution or carbon contaminates encapsulated in a hydrated layer. Unfortunately, the sample was too thick to gain a transmitted signal for any type of elemental mapping with the GIF.

![Figure 4-4: Al needle after exposure to 0.05 M NaCl\text{aq} solution for 30 minutes. a.) Low magnification b.) and c.) High magnification showing initial oxide underlying the exposure layer.](image-url)
The second sample exposed to 0.05 M NaCl\textsubscript{aq} solution for one hour is also featured in Figure 4-5 and resulted in similar structure as the needle exposed for 30 minutes. Following the exposure, the needle was again coated with a layer containing precipitate like structures or quite possibly contamination. Underneath this layer, the initial uniform 5 nm thick oxide was again observed in the TEM BF image. This sample was also too thick to perform any elemental analysis on the surface layer. The resultant layer is again hypothesized to be a hydrated layer with either chloride precipitates or trapped contaminates.

![Figure 4-5: Al needle exposed to 0.05M NaCl\textsubscript{aq} solution for 1 hour.]

A similar experiment was performed using pure water as the electrolyte (0 M NaCl\textsubscript{aq}) for two different times, 30 minutes and 3 hours. No apparent changes were observed after 30 minutes. However, after a 3 hour water exposure, a very thick, presumably hydroxide layer was observed. The TEM bright field images before and
after exposure are given in Figure 4-6. The longer exposure time permitted the oxide layer to thicken to approximately 40 nm.

![Image of Al needle and oxide layers before and after exposure](image_url)

**Figure 4-6:** a.) Al needle before exposure demonstrating uniform oxide. b.) and c.) After exposure to H₂O for three hours.

Initial examination of the oxide that resulted from the nitric etch was also investigated. Previous sample geometries were exposed to a one minute HNO₃ etch in attempt to strip away the native oxide and any contamination. This resulted in a controlled, uniform oxide that could be reliably reproduced. Needles were subjected to HNO₃ solutions for various times to determine if thickness and quality could be affected by limiting the etching time. No major changes were observed with short exposure times in the nitric etch and the oxide remained constant in thickness. Exposures in excess of one hour severely etched the metal and produced a thickened oxide structure as demonstrated with the needle in Figure 4-7. As a result, the one minute etch was adopted to produce the initial oxide on many of the needles and future geometries used in this study.
**Potentiodynamic Pitting Experiments for Dull Al wires versus Sharp Al Needles**

Although it was determined that the needles suffered radiation damage under 300 keV electrons in the microscope, electrochemical polarization experiments were pursued. Our goal was to understand the degree of field enhancement in the electrolyte in order to create preferential pitting sites at the tip of the needle. Pitting potentials and electrochemical behavior would both be affected if the field is not concentrated at the tip. A series of experiments was therefore attempted to test this approach and required a large population of needles to statistically support the findings.

Many sharp needles were made from the aluminum wire with careful attempts to maintain consistency in their preparation. Blunt samples, referred to as “dull” wires, were also made by electropolishing bulk wires for a short time. Efforts were aimed to produce a smooth surface, forming a uniform oxide yet maintaining a blunt geometry along the wire’s edges in order to avoid any sharp tip-like features. The dull wires were typically electropolished for 10-20 seconds. Each set of needles or dull wires was

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**Figure 4-7:** Al needle after exposure to HNO₃ etch for one hour.
imaged using secondary electron microscopy to gain a quick reference of the sample’s shape and size.

Potentiodynamic pitting experiments were performed on eight samples at a time using a VMP 16 multi-channel potentiostat where each sample is individually connected electrically to the potentiostat. Simultaneous testing ensured that the solution environment was constant. A schematic of the test set up and photos are presented in Figure 4-8. The samples were first exposed to deionized water at room temperature for thirty minutes. They were then immediately transferred into a beaker containing 50 mM

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**Figure 4-8:** Schematic and photographs of electrochemical set up for polarizing Al needles using VMP multi-channel potentiostat.
NaCl\textsubscript{aq} solution and electrically connected to the potentiostat. Open circuit (OC) potentials were established for each sample while sitting in solution for thirty minutes. A potentiodynamic pitting experiment was then started and the samples were ramped from their open circuit potentials at a rate of 1 mV/sec until the current limit of 1\(\mu\)A was reached. The applied potential was removed from each needle individually once the current limit was reached.

Current potential plots from the sharp needles are presented in Figure 4-9. The open circuit (OC) potentials were within 80 mV for the needles tested in the first set. Pitting potentials ranged from -589 to -714 mV, with an average -646 mV pitting potential. A second set of needles was also tested with OC potentials again within 80 mV and an average pitting potential of -601 mV. SEM images from the first set are presented in Figure 4-10. The needles are relatively blunt compared to some of the sharper needles presented earlier in this chapter with TEM, but remain consistent in tip radii (within 50 μm).

![Figure 4-9](image-url)

**Figure 4-9:** Current-potential plots for sharp electropolished needles subjected to potentiodynamic pitting experiments and pitted at the potentials given at right. OC potentials were within 80 mV for all eight samples.
nm). Many of the needles resulted in a corrosion product layer and blooms of either corrosion product or contaminants are also evident along the shank near the tip. These needles were too large for further characterization in the TEM.

Figure 4-10: SEM of needles polarized in Figure 4-9 with corrosion product blooms on and/or near tip apex.
Pitting potentials obtained from the current-potential plots for the dull wires are given in Figure 4-11. The electrochemical data indicates that pitting did occur with the dull wires. They pitted at an average potential of -419 mV, which is significantly higher than the average pitting potential of the sharp needles. The distribution of open circuit potentials for the dull wires was approximately 100 mV. SEM images from two of the dull wires are presented in Figure 4-12. These wires pitted at -555 mV (4-12a) and -574 mV (4-12b) and both demonstrate similar changes in morphology along the shank of the wire. There was no apparent preferential pitting at any tip-like features with the dull wires.

The aforementioned experiments were immediately performed after the samples were electropolished without the additional one minute nitric etch. Several sharp needles and dull wires, both subjected to the one minute nitric etch, were also tested so that pitting potentials could be compared for the samples with the two different oxides.

**Figure 4-11:** Current-potential plots for dull electropolished wires subjected to potentiodynamic pitting experiments and pitted with the exception to channel 4. Corresponding pitting potentials also given at right. OC potentials were within 100 mV for all eight samples.
Figure 4-12: SEM images of dull electropolished wires subjected to experiment in Figure 4-11. Pitting potentials were a.) -555mV in Channel 8 and b.) -574mV in Channel 3. Both samples feature similar corrosion pitting sites along the shank of the wire.
Pitting potentials and current-potential relationships are demonstrated in Figure 4-13 for the sharp needles (HNO₃ treated). Each sample pitted at potentials from -165 mV to -640 mV with the average pitting potential being -349 mV. This is significantly higher than the average pitting potential of -646 mV for the untreated sharp needles. The electrochemical behavior resulted in cleaner (with less noise) data and the higher pitting potential is indicative of a chemically different oxide structure present on the needles. This is likely a result of the one minute nitric etch treatment. Pitting was not observed for the dull wires treated in HNO₃ for one minute as demonstrated from the current-potential plots in Figure 4-14, where over a potential range of -900 to -300 mV the current limit was reached without pitting. The needles reached this current limit, set at 1 µA, without pitting and the individual anodes were electrically turned off.

**Figure 4-13:** Current-potential plots for sharp electropolished needles treated to 1 minute nitric etch and subjected to potentiodynamic pitting experiments and pitted at potentials given at right. OC potentials were within 70 mV for all eight samples.
Attempts were also made to induce pitting corrosion through application of an applied bias to the needles. There existed no prior pitting potential information so polarization was performed at a variety of applied potentials with both low and high current cut-offs. Post-exposure TEM analysis showed that the needle geometry was destroyed so that it could not be determined if pitting initiated at the tip or along the shank.

4.4 DISCUSSION AND SUMMARY

The needles offered many challenges, especially with imaging conditions in the TEM. Carbon contaminants and large increases in thickness of the needle’s surface layer did not allow imaging or analysis in the TEM. While characterizing the needles, electron beam damage became a major obstacle and unavoidable at 300 keV. Specimen drift
caused miscorrelations between pre and post-edge image acquisitions and affected jump ratio imaging.

Initial potentiodynamic experiments demonstrated the importance of radius and geometry in pitting. Sharp needles pitted at an average potential 230 mV lower than the dull wires. A summary and distribution of the samples and their pitting potentials is presented in Figure 4-15 and demonstrates a shift to the left (decrease in potential) for the sharp needle population. Needles that were treated with a nitric etch also pitted, but at a potential 300 mV higher than the untreated needles. The dull wires subjected to the same nitric etch and experiment did not pit up to potentials of -300 mV, where the passive current reached 1 µA. Therefore, a different oxide chemistry resulting from the nitric etch, drastically affects the pitting potential and electrochemical behavior. As shown in Table 4-1, sharp needles had lower pitting potentials than dull needles, while those treated with a 1 minute HNO₃ etch had higher pitting potentials. SEM data also

![Figure 4-15: Distribution of pitting potentials for needles and dull wires.](image-url)
confirmed that with sharp needles, pitting was preferred near the tip, suggesting a higher field gradient.

The needle geometry offers a means to localize pitting corrosion to a controlled location, near or at the tip. A geometric field enhancement effect was evident from the different potentiodynamic pitting experiments with the different geometries. The small variations in the pitting potentials observed among the needles are likely due to a variation in tip radius and surface area in contact with the electrolyte. The electropolishing technique used to fabricate the needles results in unique geometries, so it is very difficult to reproduce identical specimens.

Improvements in the experimental techniques employed could allow future experiments using Al needles to succeed. TEM analysis could be carried out using the Tecnai microscope, where lower accelerating voltages, down to 100 keV could be used to avoid beam damage. Each specimen can also be cleaned with an oxygen plasma to help reduce contamination problems. Better vacuum in the microscope should also minimize contamination effects. Meanwhile, similar experiments were pursued with flat electropolished wire geometries in order to avoid the problems discussed in this chapter.
4.5 REFERENCES


CHAPTER 5

ALUMINUM FLATS

5.1  INTRODUCTION

Because of problems encountered using the Al needle geometry (Chapter 4), the study then turned to experimentation and characterization of various Al flat geometries. Initial studies with flat specimens utilized bulk Al wire samples embedded in epoxy with a fine mechanical polish for initial surface preparation. Electrochemical tests were performed and after analysis in the SEM, it was determined that in order to successfully identify the different surface reactions, i.e. from mechanical polishing or pitting corrosion, a new approach for sample preparation would need to be employed. This included an electropolish of the initial surface to produce an initial smooth and uniform surface. Numerous electrochemical experiments were performed on bulk electropolished Al wires embedded in epoxy and the results and findings will be presented in the chapter.

5.2  EXPERIMENTAL

Two primary electrochemical tests were investigated for the bulk Al wire samples. Potentiodynamic pitting experiments and induction time experiments, both discussed in Chapter 3.2 were performed. Flat samples were made by embedding an Al wire, typically 125 μm in diameter, in epoxy. A single Al wire or an array of Al wires could be embedded for experimentation. Details of the preparation for the Al flats are
presented in greater extent in Chapter 2.3. During the electrochemical experiments, the entire polished aluminum surface and adjacent epoxy areas were exposed to the electrolyte.

Initial experiments were done on mechanically polished surfaces and resulted in a high population of sites representing mechanical damage and few pitting sites. The number of sites available for pit initiation that lead to metastable pitting is much larger on a surface polished mechanically compared to a smoother surface resulting from an electropolish [1-3]. These results led to the conclusion that in order to allow detailed surface characterization, an electropolish would be needed for the bulk wires. The final electropolish created a reproducible, clean surface, free from defects created via a mechanical polish and with a uniform initial oxide. This is a crucial parameter if the goal is to examine the initiation stages of pitting corrosion. Damage from a mechanical polish created numerous surface flaws, i.e. scratches [4, 5], which are likely to become sites for preferential pitting. The observed damage varied greatly from sample to sample. Consequently, a reproducible surface is achieved when an electropolish is used and any pitting sites, if present, can then be easily identified.

Induction time tests were performed on many of the wires, in particular the multi-electrode geometry, in order to create a statistically significant population of pitting potentials. One disadvantage to this type of test when sampling multiple wires at a time is that there is no control in the severity of pitting for individual wires. Typically, a pit would form and the oxide could either repassivate or the pit could continue growing until the applied potential was removed. Therefore, the preferred test for this sample geometry included potentiodynamic pitting experiments. The intent of these experiments was to
control the process of pitting corrosion by setting sensitive current limits with the belief that low currents will turn off the experiment after a single pit forms.

5.3 RESULTS

Aluminum Wire, Mechanically Polished and Polarized

The first set of flat samples was an array of wires with the surfaces prepared using a mechanical polish. Induction time experiments were performed on each wire in the array. These samples were exposed to 0.05M NaCl$_{aq}$ solution with an applied potential of -0.450 V$_{SCE}$. The current vs. time data from one Al wire demonstrates, by the sharp increase in current in Figure 5-1, that several pits initiated. Multiple current transients appeared in the current-time plot and coupled with SEM, several pitting sites were observed on the surface of the wire.

![Figure 5-1: Current-time plot from an induction time test for a wire polarized at -450 mV in 0.05 M NaCl$_{aq}$. Multiple current peaks correspond to pit initiations.](image-url)
The SEM images in Figure 5-2 show a pitted area along with some polishing damage, similar in appearance to a corrosion pit. Since the polishing damage was extensive on each wire, it was often difficult to distinguish between corrosion pits and polishing damage. The Al wire was cross-sectioned with the FIB through an area believed to be associated with pitting. TEM BF images are given in Figure 5-3 and clearly show a surface layer, approximately 30 nm thick, which is oxidized aluminum and may be associated with the corrosion product. The indentation in the middle of Figure 5-3a is believed to be a corrosion pit. It is difficult to distinguish between polishing damage and pitting corrosion due to the rough surface. The observed surface layer in these two TEM images is continuous and also fairly uniform. The thickness of this layer

Figure 5-2: a.) SEM of mechanically polished surface demonstrating both polishing damage and corrosion events. b.) SEM of damage resulting from mechanical polish. c.) SEM of area resulting from pitting corrosion.
does vary slightly across the grains, indicating there may be some orientation dependence for oxide thickness. The material above the oxide is an intentionally deposited gold-palladium layer whose purpose is to prevent charging from the epoxy and to protect the surface before the FIB is used for TEM sample preparation. This layer also adds difficulty to imaging the oxide and to elemental analysis, which was not performed on this sample due to the heavy Au-Pd surface layer. Therefore future samples had a carbon layer first deposited onto the surface oxide, resulting in a carbon layer adjacent to the oxide, giving suitable contrast for imaging and chemical analyses in the TEM. Additional Au-Pd or Pt depositions needed for FIB preparation would then be made on top of the carbon layer.

Figure 5-3: a.) TEM bright field of pitted region of mechanically polished surface. b.) BF of corrosion pit.
**Al Wire; Electropolished and Unpolarized**

The mechanically polished sample polarized in the previous section had a surface layer that was considered a corrosion product layer on a deformed surface. The next sample examined with this geometry was an Al wire that had been electropolished in contrast to mechanically polished. The surface would represent the initial starting surface for the electropolished wire samples since it had not been exposed to any corrosive environments nor applied potentials. The energy filtered TEM bright field in Figure 5-4a displays a uniform oxide across the surface. The oxide thickness is evident through

![Image](image-url)

**Figure 5-4**: a.) TEM BF of electropolished Al wire with smooth, uniform 5nm surface oxide.  
 b.) High resolution image of surface oxide.  
c.) High resolution image of oxide across boundary showing no thickness change across different grains.
examination of the high-resolution image in Figure 5-4b and proven to be approximately 5 nm. This oxide thickness on the electropolished flat wire is similar to the oxide observed on the Al needles. Such an oxide was expected to exist prior to any corrosion experimentation. A high magnification image, Figure 5-4c, was taken at a grain boundary and suggests there is no apparent thickness change present between the two orientations. Jump ratio imaging was explored with this sample and used to map Al, O and C. These results are presented in Figure 5-5.

![Figure 5-5: a.) TEM BF image of surface oxide of electropolished wire with jump ratio images obtained using b.) oxygen K-edge c.) carbon K-edge d.) aluminum L-edge.](image-url)
The initial oxide observed with this sample was important in understanding the oxide structure prior to any experimentation. With similarities between the observed oxide on the electropolished flats and the observed oxide on the Al needles, it confirms the initial oxide is amorphous and approximately 5 nm thick and uniform across the surface.

*Al Wire; Electropolished and Polarized in 50mM NaClaq*

An Al wire prepared in the same manner as the aforementioned was then examined with a presumed initial oxide as the one revealed in Figure 5-4. The sample was subjected to a potentiodynamic pitting experiment using a constant scan rate of 0.167 mV/s in 0.05 M NaClaq solution at room temperature. The corrosion current was plotted against applied potential as it constantly increased. The data was monitored throughout the experiment and the applied potential was removed after a single pit had formed. The sample was then prepped for the SEM/FIB by first depositing carbon followed by Au-Pd. SEM images of the single pit formed are shown in Figure 5-6. The smooth surface

![SEM image of electropolished wire subjected to potentiodynamic pitting experiment. Single pit formed which was site for TEM cross-sectional sample prepared using FIB.](image)
resulting from the electropolish is evident in 5-6a. The single pit formed is approximately one micron in diameter from the SEM image in Figure 5-6b. This high magnification image shows the individual pit and indicates where the FIB will thin to make a TEM sample. The red dashed line in 5-6b indicates where the final FIB will be positioned for the thinning. Regions adjacent to this line will be milled away with the ion beam and then thinned for TEM. It was determined that a cross-section through the pit, including area outside the pit would provide a valuable region for TEM characterization. Therefore, our final TEM sample contained the pit and adjacent surface regions for characterization.

The annular dark field STEM images in Figure 5-7 show evidence of two grain boundaries. Each boundary terminates at the two ends of the pit and meets below the pit. This presents the question as to whether specific sites, such as grain boundaries, are preferred sites for pit initiation. Unfortunately, since this sample geometry cannot be

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**Figure 5-7:** a.) STEM ADF image of pit in cross-section with red square encompassing a 50 nm by 50 nm area scanned for AXSIA, results in Figure 5-9.  b.) High magnification of pit in cross-section, approximately 2 μm in width and formed at grain boundary.
examined prior to polarization, it will remain a question for this specific case. This sample demonstrates the benefits of the Al needle geometry for this corrosion study and the advantage to image a sample in the TEM both prior to and following corrosion initiation.

The surface area away from the pit was then explored and was characterized in the TEM as an oxide/hydroxide structure similar to the one found on the mechanically polished surface (Figure 5-3). The thickness of this layer is approximately 30 nm. The images shown in Figure 5-8a and 5-8b are two BF images at different tilts from the surface region approximately 2 μm away from the pit. The layers are identified in Figure 5-8a to aid in understanding the steps in sample preparation. Carbon was deposited first; its low Z provides contrast against the oxide. Au-Pd was deposited to avoid charging in the SEM and Pt is deposited before cutting and milling with the FIB.

Due to the thickness and structure, the surface layer observed was originally thought to be a corrosion product layer on top of the oxide, as considered for the mechanically polished sample. Jump ratio imaging determined that the observed layer is the Al oxide or possibly a hydroxide layer above the Al metal. Jump ratio images using the Al and O edges in Figure 5-8c and 5-8d respectively; show the 30 nm thick surface layer.

Automated eXpert Spectrum Image Analysis (AXSIA) was used to determine whether chlorine was incorporated into the oxide layer or even if chlorine was present at all. The red box (50nm x 50nm) in Figure 5-7a indicates the area selected for AXSIA. The electron beam was scanned across this area and X-ray spectra collected at each point. This technique is capable of 1 nm spatial resolution; however some spatial resolution was
lost with the occurrence of specimen drift. The final analyses, compiled and processed are shown in Figure 5-9. AXSIA recognized two distinct phases in the sample. The two components identified were the Al substrate, with data shown in Figure 5-9a, and the oxide/hydroxide surface layer, Figure 5-9b. A weak signal appeared at 270 eV (consistent with the Cl L1-edge) in the oxide/hydroxide surface layer suggesting that a small amount of chlorine is present in the oxide. The presence of Cl suggests that this layer is a corrosion product layer.
Additional samples were electropolished and subjected to the same tests described above. Unlike the previous test where current-voltage data was carefully monitored, in these potentiostatic experiments the applied potential was removed after a given amount of time with the possible formation of several pits. Due to the smaller wire diameter, 25μm, it was not possible to make a FIB cut and have enough space to successfully lift the TEM sample away from the bulk material. Therefore, only SEM results will be presented. An electropolish to the Al wires (25 μm diameter) embedded in epoxy caused
the wires to become recessed in the epoxy. After polarization in 50 mM NaCl\_aq, several types of pit morphologies were observed in the SEM and are shown in Figure 5-10. A second electropolished wire subjected to potentiostatic polarization resulted in the corrosion of a large area at the wire-epoxy interface, Figure 5-11. This location along the wire-epoxy interface indicates crevice corrosion, which occurs because of solution concentration effects in high aspect ratio geometries. Corrosion initiation in this geometry was therefore not considered in this work.

**Figure 5-10:** SEM images of a corroded Al bulk wire with an initial electropolished surface. Images show different areas of attack as a result of polarization in NaCl\_aq.

**Figure 5-11:** a.) SEM of corroded Al wire demonstrating crevice corrosion. b.) High magnification of pitted area adjacent to epoxy wall.
Another 25 μm Al wire was subjected to the same conditions and formed two pits. One pit formed along the perimeter of the Al wire adjacent to the epoxy. The pits are seen in Figure 5-12 while the pit closest to the epoxy wall appears detached. A high magnification image, Figure 5-12b, shows that the wire is detached from the epoxy, most likely as a result of the electropolish during sample preparation. Again, pits so close to the wire-epoxy interface are suggestive of crevice corrosion.

![Figure 5-12: a.) SEM top down view of corroded wire. b.) and c.) Large pit formed at Al wire-epoxy contact area.](image)

An additional sample also showed evidence of crevice corrosion, suggesting that the surface exposed during the pitting potential experiments is not only the electropolished surface but also surfaces from the crevice formed as a result of sample preparation. This result is demonstrated in Figure 5-13 where an anodically polarized electropolished wire had pitted, 5-13a. Observed detachment of the wire from the epoxy walls is evident in 5-13b, which could allow the sidewalls of the Al wire to be exposed to
the solution. Additional crevices exposed to the electrolyte may serve as additional sites for pitting. A cut using the FIB was made across the epoxy and Al interface and from the SEM image in Figure 5-13c, the carbon is observed filling in the undercut material proving the Al is slightly detached from the epoxy. Inconsistency among samples may result from this effect and because crevice corrosion mechanisms are different from pit initiation mechanisms, new sample geometries were pursued.

![Figure 5-13: a.) SEM of corroded electropolished wire. b.) Outer edge of wire in contact with epoxy wall. c.) Cross-sectional FIB cut of Al wire-epoxy interface demonstrating the crevice formed (circled) from the electropolish and/or polarization.](image)

**Unpolarized Electropolished Al Wire**

The last sample of this geometry was exposed to 0.05M NaCl<sub>aq</sub> solution for 24 hours without polarization, so that pitting had not initiated. The goal was to determine whether the 30 nm thick oxide layer had formed as a result of exposure to solution alone or as a result of the applied potential it undergoes during the potentiodynamic pitting experiments. The TEM bright field images in Figure 5-14 show the formation of a
similar surface oxide. Although difficult to distinguish between the carbon coating and the oxide, the oxide layer present does not appear to be as thick as the layer observed in the previous samples that were exposed to similar experiments. The oxide layer here is approximately 20 nm. Jump ratio images collected using the O and C K-edges in Figure 5-15, helped distinguish between the carbon coating and the oxide layer and confirm the thickness.

Figure 5-14: TEM bright field images of exposed but not pitted Al wire.

Figure 5-15: a.) Energy filtered bright field TEM Image. Jump ratio image using b.) C K-edge and c.) O K-edge.
Chloride Implanted Al Wire; Unpolarized

The desire to experiment with bulk Al wires continued and interest became focused on a new means of incorporating chlorine into the sample. An aluminum wire of high purity was embedded in epoxy and the surface was electropolished. The new approach involved ion implanting chloride into the Al wire. Polarizations were then done in an environment chemically free of chloride and pitting corrosion was observed. Initial studies of the ion implantation process and its effect to the Al bulk wire are first considered. This section will cover results from the ion implanted Al wire and analyses using AXSIA.

Three TEM bright field images are given in Figure 5-16 with 5-16a identifying the various layers present as a result of FIB sample preparation. Figure 5-16b and c are

![Figure 5-16: TEM bright field images showing surface oxide.](image)

a.) Low magnification image of TEM cross-section, with layers labeled: Al, oxide, carbon (deposited for contrast in TEM), Pt (deposited to make FIB cut).
b.) Mechanically polished surface. Oxide distinct and approximately 5-7 nm thick.
c.) High magnification image; edge-on showing oxide.
two higher magnification images presenting the uniform surface oxide, 5 nm thick. The images in Figure 5-16 provide no evidence that the ion implantation process has damaged the surface or initial oxide structure. A larger field of view STEM ADF image is given in Figure 5-17a. Damage in the Al metal is evident from this image and occurs to a depth of approximately 100 nm below the surface. A 100 nm by 100 nm area (red square) at the surface was scanned for AXSIA. The individual component spectrum images are presented in 5-17b, 5-17c and 5-17d as unique phases, Al bulk wire, Cl-rich Al and Al oxide containing Cl, respectively. Each pixel in the output spectrum images represents
0.78 nm. The oxide component given in 5-17d is approximately 6-7 pixels which correspond to 4.5 to 5.5 nm. This thickness agrees with the TEM BF images of similar oxides previously characterized of the bulk Al wire and the Al needles. Chloride from ion implantation is also incorporated into the initial oxide.

It is unclear from this analysis the depth or distribution of the chloride species. A second area was then scanned for AXSIA and is shown by the 125 nm by 500 nm red area in Figure 5-18a. The height of this collection area will include the top surface, oxide, and depth into the bulk past where the implanted species stops. Again the individual component spectra and images are given in Figures 5-18b-d. Results provided show the depth of the Cl\textsuperscript{−} species from ion implantation is just under 100 nm. A column of pixels (using the strongest intensity) from an area of the Cl-rich Al component was used to integrate over the 500 nm depth to produce a profile of this component, given in Figure 5-19. The integration area started at the top surface and continued down into the bulk of the Al wire. The profile shows a small concentration of Cl\textsuperscript{−} in the oxide followed by a small Cl\textsuperscript{−}-depleted layer. The remaining Cl\textsuperscript{−} profile into the depth of the Al wire is Gaussian.

These preliminary results on chemical and structural properties of the Al wires implanted with chloride suggested a viable approach to using and investigating Cl\textsuperscript{−} in corrosion pit initiation. Although these initial results showed no obvious damage from ion implantation or changes in structure or thickness to the initial oxide, further studies would allow the effect of implanted Cl\textsuperscript{−} concentration on pit initiation to be investigated. Thin films were chosen as the final geometry for a variety of reasons discussed in the following chapter.
Figure 5-18: a.) ADF STEM image with red box of dimensions 125 nm by 500 nm scanned for AXSIA. Individual component spectrum images (0.977 nm/pixel) identifying 3 phases; b.) Al bulk wire c.) Al oxide d.) Cl-rich Al with Ga.
5.4 DISCUSSION AND SUMMARY

The Al needles are ideal for this study because they may be characterized in the microscope both prior to and following electrochemical experimentation. Successful experiments were employed using the wire geometry however a disadvantage with this geometry arises from not being able to characterize the material in the TEM prior to any experimentation. Therefore, the initial oxide is assumed to be uniform and 5 nm and no additional information about the initial microstructural can be stated. The bulk wires also expose a larger surface area during electrochemical testing, which reduces the probability of predicting where pit initiation occurs. Therefore, localization of corrosion pitting is inherently more difficult.

The importance of surface preparation was the biggest accomplishment realized resulting from the geometry change. Numerous investigations into corrosion pit initiation were made in the past with poor and inconsistent sample preparation. Results from this
chapter prove that a mechanical polish introduces damage to the surface that can serve as sites for preferential pit initiation. Not only are additional sites created using a mechanical polish, the oxide along the surface becomes more difficult to characterize in the presence of such mechanical surface damage. Grain size is another microstructural parameter that varies with the bulk Al wires. Wires of two diameters, 25 and 125 μm, were characterized in this chapter, both with a different grain size. Damage from the initial mechanical damage may vary amongst grain size, along with crystallographic orientation of the surface grains. These factors may change oxide structure and/or pitting behavior. In order to properly use this geometry for analysis, Al wires must be consistent with microstructure, including grain size.

Another variable considered for corrosion pit localization is the surface area exposed during electrochemical experiments. The exposure area greatly influences electrochemical behavior and should be minimized to better predict the locality of a corrosion pit. The entire surface of the wire was in contact with the electrolyte providing a large area for corrosion reactions, which is demonstrated nicely in this chapter. Although this is a negative aspect of the wire geometry, it shows the advantage of the small surface area associated with needles and it gives insight to needed changes in experimental variable for future samples.

Other interesting features resulted from the wire sample geometry. The initial oxide was uniform in thickness and had a similar structure to the oxide characterized on the needles. A thickness change was observed in the samples subjected to NaCl\textsubscript{aq} consisting of an increase from 5 nm to 20-30 nm. A morphology change seemed evident
in many cases and both jump ratio imaging and AXSIA were utilized to confirm the presence of a thickened oxide layer containing a low chloride concentration.

The AXSIA technique was better supported with the bulk wire implanted with chloride. TEM shows the oxide is again 5 nm and uniform across the surface. Ion implantation did not introduce any apparent changes to the oxide. The bulk of the implanted species is identifiable in both the TEM BF and STEM ADF images. AXSIA also detected chloride in the surface oxide layer.

As stated in the abstract, a so called “evolution” of sample geometries occurred during the length of this study. The bulk Al wires were a critical intermediate phase of this study which provided valuable data to better define the initial starting material for corrosion studies. It also demonstrated the need for controlled exposure areas to achieve localization of pitting corrosion. Along the way, the bulk wire sample geometry also demonstrated the capabilities of the various characterization techniques that were proposed and will be employed for future work.
5.5 References


CHAPTER 6

CHLORIDE IMPLANTED ALUMINUM THIN FILMS

6.1 INTRODUCTION

Chloride plays a critical role in pitting corrosion. Previous experiments varying chloride concentrations in solution demonstrated the importance of concentration in determining the susceptibility to pitting [1-4]. Such results motivated the work to experiment with a new sample geometry consisting of aluminum thin films and will be discussed in this chapter.

Thin aluminum films can be grown with high purity and allow the initial microstructure to be defined and consistently uniform among the samples tested. Chloride is incorporated into the Al films through ion implantation. Careful selection of ion implantation energy and fluence allows the concentration profile of the chloride species to be controlled [5]. As a result, a well defined sample is readily available for experimentation with a known initial microstructure and chemical makeup.

The chloride implanted films are observed to pit when anodically polarized in a Cl-free electrolyte such as potassium sulfate (K₂SO₄) solution. The pitting potential is a function of both implantation energy and ion fluence [6, 7]. Both parameters were investigated in order to determine the optimum conditions for ion implantation. The Cl⁻ depth profile, calculated using TRIM-92 software [8], in Figure 6-1 is for a fluence of 3 x10¹⁶ Cl/cm² implanted at three different energies; 20, 35 and 50 keV. Increasing the implantation energy decreases the peak in concentration and increases the depth at where
the concentration peak occurs. This ultimately changes the concentration of Cl\(^-\) within the oxide layer and near the oxide-metal interface. These two regions in our samples are of particular interest in the corrosion investigation because the pit initiation process occurs within these areas. The resistance to pitting corrosion also increases with an increase of implantation energy [7].

A second parameter to consider is ion fluence, or the number of ions implanted into the sample per an area of one square centimeter. Increasing the fluence decreases the resistance to pitting by decreasing the anodic over-potential required for pitting without changing the depth at which the concentration peak occurs, as seen in the depth profile in Figure 6-2 [6]. The profile shows atomic % Cl\(^-\) versus depth for three different fluences each implanted at 35 keV. The depth at which the peak in concentration occurs remains constant with the peak height varying as a function of ion fluence. The maximum concentration at the peak in the profile thereby decreases with decreasing ion fluence. Figure 6-2 also demonstrates that a lower fluence produces samples with a smaller Cl\(^-\)
concentration in the oxide and near surface layer. Various implantation fluences were investigated to determine the critical concentration of Cl\(^-\), above which pitting will occur in a Cl\(^-\) free electrolyte.

![Figure 6-2: Cl\(^-\) depth profile using 35 keV Cl ions for four different implantation fluences.](image)

In summary, implantation energy and fluence are two important factors that will affect the initiation process of corrosion pitting in the aluminum thin films. The chloride profile can be shifted in peak height and depth through manipulation of these two parameters. Similar Cl\(^-\) concentrations within the oxide can be achieved using specific implantation energies with specific ion fluences. Therefore, in order to fully understand what changes occur in the pitting process, these parameters are carefully chosen and controlled for the results presented in this chapter.

Microstructural variations play an important role in pitting corrosion. Using ultra high purity Al thin films to control the microstructure with various implants for corrosion experiments allows the initial microstructure to be constant, thereby eliminating one
variable that contributes to pitting. The thin film geometry was pursued in order to reproduce a similar initial microstructure for analysis and comparison throughout electrochemical tests.

TEM characterization and microanalysis focused on the as-deposited and implanted aluminum thin films in order to distinguish changes in initial microstructure and changes resulting from ion implantation. TEM will also serve as a powerful tool to identify differences occurring in the films as a result of anodic polarization by characterizing changes in the surface oxide microstructure and morphology. The different techniques employed each present unique opportunities in characterizing the aluminum films. TEM BF/DF imaging and diffraction will aid in characterizing the microstructure, including surface oxide and chloride precipitates. Microanalysis with AXSIA also allows detailed elemental mapping and characterization of the Cl\(^{-}\) species especially with sensitive/low concentration levels. AXSIA’s software uses advanced counting statistics that detects and recognizes small concentration levels present with excellent spatial resolution. Combination of sophisticated imaging and analysis techniques employed in the TEM will contribute new information to pitting corrosion in the aluminum films.

### 6.2 Experimental

99.9999% aluminum thin films were deposited onto SiO\(_2\)/Si substrate at ambient temperature by electron beam evaporation in an ultra-high vacuum system. Approximately 2000 Å thick polycrystalline films were evaporated at a rate of 1 Å/sec.
A uniform 4-5 nm thick oxide was formed by exposing the aluminum film to ultra-high purity oxygen in a load lock chamber after growth [9].

Preliminary experiments and tests using implantation energies of 20, 35 and 50 keV determined the optimum implantation energy for the thin film sample geometry to be 35 keV. This implantation energy produced a small concentration of Cl\textsuperscript{-} in the oxide layer with allowable resistance to pitting corrosion for the investigation. Several fluences were explored and it was found that a critical Cl\textsuperscript{-} concentration for pitting in 50 mM K\textsubscript{2}SO\textsubscript{4} solution occurred for an ion fluence between 2 and 3 \times 10^{16} \text{ Cl/cm\textsuperscript{2}} [7, 9]. The samples characterized with TEM and reported on in this chapter are films implanted at 1, 5 and 7 \times 10^{16} \text{ Cl/cm\textsuperscript{2}} using 35 keV Cl\textsuperscript{+} ions.

Electrochemical experiments were performed using a 3-electrode cell with a Pt counter electrode, a sulfated silver wire reference electrode, and the aluminum film working electrode. The thin films were exposed using a micro-capillary test cell set up shown in Figure 6-3 located at Sandia National Laboratories. A 1 mm diameter capillary defines the exposed area. 50 mM K\textsubscript{2}SO\textsubscript{4} is held within the capillary and set onto the sample surface by a measure of force. The electrodes are then electrically connected to

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6_3.png}
\caption{Figure 6-3: a.) Three electrode cell set up for thin films. b.) 1 mm capillary used for exposure.}
\end{figure}
the potentiostat and a potentiodynamic pitting experiment is conducted. The sample sits at open circuit potential for 100 seconds. The sample is then polarized to -1.0V relative to the reference electrode and the applied potential is then increased anodically at a constant rate of 1 mV/sec. The current-voltage relationship is recorded and used to correlate any abrupt changes in corrosion current to pitting events. Pitting events in the current-voltage plots are identified by a sharp rise in current density above a threshold value of several microamps/cm². Smaller individual current transients are also observed below the pitting potential, but do not lead to stable pitting.

The exposed and polarized area is thereby only 1 mm in diameter. It is prudent to thin material from this area. Therefore, careful precautions such as precise measurements and markings were made during the electrochemical test to allow for successful TEM sample preparation from the 1 mm polarized area.

6.3 RESULTS: Al THIN FILMS

The results discussed in this section consist of several comparisons. Thin films of aluminum were grown and implanted with chloride at fluences of 1, 5 and 7 x10¹⁶ Cl/cm². Areas of the implanted films were polarized in 50 mM K₂SO₄ solution as described in the previous section. Atomic force microscopy (AFM) was done on the unpolarized unimplanted films as well as the different implanted (and unpolarized) films to obtain information on surface morphology. TEM cross sections were made from each of our samples using the focused ion beam technology discussed in section 2.3. TEM plan-view samples were also made using the FIB. Conventional plan-view samples were
later made to eliminate Ga effects from the FIB-prepared samples. These effects will be discussed in more detail later in the results section.

The remaining analysis and characterization made on the films after AFM included numerous TEM techniques. TEM BF/DF, diffraction, EELS were each employed in the characterization process of the aluminum films, both unpolarized and polarized. AXSIA was of importance in characterizing the implanted films by demonstrating capabilities in sensitive detection limits to the small concentrations of chloride present.

In summary, TEM samples were made in both cross-sectional and plan-view from the unimplanted films as well as the films implanted at 1, 5 and 7 x 10^{16} Cl/cm^2. Samples were made from both unpolarized material as well as polarized material. This chapter will first compare and discuss TEM results from the samples implanted with 3 different Cl^- fluences relative to the unimplanted sample. Because the critical concentration for pitting was determined to lie between 2 and 3 x 10^{16} Cl/cm^2, further investigation of the 5 x 10^{16} Cl/cm^2 implanted sample (above the critical concentration) will then be presented for polarized versus unpolarized films. The results from this chapter will then be concluded with a short discussion.

6.3.1 AFM RESULTS

Figure 6-4 contains high magnification AFM images which show a change in morphology occurring for samples implanted with fluences of 3 x 10^{16} Cl/cm^2 and above. Distinct “domains” are observed with boundaries that encompass one to several of the Al grains. The origin of these boundaries is not understood in detail, but is thought to arise from preferential sputtering during the implantation process. We note however that this
distinct change in surface morphology first appears above the critical concentration for pitting. The unimplanted Al films have a similar morphology to the samples implanted with a fluence of $1 \times 10^{16}$ Cl/cm$^2$. The Cl$^-$ concentration of $3 \times 10^{16}$/cm$^2$ is critical and results in pitting in sulfate as well as a significant change in morphology. This leads to the question of whether pit initiation results from a significant chemical presence of Cl$^-$ in the oxide and near surface area or does it result from the change in morphology due to ion implantation? It is also desired to know whether the Cl$^-$ distribution is uniform laterally or is concentrated at these boundaries.

The significant change in surface morphology as a result of increasing ion implantation fluence leads to the question of whether other changes occur simply due to the interaction of the ions with the aluminum film, independent of the specific change in
Cl⁻ concentration. For example, could there be microstructural changes to the individual Al grains as a result of implantation? Is there any evidence for ion damage or grain growth in the metal grains and has the oxide thickness changed as a result of implantation? Through electrochemical experimentation and TEM analysis, we hope to find evidence which can answer such questions.

6.3.2 Unpolarized Thin Film Samples in TEM Cross-section

Before we can understand any changes that result from anodic polarization and pitting, the initial material should first be carefully characterized. This section will present results from TEM cross-sectional samples that were made from the three implanted materials. TEM cross-sections were made using the FIB for samples implanted with fluences of 1, 5 and 7 x10¹⁶ Cl/cm².

1 x10¹⁶ Cl/cm² Al Film

A STEM dark field image of the 1 x10¹⁶ Cl/cm² Al film on SiO₂/Si substrate is presented in Figure 6-5. This particular implantation fluence is below the critical concentration for pitting to occur in sulfate solution. The different layers of substrate are identified along with the, approximately 200 nm thick, Al film and a top layer of deposited platinum which is needed for surface protection during the sample preparation process, as discussed in Chapter 2. The annular dark field image shows columnar grains across the polycrystalline film with a grain size ranging from 50-150 nm. A large area was selected to analyze using AXSIA to test the technique and to try to spatially and spectrally resolve chloride in our material. The red rectangle, labeled 1, in Figure 6-5 is a 400 by 800 nm area that was scanned and EDS data was collected in a 128 by 256 matrix.
This results in each pixel equivalent to 3.125 nm for our spectral image seen in Figure 6-6. AXSIA results consisting of an overlay of individual spectral components is given in Figure 6-6 along with the RGB image overlay of the different components. The blue

![Figure 6-6: EDS component spectra overlay from AXSIA and corresponding RGB overlay image (3.1 nm/pixel) showing the output components from area in Figure 6-5.](image)
pixels in the RGB image and blue spectrum (with Si and O) correspond to the film’s substrate. The green pixels and spectra and red pixels and spectra correspond to the Al film and Al combined with the implanted species, chloride, respectively. This sample demonstrates the ability for AXSIA to detect small concentrations of different chemical species with good spatial resolution.

**5 x10^{16} Cl/cm^2 Al Film**

Analysis then focused on the 5 x10^{16} Cl/cm^2 sample, which is above the critical concentration for pitting. The high resolution TEM bright field image in Figure 6-7a, shows a uniform 4-5 nm thick oxide at the smooth film surface while diffraction contrast evident in the left side of the image contributes to some imaging difficulty. The oxide characteristics observed with this sample are also similar to the oxides observed in the

![Figure 6-7: a.) TEM BF image, 390kX showing 4-5 nm surface oxide b.) STEM ADF image of film implanted 5 x 10^{16} Cl/cm^2. The red area (labeled 1) is a 400 by 800 nm region used for AXSIA.](image)
previous sample geometries investigated. Figure 6-7b is a STEM annular dark field image showing an extended view of the implanted film and the various layers are again labeled. A 400 by 800 nm region, again labeled 1, was scanned and EDS spectra were collected for analysis with AXSIA. The output data will again have 3.125 nm associated with each pixel. The overlay of component spectra shown in Figure 6-8 contains four distinct components. The four individual component spectra are blue, green, red and magenta corresponding to the SiO$_2$ substrate, Al film, Cl$^{-}$ implanted species and Al oxide, respectively. The inset of the RGB image clearly identifies the oxide component, which is the 1-2 pixel thick magenta layer corresponding to approximately 3-6 nm. Although the area scanned is larger and results in lower spatial resolution, the AXSIA technique can spatially and spectrally resolve the individual components including the thin surface oxide. This is particularly of benefit when exploring and comparing our polarized material as will be presented later in this chapter.

![Figure 6-8: EDS component spectra overlay from AXSIA and corresponding RGB overlay image (3.1 nm/pixel) showing the output components from area in Figure 6-7.](image)
7 x 10^{16} Cl/cm^2 Al Film

The 7 x 10^{16} Cl/cm^2 implanted sample was then characterized in cross-section. This particular implant fluence has little resistance to corrosion in a Cl-free environment.

Figure 6-9 is a collection of TEM BF and STEM ADF images from the 7 x 10^{16} Cl/cm^2 implantation damage.

![Figure 6-9: TEM bright field images of film implanted 7 x 10^{16} Cl/cm^2 showing a.) implanted region b.) implantation damage across low angle boundary c.) and d.) near surface region & uniform 4-5 nm oxide. e.) and f.) STEM ADF images showing density changes (arrows) correlated to implantation damage & Cl ppts.](image)
implanted film. It is first easily observed that implantation damage is more predominant in this sample compared to the lower fluences. Images 6-9a and 6-9b show the depth of this damage and across a low angle grain boundary. Images 6-9c and 6-9d demonstrate the damage from different tilts in the TEM where it appears Cl-rich precipitates may be present. The two DF images, 6-9e and 6-9f, show clear density changes along the implanted region in this sample with several occurring along boundary points, as well as a higher density of threading dislocations in some grains that may be a result of the high implantation fluence.

When the high resolution TEM images in Figure 6-10 are compared to images of the other samples, a similar oxide layer, uniform in thickness and approximately 4-5 nm was again observed and was also not affected by the high ion fluence. There also exist crystalline domains near the surface oxide that range 3-10 nm in diameter. These regions may be Moiré fringes, however due to the size and comparison to some of the plan-view results, as discussed further below, they may be indicative of Cl-rich precipitates.

![Figure 6-10: HRTEM images, 7x10^16 Cl/cm², near surface showing oxide and crystalline regions.](image-url)
A similar 400 by 800 nm area, with the red region labeled 1, was selected for AXSIA in Figure 6-11, using EDS for analysis. AXSIA results are shown in Figure 6-12, recognizing three distinct components. As seen with the previous samples, we have the blue, green and red spectral components directly corresponding to the substrate, Al film and implanted chloride species. The RGB component image also has a pixel value 3.125 nm. The absence of a distinct spectrum corresponding to a thin surface oxide in the vacuum.

![Figure 6-11: STEM ADF image of film implanted 7 x 10^{16} Cl/cm^2. The red area (labeled 1) is a 400 by 800 nm region used for AXSIA.](image)

AXSIA results is noted for this sample and also for the lower implant fluence 1 x 10^{16} Cl/cm^2 sample. While the oxide was easily identified as a unique component in the AXSIA output for the sample implanted with 5 x 10^{16} Cl/cm^2, this is attributed to better sample tilt in the TEM and the oxide being edge-on with the electron beam. Because the oxide is only a few nanometers thick, if the electron beam is not edge-on with the aluminum and aluminum oxide interface, it may not be spectrally resolved using AXSIA.
and consequently, the oxide component will not appear as a distinct phase in the output data. However, from examination of several TEM BF images, it is observed that the oxide remains uniform in thickness, approximately 4-5 nm.

![Figure 6-12: EDS component spectra overlay from AXSIA and corresponding RGB overlay image (3.1 nm/pixel) showing the output components from area in Figure 6-11.](image)

Higher spatial resolution areas were also scanned for this sample and the film implanted with \(5 \times 10^{16}\) Cl/cm\(^2\). BF TEM images are given with AXSIA results (1.56 nm/pixel), in Appendix A for areas 200 by 200 nm. More clustering of the Cl\(^-\) component is observed with the \(7 \times 10^{16}\) Cl/cm\(^2\) implanted specimen (Figure A-2). From examination of the STEM ADF images, implantation damage including dislocations and local density changes of either precipitates or voids is more prevalent as the implantation fluence is increased. From these results, we conclude that the \(7 \times 10^{16}\) Cl/cm\(^2\) fluence causes significant ion implantation damage to our films.
Summary

All three implanted samples are observed to have similar surface oxides, in both thickness and morphology prior to polarization. AXSIA proved to be a powerful tool in identifying unique components and allows the oxide, Cl species and bulk film material to be spatially resolved. The implanted depth for all three samples was approximately 75 nm, which agrees with the calculated depth profile in Figure 6-1. The surface oxide for the different implanted films is uniform in thickness and consistent for the different fluences investigated. The highest fluence \(7 \times 10^{16} \text{ Cl/cm}^2\) demonstrated the function of damage with ion fluence and produced additional defects in the film. Pitting occurs in this sample and as a result of the additional damage, it is determined the \(5 \times 10^{16} \text{ Cl/cm}^2\) is a better fluence to study among the samples available for corrosion pitting.

6.3.3 Unpolarized Thin Film Samples in TEM Plan-view

Conventional TEM plan view samples were made from the same implanted films described in the previous section. All three samples were analyzed using AXSIA to characterize the spatial distribution of Cl-rich species and to provide a baseline for comparison to the polarized material. Samples nearest the critical concentration for pitting \(5 \times 10^{16} \text{ Cl/cm}^2\) and above are characterized further in the microscope using EELS in STEM spot mode and also with other TEM imaging techniques. Further characterization of these particular fluences with additional techniques in the microscope is aimed to provide more structural and chemical information that may influence pitting corrosion in the implanted films. The results for the conventional TEM plan-view samples will be discussed in this section for the unpolarized implanted Al thin films.
**AXSIA using EDS in STEM Mode**

Again, AXSIA has been deemed very valuable in analyzing our implanted material. In particular, characterization of the spatial distribution of each significant chemical species in our sample is easily achieved. As will be seen later in this section, typical BF/DF imaging and EELS do not provide enough information to allow a comprehensive analysis of the implanted films.

The DF image in Figure 6-13a is a large field of view showing the grain size in our film ranging from 50-100 nm. This film was implanted with $5 \times 10^{16}$ Cl/cm$^2$ and when imaged in plan-view, demonstrates contrast along the boundaries similar to the AFM image (Fig 6-4). The DF image is collected in STEM mode using a high angle annular detector and the contrast is from electron scattering at larger angles collected on the annular detector. The scattered component represents Rutherford scattering and has strong Z-dependence, so the intensity difference seen in the STEM DF images is from Z-contrast instead of diffraction contrast.

A 400 by 400 nm region that encompassed several grains was selected for AXSIA (red square labeled 1 in 6-13a). Two distinct components resulted and are identified in Figure 6-13c. The Al film and an aluminum component rich in Cl$^-$ are blue and green respectively in the component spectra, 6-13c and RGB overlay image, 6-13d. The individual Cl-rich Al component spectral image is also shown in 6-13b, where the blue to red scale represents an increasing intensity scale of the Al and Cl spectral component. The data was collected in a 128 by 128 matrix for this analysis, which corresponds to 3.125 nm/pixel. Larger clusters of the Cl-rich Al phase appear preferentially along the boundaries in this image. The clusters are 3-6 pixels in diameter, suggesting that areas as
large as 18 nm of the Cl-rich phase, possibly precipitates, are present along the boundaries. Smaller Cl-rich clusters are also uniformly distributed on the grain faces.

Figure 6-13: a.) STEM ADF image of film implanted 5 x 10^{16} Cl/cm². The red area (labeled 1) is a 400 by 400 nm region used for AXSIA. b.) Spectral component image for Cl-rich Al phase (3.125 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase and blue=Al matrix.

Figure 6-14 is another area from the same sample where the red box labeled 1 is a 300 by 300 nm area scanned for AXSIA. The Cl-rich Al spectral image, 6-14b, is also given with each pixel representing 2.34 nm. Again, larger clusters of the Cl-rich Al phase are observed along the boundaries seen in the STEM ADF area selected. The areas
Figure 6-14: a.) STEM ADF image of film implanted 5 x 10^{16} Cl/cm². The red area (labeled 1) is a 300 by 300 nm region used for AXSIA. b.) Spectrum component image (2.34 nm/pixel) for Cl-rich Al phase. c.) and d.) TEM BF images of area scanned for AXSIA at different tilts showing the alignment of Cl component with grain boundaries. e.) Z-contrast image of blue region in a.
along the boundaries are 3-9 pixels across, representing Cl-rich regions or precipitates as large as 20 nm. The two BF images in 6-14c and 6-14d are taken at different tilts from the area selected in the STEM image. Both images show varying diffraction contrast which aids in the identification of the grain boundaries and also helps show the alignment of the Cl-rich areas along them. The blue area selected in Figure 6-14a is an area that was focused in on after AXSIA data results were collected and processed. Imaging conditions, such as using a shorter working distance, were optimized and a higher magnification STEM DF image was collected in Figure 6-14e. This image represents a truer Z-contrast image and the varying intensities observed directly correspond to changes in local density. The larger clusters, averaging 10 nm in diameter, could indicate distinct Cl-rich precipitates along the grain boundaries, while smaller Cl-rich clusters or precipitates are uniformly distributed across the grain faces.

Thus far, from examination using AXSIA on the 5 x10^{16} Cl/cm² implanted film, a higher concentration of Cl⁻ is observed along boundaries relative to that on the grain faces. Two more areas were examined on this sample. The results are shown in Figures 6-15 and 6-16. Here a depletion of the Cl-rich Al phase exists along the boundaries, in opposition to the results obtained on the previous area. It is important to note the differences observed in the DF image compared to the previous results from this sample. There is no faceting of the grain boundaries and dark oxide spots are present. There are several reasons for why such opposing result can occur from within one sample. Different areas being imaged may give different results, especially if one area is extremely thin compared to another. Imaging conditions could also be varied between these two analyses because they were imaged on different dates.
Figure 6-15: a.) STEM ADF image of film implanted 5 x 10^{16} Cl/cm^2. The red area (labeled 1) is a 500 by 500 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (3.9 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase and red=Al matrix.
When compared to the lower implant, $1 \times 10^{16}$ Cl/cm$^2$, AXSIA identified two unique components, Al with Cl and Al oxide as seen in Figure 6-17. The oxide signal in the aluminum component is likely a result from being in a very thin region and some X-rays from the surface oxide are contributing. The Al film component contains a much smaller Cl signal than what was observed for the $5 \times 10^{16}$ Cl/cm$^2$ sample. However there is enough Cl present for AXSIA to identify two distinct phases, one pure Al and the other Al plus Cl as observed for the higher implant fluences. The most striking difference though is that there is no clustering of the Cl-rich component. Instead, the Cl is uniformly distributed laterally.
AXSIA was then performed on the $7 \times 10^{16}$ Cl/cm² conventional plan-view sample. A 200 by 200 nm area, labeled 1, in the ADF image in Figure 6-18 was scanned and EDS data was collected for AXSIA. Three unique phases resulted; Al (red), Cl (green), and Al oxide (blue). The Cl (green phase) independent spectrum image is given, 6-18b along with the RGB overlay image of all three components, 6-18d. A large cluster of Cl is present near a triple boundary point in the center of the spectrum image with a depletion of aluminum. The oxide and Al components are both fairly uniform over the 200 by 200 nm area but stronger along the boundary in the center of the image. The
spectral images in Figure 6-18 have a pixel size of 1.56 nm, which relates to the large cluster in this spectral image being approximately 75-80 nm.

Figure 6-18: a.) STEM ADF image of film implanted 7 x 10^16 Cl/cm². The red area (labeled 1) is a 200 by 200 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (1.56 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase, red=Al matrix and blue=Al oxide.
In order to determine the distribution of Cl\textsuperscript{-}, a larger area was then scanned for AXSIA. A 500 by 500 nm region was scanned and AXSIA results using a 128 by 128 pixel matrix (3.9 nm/pixel) are given in Figure 6-19. Three components were again

![Figure 6-19: a.) STEM ADF image of film implanted 7 \times 10^{16} \text{Cl/cm}^2. The red area (labeled 1) is a 500 by 500 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (3.9 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase and red=Al matrix with circled regions are indicative of adjoining clusters.](image-url)
identified as in Figure 6-18. Cl clusters were again observed while on the larger side being approximately 9-11 pixels, ~43 nm. Although not as large as the cluster seen in the previous spectral image, there are a few clustered areas where the regions are adjoining. These regions are circled in Figure 6-19d and could possibly be interpreted as one cluster, which would result in a cluster size of ~80 nm. While the spectral image in Figure 6-19 appears lost midway in the raster direction, the data acquisition is drift corrected and corrected after every other raster. This enables the left side of this particular spectral image to be useful and therefore the results were included to give perspective with a larger field of view. The 7 x10^16 Cl/cm² implanted film clearly has larger clustering of Cl-rich regions that appear more often near grain boundaries rather than grain faces.

**Electron Energy Loss Spectroscopy**

EELS was then pursued on the conventional plan-view samples for several reasons. It was hoped that EELS and Z-contrast imaging could further spatially resolve Cl⁻ in the film. EELS near edge fine structure over regions rich with Cl⁻ could also aid in the identification of the chloride phase present. The 5 x10^16 Cl/cm² sample was therefore characterized in the JEOL 2010 TEM at NCSU. An EELS spectrum using an aperture over a 1 micron area in Figure 6-20 was collected and multiple electron energy loss signals are present. The Al-L3 edge occurring at 73 eV and the hydrogenic Al-L1 edge at 118 eV are both present. A Si-L3 edge is present at 100 eV and most likely a result of remaining substrate material not completely removed during the thinning or ion milling stages of the sample preparation process. At 200 eV there is also small Cl⁻ L3 peak, shown in black using background subtraction in Figure 6-20. The alignment of the microscope in STEM mode is for true Z-contrast and the image in 6-20 shows a higher
density region encompassing many of the grain boundaries. The figures to follow will consist of several Z-contrast and BF images with EELS spectra obtained using STEM in spot mode to correlate contrast observed in the image to the chemical species chloride. Data will be presented from the sample implanted with $7 \times 10^{16}$ Cl/cm$^2$ because imaging conditions could not be optimized for the $5 \times 10^{16}$ Cl/cm$^2$ sample shown in Figure 6-20 well enough to observe contrast as previously seen.

The grain boundaries in the $7 \times 10^{16}$ Cl/cm$^2$ are quite prevalent and show contrast as seen in the DF image in Figure 6-21a. In STEM, the electron beam was used in spot mode to collect an EELS spectrum from the boundary triple point indicated by the red arrow in Figure 6-21. This area has a higher density in the DF image and when compared...
to the BF image, 6-21b, also contains much diffraction contrast in the appearance of precipitate like features. The Cl-L3 edge is present in the EELS spectrum indicating Cl\(^-\) in this junction.

![Image](image_url)

**Figure 6-21:** a.) DF Z-contrast image (sample implanted 7 x 10\(^{16}\) Cl/cm\(^2\)) with arrow pointing to triple boundary point where EELS spectrum was taken using electron beam in spot mode in STEM. b.) Corresponding bright field image.

The sample was then translated to a different area to collect more EELS data at a slightly higher magnification. Figure 6-22a is a BF image of a few grains with the corresponding DF Z-contrast image, 6-22b. Two spectra were again collected in spot mode from the areas indicated in 6-22b. Again, the data follows the trend of higher Cl at the boundary triple point as compared to within the grain. Spectrum 1 was collected from a grain boundary triple point and has a stronger Cl peak while spectrum 2 was obtained
with the beam in spot mode at the center of the grain. Both spectra were collected under the same conditions including acquisition time.

Figure 6-22: a.) BF image (sample implanted 7 x 10¹⁶ Cl/cm²) and corresponding b.) DF image with two arrows indicating areas where EELS spectra were collected in STEM spot mode. c.) EELS spectra from regions indicated in b showing higher Cl concentration at boundary triple point (Spectrum 1) compared to within the grain (Spectrum 2).
A thinner area near the edge of this sample was analyzed at a higher magnification and BF/DF images are given in Figure 6-23. Two EELS spectra in 6-23c were acquired at different points across the boundary. This area was chosen because it was very thin and had good diffraction contrast in the BF image. The probe was moved across the boundary and EELS spectra were acquired sequentially at each point a-f.

Figure 6-23: a.) DF image (sample implanted $7 \times 10^{16}$ Cl/cm$^2$) showing points where EELS spectra were collected in STEM spot mode across the boundary. b.) Corresponding BF image. c.) EELS spectra from regions a and c showing higher Cl concentration within the grain (spectrum a) than at the boundary (spectrum c).

Spectra from point a and c are given. There is a stronger signal from chlorine at point a away from the boundary as compared to the spectrum from point c, which is right along the boundary. One possible explanation for this discrepancy may be that the Cl-rich large
clusters in the $7 \times 10^{16}$ Cl/cm$^2$ were so extensive that they did not necessarily follow the grain boundaries but were also distributed on the grain faces.

Sample drift may have also affected EELS acquisitions in spot mode. In order to eliminate drift, the sample was allowed to sit in the microscope for a short time to stabilize and a new DF image was collected from the same area, Figure 6-24a. Six more EELS spectra were acquired in spot mode at different points seen in 6-24a. The resulting

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure6-24.png}
\caption{a.) DF image from the same region as in Figure 6-23, only with a series of EELS spectra collected in STEM spot mode from different areas. b.) EELS spectra from some of the different points. Spectra $b$ and $d$ both along boundary with one showing significantly more Cl than the other. Spectra $a$ and $f$, one at boundary triple point and one within the grain indicating more Cl at triple point.}
\end{figure}
EELS spectra from four of these points are shown. The spectra at points $b$ and $d$ both are from along the boundary, while spectrum $d$ contains a stronger Cl signal compared to spectrum $b$. A comparison of spectrum $a$ to spectrum $f$ shows that again there is a stronger Cl signal from the triple boundary point in $a$ as compared to within the grain in $f$. Again, due to the prevalence of large Cl-rich clusters across the sample surface, the intensity of the Cl signal will vary, depending on whether the beam is on a cluster or not. Another possibility is that an orientation dependence may exist where Cl prefers to migrate along specific grain boundaries during the implantation process.

AXSIA is a statistical approach to chemical mapping and small concentrations of chemical species, like Cl in the samples presented here, will always be present in the resulting output spectrum images. All points with a Cl-signal are then acknowledged in images when characterized with AXSIA with a spectral related intensity scale. In comparison, AXSIA demonstrates Cl$^-$ interpretation better than Z-contrast and EELS alone for the chloride implanted aluminum films. EELS mapping may also show the clustering observed yet in spot mode, it is difficult to tell if you’re on a cluster or not so the heterogeneity in the EELS results is consistent with Cl-rich clusters.

**Additional TEM Results**

BF/DF image pairs captured of the $7 \times 10^{16}$Cl/cm$^2$ are given in Figure 6-25 from the same area at two magnifications. Precipitates on the order of 5 nm are observed along certain boundaries and are also seen within some grains. A selected area diffraction pattern, indexed in Figure 6-26a, and a DF image were captured using the objective aperture over the given reflection circled, which corresponds to a d spacing of 1.67 Å. The d spacings for AlCl$_3$ are very close to Al (Table 6-1) and the reflection used
for the DF image in 6-26b is associated with AlCl₃ and not Al. In the corresponding DF image, Figure 6-26b, we again see bright Cl⁻ precipitates scattered throughout the plan-view field. Many Al grains are also brighter in this DF image, likely due to the aperture size permitting the contribution of the adjacent ring reflection.
Table 6-1: Lattice (d) spacings for given hkl in pure aluminum and AlCl₃.

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<td>(1 3 3)</td>
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BF/DF TEM image pairs are also shown for the $5 \times 10^{16}$ Cl/cm$^2$ sample in Figure 6-27. Small precipitates are scattered randomly in the DF images that were imaged using the same 1.67Å reflection. They range in size from a few nanometers to larger precipitates approximately 20 nm in size. Strain contrast is observed in many of the precipitates and show up as dark lines running through the bright precipitates in the DF images. EELS and BF/DF imaging are useful techniques in characterizing the implanted films but are not capable of fully analyzing the chloride present in the sample.
6.3.4 SUMMARY OF UNPOLARIZED Al FILMS

AXSIA was employed for analyses in both cross-sectional and plan-view samples. Excellent spatial resolution was achieved with the technique. The surface oxide is similar among the unimplanted and three implanted specimens in uniformity and \( \sim 5 \, \text{nm} \) thickness. The depth of Cl agrees with the calculated depth profile for 35 keV Cl\(^+\) ions. As the implant fluence is increased, Cl-rich clusters are observed only for implant fluences above the critical fluence of \( 3 \times 10^{16} \, \text{Cl/cm}^2 \). The cluster diameter and implant...
damage increases with fluence. TEM plan-view samples provided results for the lateral distribution of Cl\(^-\) in the thin films. For the 5 \(\times 10^{16}\) Cl/cm\(^2\) implant and above, AXSIA showed larger precipitates along many of the grain boundaries, this was not observed in the lower fluence. While in other AXSIA results of the 5 \(\times 10^{16}\) Cl/cm\(^2\) implant, a depletion of Cl\(^-\) was apparent along the boundaries, it is contributed to a thickness difference in the region of analysis. Chloride was also detectable using EELS and significant correlations between intensity contrast and local density were made.

### 6.3.5 Polarized Thin Films in TEM Cross-section

Anodic polarization of the chloride implanted Al films in sulfate solution to potentials just below the average potential observed for pitting may result in microstructural changes associated with metastable pitting. Techniques with the TEM could then be used to further characterize the films after polarization and prior to pitting. The implanted aluminum films were then subjected to potentiodynamic polarization experiments in sulfate as described in section 3.2 and in more detail for this sample geometry, section 6.2. TEM cross-sectional samples were prepared in a novel way, using FIB technology and will be presented in this section. The samples were anodically polarized to just below the average pitting potential, which was determined from several previous pitting experiments with other implanted thin film samples.

An unimplanted Al thin film, grown under identical conditions as the films that were implanted, was also polarized using 50 mM NaCl solution to just below its anticipated pitting potential to determine if pitting could be induced similarly to the Cl\(^-\) implanted films in sulfate. The STEM ADF image in Figure 6-28a is of the film in cross-
Figure 6-28: a.) STEM ADF image in cross-section of unimplanted sample that was polarized in 50 mM NaCl with a 200 by 200 nm area labeled 1, selected for AXSIA analysis. b.) Three components computed using AXSIA, Al=red, Al oxide with Ga=blue, and Al oxide plus surface contaminants=cyan. c.) RGB overlay image of components (1.56 nm/pixel).

AXSIA was performed on the red area labeled 1 and the individual spectral components are presented in Figure 6-28b. Three distinct phases resulted from the analysis. The red component represents the Al film while the blue and cyan components are an Al-oxide without the presence of chlorine. Only a trace concentration of Cl is incorporated into the oxide and film by using NaCl solution and it is therefore not as easily detected with AXSIA. The RGB spectral image is also given in Figure 6-28c and the 200 by 200 nm area sampled for AXSIA defines a pixel value of 1.56 nm/pixel in the output spectrum images. The blue oxide component is most representative of the surface
oxide, while the cyan has additional peaks of the surface layers from sample preparation and contaminants. The blue oxide component is 3-4 pixels thick giving an approximate surface oxide thickness of 4-6 nm, which is similar to the other oxides observed in cross-section. While the pitting potential was nearly approached but not reached, the oxide remains in tact and uniform in thickness across the surface.

In order to demonstrate how a sample is polarized to just below the pitting potential, if the average pitting potential was know, for example -0.5 V, then an experiment might anodically polarize to 50 mV below this potential. This approach is demonstrated with the polarization curve in Figure 6-29. The blue data is actual current-potential data from an experiment up to where it was terminated and the dashed red line is an imaginary extension of the data indicating where the pitting potential would occur, by the sharp rise in current, if the experiment were allowed to continue.

![Figure 6-29: Hypothetical polarization curve demonstrating experimental data (blue) and experiment termination at a potential below what is anticipated for pitting (red).]
The sample implanted with $5 \times 10^{16} \text{ Cl/cm}^2$ was also anodically polarized to 60 mV below the average pitting potential in 0.05 M K$_2$SO$_4$. Current-potential data is given in Figure 6-30. The STEM ADF image of this sample in cross-section is presented in Figure 6-31a. There is a significant amount of contrast present in the near surface region signifying regions of lower density and possible voids. The lower density regions and contrast observed here are much more significant than what was observed prior to polarization. The 200 nm by 200 nm area labeled 1 in Figure 6-31a was selected for AXSIA. Three distinct components were observed as shown in 6-31b. The red, green and blue components correspond to the Al film, Cl-rich Al and Al oxide with chlorine phases respectively. This analysis again assigns a pixel value of 1.56 nm.
Individual component spectral images are given in Figure 6-32. In the Al oxide containing Cl spectral image, 6-32b, we see an increase in oxide thickness locally occurring. While the Cl-rich Al component spectral image (6-32a) at first glance appears to have a Cl-depleted area, it isn’t necessarily showing a depletion of chloride, yet only an increase in oxide. As compared to the pure Al film spectral image (6-32c) it is certain that a change is chemically and quite possibly morphologically occurring in the near

**Figure 6-31:** a.) STEM ADF image in cross-section of sample implanted $5 \times 10^{16}$ Cl/cm$^2$ that was polarized in 50 mM K$_2$SO$_4$ with a 200 by 200 nm area labeled 1, selected for AXSIA analysis. b.) Three components computed using AXSIA, Al=red, Cl-rich Al=green and an Al oxide w/Cl=blue. c.) RGB overlay image of components (1.56 nm/pixel).
surface region. It is important to note the surface oxide in the top right area of Figure 6-32b is uniform and of the original oxide thickness, approximately 3 pixels or 5 nm. The increased oxide component appearing centrally in Figure 6-32b thickens from 3 pixels to 15-20 pixels, which relates to an increase from 5 nm to 30 nm.

Figure 6-32: Individual component spectrum images from AXSIA results in Figure 6-31. a.) Cl-rich Al component b.) Al-oxide containing Cl and c.) Al matrix. Each pixel is the equivalent of 1.56 nm.
A second AXSIA scan was collected from the surface region to determine any additional changes that may have resulted from polarization; however the scan lost itself part way through the data collection. Fortunately, AXSIA results from the top surface region were preserved and not affected by the drift and confirmed the surface region in this scan contained a uniform 5 nm oxide. Therefore, a localized change and increase in oxide thickness is occurring as a result of polarization. These AXSIA images may provide the first chemical image of a metastable pitting site.

As previously discussed, above the critical Cl⁻ concentration for pitting, (e.g. the 5 x 10¹⁶ Cl/cm² implanted sample) when polarized in an environment chemically free of chloride, pitting will occur. Just prior to reaching the pitting potential, changes in the surface oxide are observed such as a localized increase in thickness and Cl⁻ incorporation. By comparison to other surface scans with AXSIA, these changes appear localized and not randomly dispersed across the sample surface.

6.3.6 Polarized Thin Films in TEM plan-view

Plan-view samples were made from the polarized implanted films using a nontraditional technique in the FIB. The purpose of using the FIB for plan-view sample preparation is to ensure that the 1 mm polarized area is the region thinned for TEM. This deemed a difficult task to accomplish using conventional sample preparation techniques so the FIB was used to cut a square area from the surface. This region was then lifted up, removed from the bulk material and attached to a TEM sample holder using electron beam deposited Pt for a weld. The TEM holder and affixed sample material was tilted 90 degrees and the ion beam was used to slowly thin in successively finer steps from the
backside until the material was electron transparent. This particular FIB lift-out and thinning technique has been demonstrated before for cross-sectional specimens, however the advances made with the implanted films and preserving the top surface in plan-view using the FIB is a new technique.

The first FIB-made plan-view sample characterized was the 1 x 10^{16} Cl/cm^2 sample. This sample was polarized up to 10 volts versus the reference electrode but did not show evidence of pitting most likely due to the concentration of Cl being too low. The ADF image in Figure 6-33a shows the film and the 300 by 300 nm area for AXSIA. Two components resulted. The Ga (red) and Al (blue) spectral components are seen in the RGB overlay image along with the corresponding component spectra in 6-33b. The

![Figure 6-33: a.) STEM ADF image of sample implanted 1 x 10^{16} Cl/cm^2 and polarized in 50 mM K_2SO_4 in plan-view made via FIB. Region labeled 1 is a 300 by 300 nm area selected for AXSIA. b.) Spectrum image (RGB overlay) showing two components, Al and Al w/Ga and no chlorine components. Each pixel is 3.125 nm.](image)
Ga phase is not desired and likely results from using the Ga ion beam in the FIB during sample preparation. It is possible that the Ga has interacted with the sample in such a way as to limit our ability to detect a Cl-rich phase.

The STEM ADF image of the film implanted with $5 \times 10^{16}$ Cl/cm$^2$ following polarization is given in Figure 6-34a. Grain boundary facets are observed as seen prior to polarization on the conventionally prepared plan-view samples. These faceted boundaries between grains are consistent with those observed at the film surface by AFM. The region labeled 1 in 6-34a is a 300 by 300 nm area selected for AXSIA. Four components are computed from AXSIA as seen in Figure 6-34b, although the red component combined with the blue component are both attributed to the same phase, the Al film. A Cl-rich Al component is also observed as the green phase and a new distinct phase appears that heavily decorates the grain boundaries. This component (cyan in this output spectrum) contains Ga, mainly due to the Ga ions used during FIB sample preparation. The impact of the presence of Ga on the analysis will be discussed in the following section.

The RGB overlay spectrum image is given in Figure 6-34c along with the spectral image from the Cl-rich Al phase in Figure 6-34d. The pixel resolution for these spectral images is 2.34 nm/pixel. Large clusters, rich in chlorine, are easily recognized in the RGB image as the green phase. Using the Ga phase to identify the grain boundaries, it appears that the chlorine-rich clusters are not preferentially localized to the grain boundaries. The most striking difference is that the clusters are larger in size compared to the unpolarized samples. A more careful inspection of the Ga (cyan) component shows evidence of a small Cl peak at 2.6 keV occurring in the component spectrum. The
Figure 6-34: a.) STEM ADF image of film implanted 5 x 10^{16} Cl/cm² and made in plan-view using FIB. The red area (labeled 1) is a 300 by 300 nm region used for AXSIA. b.) Individual spectrum component images for component spectra, red=Al, green=Cl-rich Al, blue=Al and aqua=Ga. c.) RGB overlay spectrum image (2.34 nm/pixel). d.) Spectrum image for Cl-rich Al component showing larger clusters away from boundaries.
presence of the Cl spectral peak coupled with the Ga limits our ability to resolve small Cl-rich clusters along the grain boundaries. Therefore, we cannot rule out their presence. The spectrum image for the chloride component in Figure 6-34d shows that the clusters range in size from 4 to 15 pixels or 9-35 nm. Although the majority of these clusters are present within the grains, there are a few regions along the boundaries where the green Cl phase is predominant and intermixes with the Ga component, suggesting that some of the Cl-rich phase may also be found along the boundaries.

Similar results are again observed from another area of this sample and AXSIA data is given in Figure 6-35. The Ga component (purple) again appears strongly along the grain boundaries. Figure 6-35 b and c show the Al (red) and Cl-rich Al (green) components. A Si particle (cyan) is also present. This is most likely a contaminant particle scattered from the substrate onto the sample during the ion beam milling process. At 2.34 nm/pixel, the larger Cl clusters seen in the RGB image and Cl spectrum image again range in sizes up to 30-35 nm. The RGB spectrum image highlights many of the smaller Cl-rich precipitates or clusters. Again, there appears to be no preference for these clusters to segregate to the grain boundaries.
Figure 6-35:  a.) STEM ADF image of film implanted 5 x 10¹⁶ Cl/cm² and made in plan-view using FIB. The red area (labeled 1) is a 300 by 300 nm region used for AXSIA.  b.) Individual spectrum component images for component spectra, red=Al, green=Cl-rich Al, blue=Ga and aqua=Al-Si contaminant particle.  c.) RGB overlay spectrum image (2.34 nm/pixel).  d.) Spectrum image for Cl-rich Al component showing larger clusters away from boundaries.
**Ga effects from FIB for TEM sample preparation**

The individual spectral components from AXSIA for the sample in Figure 6-34 are given in Figure 6-36. The spectrum images demonstrate the severity of Ga effects which result from FIB sample preparation. Ga heavily decorates the grain boundaries. A Cl peak is present in the Ga component which allows for the possibility that some Cl-rich clusters may also exist along these boundaries. However, because the Cl component is linked to the Ga component, which saturates the grain boundaries, distinct Cl-rich precipitates on the boundaries cannot be distinguished. Another possibility is that Ga may displace Cl along the boundaries. Therefore the main conclusion we can draw from the plan-view samples prepared using the FIB is that larger Cl clusters are observed following polarization. Additionally, there is no preference for these larger clusters to lie along the grain boundaries or to be excluded from the boundary regions. Both large and small clusters are found randomly dispersed across the surface. Figure 6-36c does show localized regions where the Cl-rich phase is absent, but these regions do not correspond to any identifiable features in the underlying microstructure.
Figure 6-36: Spectrum images for individual components from AXSIA results in Figure 6-34. 

a.) Al with some Ga from FIB  
b.) Ga from FIB decorating the grain boundaries and  
c.) Cl-rich Al showing up as larger clusters and segregated away from boundaries.
In order to rule out the effects of Ga in our results, conventional TEM plan-view samples of the polarized implanted films were used for comparison. Careful measurements and cuts were made and the polarized area of a sample implanted with $5 \times 10^{16}$ Cl/cm$^2$ was centered onto a TEM ring for further thinning. This sample was polished from the backside and ion milled only from the backside with the front shielded to preserve the surface of our film. A successful TEM plan-view sample was made with good thin area. It was then characterized using AXSIA from a region encompassing several grains in order to compare to our FIB-prepared plan-view samples.

The ADF image in Figure 6-37a identifies a 300 by 300 nm area where EDS spectra were collected for AXSIA. Two distinct components resulted, 6-37c, aluminum film (red) and a Cl-rich Al component (green). From examination of the component spectra and RGB overlay image (6-37d), it is evident that the larger clusters of Cl-rich phase lie preferentially along the grain boundaries. These Cl-rich clusters decorating the grain boundaries and shown in the spectral image in 6-37b are relatively uniform in size, 6-10 nm. The smaller clusters are uniformly distributed on the grain faces.

It is therefore clearly evident that very different results are obtained when characterizing a TEM plan-view sample made conventionally versus a FIB made plan-view sample. When considering the results from conventionally prepared plan-view samples and comparing the effects of polarization on the $5 \times 10^{16}$ Cl/cm$^2$ sample, it appears that polarization does not influence the distribution of Cl-rich clusters over the whole sample surface. Instead, only local differences in oxide growth were observed. These local regions may be indicative of metastable pitting sites that re-passivated before pit growth was stabilized.
**Figure 6-37:** a.) STEM ADF image of film implanted $5 \times 10^{16}$ Cl/cm$^2$ and polarized in 50 mM K$_2$SO$_4$. Sample was prepared via conventional sample preparation in contrast to the plan-view polarized samples seen in Figures 6-34 and 6-35. The red area (labeled 1) is a 300 by 300 nm region used for AXSIA. b.) Spectrum component image for Cl-rich Al phase (3.125 nm/pixel). c.) Individual component spectra, color coded, and overlay of spectra. d.) RGB overlay spectrum image; green=Cl-rich Al phase and red=Al matrix.

**Additional TEM results**

While the majority of the characterization of these films focused on AXSIA, TEM BF images were also captured. A few high resolution images are presented in Figure 6-38 and demonstrate various features seen in the polarized plan-view samples. There are regions that appear amorphous and Moiré fringes are also observed. The image on the right, slightly over focused, shows a region which may be a chloride precipitate. Many of
the clusters observed are of the same size scale as those identified by AXSIA data as the Cl-rich Al phase. Coupled with the diffraction data presented earlier, we hypothesize that these ordered regions may indicate AlCl$_3$ precipitates.

![Figure 6-38](image)

**Figure 6-38:** Three BF images from the sample implanted $5 \times 10^{16}$ Cl/cm$^2$ and polarized in 50 mM K$_2$SO$_4$ and made using FIB. Moiré fringes and precipitates present with possible effect of amorphization from FIB preparation.

The BF images in Figure 6-39 are representative of the types of diffraction contrast seen in the implanted films. Diffraction contrast in the films is attributed to the varying orientation of the grains as well as implantation damage from the chloride and/or chloride precipitates and difficult to characterize in BF alone.

![Figure 6-39](image)

**Figure 6-39:** BF images from polarized sample implanted $5 \times 10^{16}$ Cl/cm$^2$ showing various types of diffraction contrast observed.
Selected area diffraction patterns were also taken from interesting regions of the polarized plan-view samples. Any reflections attributed to AlCl₃ were very weak (Fig. 6-40), and often hard to image due to the low concentrations of Cl present. Many of the $d$ spacings, Table 6-1, for AlCl₃ are very close to those for Al so that isolating the AlCl₃ was difficult. DF images were captured by rotational tilt around a given reflection, and as shown in Figure 6-41, different chloride precipitates appear in the different DF images. This is one example of how important the AXSIA technique can be when trying to spatially resolve a precipitate structure within a matrix. Conventional microscopy imaging techniques like capturing multiple BF/DF pairs, cannot provide the chemical component information that could be determined from one single analysis using AXSIA. BF/DF pairs such as the one seen in Figure 6-42, are useful in correlating specific features observed, for example in diffraction contrast. In the images here, several precipitates that appear bright in the DF images are located at boundary points and can be directly linked to unique features and contrast seen in the BF image.
Figure 6-41: Series of DF images captured by rotating aperture around central spot. Several precipitates appear at different tilts which denote the value of AXSIA technique and the ability to "see" all precipitates with one data collection.

Figure 6-42: a.) BF TEM image of polarized and implanted sample. b.) – e.) DF images at different rotational tilts showing various precipitates for comparison to diffraction contrast observed in BF image.
6.3.7 SUMMARY OF POLARIZED Al FILMS

The aluminum thin films were polarized in 50 mM K$_2$SO$_4$ solution and polarized to just below the expected pitting potential. TEM cross-sectional AXSIA results provided interesting changes in thickness and chemistry occurring within the oxide layer. Oxide thickness increased and contained more chlorine as a result of polarization and the change also occurred locally. Plan-view samples made with the FIB showed that Ga decorated the grain boundaries, potentially masking changes that may have occurred as a result of polarization. Another interesting feature was the larger sizes of the Cl-rich areas occurring within the grains relative to the unpolarized samples. Additional plan-view samples were made using conventional techniques to eliminate the Ga effects from the FIB and AXSIA results were obtained. Results from these samples confirmed that the Cl-rich precipitate structure was similar to the structure observed in the unpolarized films and polarization did not affect the Cl$^-$ distribution. Some traditional TEM imaging techniques were also employed to compliment the analysis of the polarized Al films.

6.4 DISCUSSION AND SUMMARY

In conclusion, the aluminum thin films have offered further insight into the characterization of our material prior to pitting corrosion and after anodic polarization. The initial oxide is uniform for the different implanted films and was spatially resolved with AXSIA. The uniform 4-5 nm thick oxide was identified as an individual component and in its EDS component spectrum, chloride is not included in this phase. After exposing an area to a potentiodynamic pitting experiment, a TEM cross-section was made from the polarized region. A significant change in oxide chemistry and
morphology was observed. The oxide thickened by a factor of 6X over a localized area approximately 100-150 nm wide, while the remaining surface was a uniformly 5 nm thick oxide. Density changes in the near surface region of the polarized film are also more pronounced in the TEM cross-section compared to the unpolarized material of the same implantation. The oxide and near surface aluminum regions thereby play an important role in the pit initiation process. Changes are noticed in these regions, most specifically with the oxide.

The implanted material created controversy to the ability for these samples to mimic real world environments for corrosion opportunities. This sample geometry was employed in order to precisely control the concentration of Cl in the surface and near surface regions. Implantation damage is unavoidable using 35 keV ions especially at higher fluences. Damage can be misinterpreted for chloride precipitates and dislocations along with other defects may also be created from the implantation process. Such changes in the films are neglected under the assumption that pitting events are reserved to the surface and near surface regions, so the depth of the film where most damage exists is ignored.

An advantage considered for the implanted Al is that through precise control of [Cl], pitting sensitivities could also be controlled and ion implantation processes could be manipulated to better define a critical concentration for pitting. The data currently provides a critical concentration between 2 and 3 x 10^{16} Cl/cm^2. Characterization and analysis of films implanted above and below this critical fluence concludes significant changes occurring on a microstructural level. It is thereby desired to continue analysis and characterization of implanted Al films with samples that have a higher sensitivity to
pitting. For example, samples could be implanted so [Cl] is closer to the critical concentration. Microstructural and chemical changes would then be more valuable to gaining insight into the initiation process of pitting corrosion.

Sample preparation was difficult for the implanted films and was best accomplished using the FIB. Undesired Ga effects prevented valuable AXSIA data from being obtained. Ga effects may include the displacement of chlorine away from the grain boundaries, but most importantly affect analysis by heavily decorating the grain boundaries. Therefore, conventional TEM sample preparation must be performed in order to make a fair comparison of results. This task was more difficult with the polarized material because the exposed area must be centered for mechanical thinning, dimpling and ion milling.

AXSIA benefited the characterization of the plan-view samples by providing information about the Cl spatial distribution and precipitate/cluster sizes. Although the plan-view FIB samples resulted in larger Cl-rich areas within grains, the conventional plan-view samples of both the polarized and unpolarized films demonstrated precipitates present along the grain boundaries. These precipitates ranged in size from 6-20 nm between the two samples. The variation in Cl precipitate size or cluster size may be attributed to the thickness of the area being examined. Figure 6-43 is a schematic of this effect. Several AXSIA scans presented in this chapter were made from different areas of the plan view sample. The resulting spectrum images of the Cl-rich Al phases demonstrated a depletion of Cl along the boundaries. Depending on the thickness of the imaged area, a change in [Cl] may differ greatly and affect the size and/or distribution of Cl. For example, the orange, green and red arrows in 6-43a when translated to a
Figure 6-43: Schematic showing possible imaging depths because precipitates are seen both along boundaries, yet also depleting boundaries in AXSIA results. Schematic demonstrates the dependence of region being characterized and sensitive depth profile. The orange, green and red arrows in a.) when translated to a particular depth profile in b.) show that Cl concentrations can vary from 2-10 at\% over a 20 nm thickness difference.

Figure 6-44: a.) AXSIA results from sample implanted 5 x 10^{16} Cl/cm^2 with Cl-rich spectral image showing depletion of Cl along the grain boundaries. b.) AXSIA results from sample implanted 5 x 10^{16} Cl/cm^2 with Cl-rich spectral image showing precipitates of Cl along the grain boundaries. Proposed phenomenon in Figure 6-43 is an effect of imaged areas differing in thickness.
particular fluence in the depth profile of 6-43b varies from 2 to 10 atomic %Cl. Two possible analyses are proposed to demonstrate this affect in Figure 6-44. The results in 6-44a may be recorded from a region thinner than those obtained from 6-44b and consequently, the lower concentration of Cl may be the reason behind the Cl-depleted regions and Cl-precipitate enhanced grain boundaries or vice versa. Regardless, important characterization results are available from plan-view samples and AXSIA and can be better controlled for future work.

A variety of techniques were utilized to fully characterize these films, with the emphasis on the use of AXSIA in STEM mode. AXSIA revealed to be a unique tool and provided detailed chemical mapping with excellent spatial resolution. In comparison to EELS, it also proved to be better in displaying complete detection, chemically and spatially, of chloride in our implanted Al films.

In conclusion, the implanted films have paved a path for future work where advanced analytical techniques in the TEM can be utilized for investigation of the corrosion pit initiation process. The observed increase in oxide thickness and the locality of this behavior implies that the initiation process of corrosion pitting may be more dependent of oxide structure and morphology rather than a particular role of Cl in the aluminum and/or oxide. Several imaging and analytical approaches were successfully made on the implanted films discussed in this section. These tools can again be applied to a better defined sample and coupled with additional microscopy techniques such as electron energy loss near edge fine structure, ELNEFS, a more thorough analysis of the initiation process may be made.
6.5 References

CHAPTER 7

SUMMARY, CONCLUSIONS AND FUTURE WORK

7.1 SUMMARY OF RESULTS

A detailed investigation of the initial stages of pitting corrosion in aluminum was performed by characterizing and electrochemically testing novel sample geometries that reduced the lateral scale for which pitting occurred. Three different geometries were employed and the results were presented. Al needles offered specific characterization benefits, but presented several experimental difficulties. Flat Al samples were then investigated and different advanced characterization and microanalysis techniques were established, which led finally to using an Al thin film geometry.

Sharp Al needles had the ability to be characterized in the TEM both before and after electrolytic exposures and/or corrosion experiments. Their unique sharp tip radius served as a feature that, with appropriately controlled bias application, confined pitting events to the tip area. Localization of corrosion pit initiation could thereby be achieved and studied more intensely due to the ability for multiple characterizations in the TEM at various stages of experimentation. However there were several problems with this geometry. Radiation damage was prevalent with many of the needles in the TEM imaged with 300 keV electrons. For example, it was observed that needles with smaller radii, which are more electron transparent for TEM investigation, were damaged considerably more quickly by the electron beam than the larger needles. Contamination was also evident with many of the needles, due to either poor vacuum conditions and/or
cleanliness of the sample itself. Localized heating undoubtedly occurred. Collectively
the radiation damage presented too many difficulties for TEM characterization of the Al
needles to be considered reliable.

Several attempts were made to examine the needles prior to corrosion
experimentation. The initial oxide was established 4-5 nm thick uniformly covering the
needle’s smooth surface. An Al needle was single crystalline with the tip of constant
radius approximately a hemisphere. Thus, the crystallinity of a tip is different for each
tip and can come from a wide range of crystallographic orientations. The oxide thickness
remained constant in all the needles examined resulting in no orientation dependence for
thickness. Jump ratio imaging was useful in confirming the presence of the thin oxide;
however EELS acquisitions of the film failed primarily due to specimen drift in the
microscope and film thickness being only a few nanometers. Several samples were also
subjected to electrolyte exposure experiments and also variations to the HNO₃ etch, used
to form the initial oxide. The resulting products from these loosely defined experiments
were too thick for TEM characterization or imaging and also resulted in contamination
build up.

Even though initial microscopy attempts were not completely successful, several
sharp needles and dull wires were subjected to potentiodynamic pitting experiments in
aqueous NaCl solutions. Pitting occurred for the population of needles and wires tested
and all held reliable open circuit potentials within 100 mV. Lower pitting potentials
were obtained with the sharp Al needles. The proposed field enhancement effect with
this particular geometry was thereby confirmed. SEM served as a valuable tool for
characterizing pitting activities on these samples, high in population.
The flat geometries also provided several interesting results when investigated. Initial studies and TEM sample preparation using the FIB/SEM proved the importance of initial surface features and emphasized the need for an electropolish to minimize damage from a mechanical polish. Polishing damage lead to additional preferred pitting sites and thus samples prepared in this manner were undesirable in investigating the initiation stages of pitting corrosion. The initial oxide from the electropolished aluminum wires was again uniform in thickness and 4-5nm, as observed with the needle geometry.

Potentiodynamic pitting experiments on the individual wires were carefully controlled by close monitoring of the current-potential data. One experiment was terminated after the formation of a single pit signified by a sharp rise in current in the current-potential data. FIB was employed to make a site-specific TEM cross-section through the center of the pit. The oxide formed on this sample after exposure to NaCl solution and pitting had thickened to 30 nm and also contained chlorine, detected with AXSIA. The pit had formed at a grain boundary. Unfortunately the sample geometry did not allow a prior knowledge of the initial grain structure prior to pitting, resulting in some uncertainty; however a grain boundary is likely to serve as a site for preferential pitting. It is assumed that the initial oxide was 5 nm based on characterization results from the unpolarized and electropolished Al wire. Exposure to aqueous NaCl with pitting conditions changed the oxide in both structure and thickness. Other electropolished wires were similarly prepared and tested and experienced several pitting events. TEM samples were not made from these wires; however, SEM data provided valuable information that led to investigations of the electrochemical variables.
The oxide layer thickened by a factor of 5-10 and contained voids when subjected to pitting experiments and by comparison with the initial flat sample and the needles. The structure of the oxide thereby changed drastically. Chlorine was also detected in the surface oxide for the sample exposed to NaCl solution and was even more distinctly observed using AXSIA for a wire implanted with chloride ions.

Microscopy techniques such as jump ratio imaging and AXSIA proved their value with the needle and wire geometry. AXSIA was especially important in detecting sensitive chemical species present like chloride. Several variables and experimental parameters were determined and controlled through the initial investigations using these two geometries. These studies focused on employing the acquired knowledge by performing more defined experiments using high purity aluminum thin films grown by electron beam evaporation.

The precise concentration levels of chloride needed for pitting sensitivities was achieved using ion implantation as a means for Cl\textsuperscript{-} incorporation. Various implant fluences were investigated and electrochemically tested and a critical fluence, chloride concentration, was determined for the Al thin films. Films implanted above and below the critical fluence of \(3 \times 10^{16}\) Cl/cm\(^2\) were characterized using AXSIA and TEM BF, and both confirmed the presence of the thin surface oxide unaffected in morphology by the ion implantation process. The initial oxide on the thin films was also consistent with other geometries, approximately 4-5 nm thick.

Precipitates, or possibly large clusters of the chloride species, were observed along the grain boundaries, while smaller AlCl\textsubscript{3} precipitates were observed within the grain faces. The films were anodically polarized to 50 mV below the average pitting
potential using a 1mm microcapillary test system. TEM plan-views and cross-sections were made and characterized. Polarization did not have a major effect on precipitate size or distribution as deduced from examination of the plan-view specimens. The chloride precipitates remained larger along the grain boundaries (up to 20 nm) and smaller within the grains (a few nm).

Upon examination of the polarized film in cross-section, a local increase in oxide thickness was observed and which also contained chloride from the X-ray spectrum. AXSIA results are given in Figure 7-1 demonstrating the localized increase in the oxide layer which is richer in chloride. Chloride is incorporated into the oxide layer and the concentration is large enough to prevent repassivation of the oxide. The cross-sectional data corresponds to changes associated with metastable pitting. Further polarization then results in the dissolution of aluminum through the thickened oxide, which will lead to pitting.

![Figure 7-1: RGB spectrum image overlays of aluminum film implanted with 5 x 10¹⁶ Cl/cm² at 35 keV. Red = Al, Green = Al-Cl for both. a.) As-received, before anodic polarization, with image enlarged to equate with scale in 7-1b, blue = Al-oxide. b.) After anodic polarization to 60 mV below pitting potential, blue = Al-oxide w/chlorine.](image)
7.2 CONCLUSIONS & DISCUSSIONS

The spatial distribution and sizes of the chloride precipitates, or even large clusters of the chlorine species, may directly contribute to the initiation stage of pitting corrosion. Their presence may support the need of a critical concentration present to induce metastable pitting events which then further lead to stable pit nucleation and growth. The surface oxide present on the aluminum samples explored throughout this dissertation has been uniform and constant, approximately 4-5 nm thick. The oxide is consistent using Al needles, electropolished Al wires and Al thin films and its thickness does not have crystallographic orientation dependence.

The thickness of the oxide increases significantly when exposed to potentiodynamic pitting experiments in 50 mM NaCl$_{aq}$ solution. Both the Al wires and thin films demonstrated this effect. The Al wire was electrochemically tested until pitting occurred and the film was electrochemically turned off just prior to pitting. In both cases, the oxide was approximately 30 nm thick. AXSIA was an especially useful tool in the detection of chlorine in the various samples, producing spatially resolved spectrum images of the chloride species. Chlorine was incorporated into the oxide on the wire in trace amounts from the NaCl$_{aq}$ solution and chlorine was also present from ion implantation in the Al films. A thickness increase inherently produced a structural change of the oxide layer as observed in both the TEM BF and AXSIA spectrum images.

A critical concentration of chloride is needed to permit metastable pitting. The chloride concentration is incorporated into the oxide and causes a chemical change of the surface layer. Enough Cl$^-$ incorporation prevents the oxide from reforming during anodic polarization and eventually results in metastable reactions which ultimately lead to
pitting. The oxide, rich in chlorine, eventually breaks down and allows metal dissolution resulting in pitting. Chloride is clearly a critical species that plays a very important role in the pitting phenomenon. The concentration of chloride is most important and especially its role as incorporated into the surface oxide. Pitting was not observed in the film implanted at the lower fluence, which also demonstrated no local concentrations of the Cl⁻. Thus, spatial distributions and precipitate sizes appear to be critical and affect the initiation process. The Al film implanted above the critical concentration for pitting had local areas rich in Cl⁻ and also showed signs of more Cl⁻ incorporated into the oxide layer. Several unique sample geometries combined with advanced microscopy and microanalysis techniques proved to be a powerful combination to aid in the investigation of corrosion pit initiation.

It has also been determined that the oxide and changes therein are critical parameters in the initiation process of corrosion pitting. Numerous attempts were made to localize this process and to characterize it using advanced TEM techniques. Advances in microscopy may allow a more comprehensive investigation of these critical parameters. The three sample geometries employed have evolved during this dissertation project and have led to the evaluation of several important microstructural considerations. Sensitive electrochemical data was also optimized during these studies and produced the precision needed to further explore pitting corrosion in its initial stages.

The importance of microstructure at the nanometer scale was realized throughout the evolution of sample geometries. Initial microstructure, including available surfaces and oxides, was determined necessary to permit corrosion localization and to physically characterize changes resulting from polarizations. TEM imaging techniques, including
energy filtered imaging, offered a new insight into the examination of corrosion in Al. Microanalysis methods using AXSIA were established for the Al-Cl corrosion system. A high spatial resolution was achieved using STEM and EDS for spectrum imaging and offered the identification of unique components with shared elements, i.e. Al, Al-O, Al-Cl, thereby becoming a very useful tool in this study. AXSIA complemented other TEM analyses and allowed for a significant improvement in a complete characterization.

7.3 SUGGESTED FUTURE WORK

Combining the advanced TEM microanalysis and characterization techniques discussed in this dissertation with well-defined and controlled potentiodynamic pitting corrosion experiments in future work can aid in providing a more detailed explanation of the role of the oxide and, more importantly, the role that chlorine plays in pitting corrosion. Additional techniques can and should be employed. Most particularly, EELS near edge fine structure and/or low loss spectrum imaging can especially aid in structurally mapping the changing occurrences of the oxide resulting from polarization, metastable pitting, and pitting. Any local density changes, including bonding information, can be achieved using these same techniques. Chlorine incorporated into the oxide can then be chemically identified and mapped throughout electrochemical changes. Automated eXpert Spectrum Image Analysis can use either EDS or EELS data. Although difficulties are presented using an EELS signal, the technique if optimized, could offer valuable chemical structure information at a much higher spatial resolution. EELS spatial resolution (sub-Angstrom) could thereby better map $\text{Cl}^-$ within the 5 nm
oxide. These techniques coupled with a sample geometry capable of confining pitting corrosion offers a major opportunity to further investigate the initiation stage of pitting.

One sample geometry pursued at the end of this study consisted of punched 3 mm disks from a high purity Al foil. Information and initial results are presented in Appendix B and will not be discussed in detail here. Sample geometry is a key feature to successfully localize pitting corrosion. It is also important for microscopy and analysis. Optimizing the geometry to satisfy these two conditions is the ultimate goal for any future work. It is desired to characterize a sample throughout the corrosion investigations without alterations or destruction of the specimen for TEM; that is, the closest to in-situ for characterization of the initiation process of pitting corrosion.

The appropriate sample geometry is thereby critical to make this work a success. The Al needle geometry is unique in offering multiple imaging and analysis capabilities without sample destruction. The field enhancement effect has been verified and with an appropriate sample population and electrochemical data including pitting potentials could be collected. Experiments must be conducted with the required sensitivities to induce pitting and the sample characterized throughout the stages from metastable pitting through pit formation. Microscopy conflicts can be overcome with careful precautions. Sample storage and plasma cleanings can keep the samples free from contamination and imaging at low accelerating voltages (100-200 keV) can eliminate radiation damage. Although this geometry was abandoned during the early stages of this work, the needles are considered a very viable approach to localizing pitting corrosion for initiation studies. The needles will require detailed control in sample radius, yet with the techniques and capabilities now developed and available, the Al needles can serve as an innovative
approach to establishing ground breaking results in the initiation process of pitting corrosion.

In conclusion, several novel techniques in the electron microscope have demonstrated the power to analyze pitting corrosion at the nanometer level. The addition of electron microscopy to complement the existing corrosion efforts has resulted in significant findings and highlighted several microstructural features that would otherwise be entirely missed. When investigating an initiation stage of any process, especially pitting corrosion, every feature at the nanometer level may contribute and should be considered and controlled, if feasible. Advances in microscopy are now allowing such features to be characterized. Using what has been learned throughout this project with better controlled electrochemical experiments can now lead to future investigations that will result in a considerable increase of pertinent information to finally understand pitting corrosion.

A Final Note on EELS for Future Work

Although not employed in the work presented, it was considered that energy loss near edge fine structure (ELNEFS) analysis could serve as a powerful tool in this study. Similar to observing a chemical shift in the core level binding energies with XPS, the ionization edge threshold energies in EELS, when carefully examined, can also exhibit a shift in energy or change in edge structure. The ionization edge threshold energy observed in EELS represents the difference in energy between the core level initial state and the lowest energy final state of an excited electron which occurs below the vacuum level. Chemical shifts in EELS depend on the valence electron configuration; therefore important bonding information can be gained from the sample. Careful examination of
the ionization edge reveals that it exhibits oscillations within the first 20-30 eV of the edge onset which gives rise to a fine structure in the edge. As a result, the ionization edge may shift in energy or change in shape or structure corresponding to any differences in local bonding or valence states.

Detailed interpretation of the near edge fine structure in EELS is a very useful tool for characterization. A change in the ionization edge structure states a change in the chemical environment (bonding characteristics) around a particular element. For the corrosion experiments performed in this dissertation, bonding characteristics and changes within the oxide including Cl⁻ adsorption, state of hydration and defect concentration, could possibly be interpreted through careful inspection and fingerprinting of the oxygen near edge fine structure. This technique appears promising for microanalysis of the various oxides present in our samples and should be considered for future analysis of the polarized and unpolarized aluminum surfaces. Although not fully utilized in this study, ELNEFS involved in future work with pit initiation could further aid in understanding the oxide bond structure and relationship to the pitting process.
APPENDICES
APPENDIX A

ADDITIONAL THIN FILM RESULTS

Additional results discussed in Chapter 6 are presented here for the aluminum thin films. Several data sets for AXSIA processing were collected in numbers and while not all can be presented, two additional results are provided below.

Figure A-1: STEM ADF image (top left) and resulting spectrum image (top right) with component spectra for sample implanted $5 \times 10^{16}$ Cl/cm$^2$. 
Figure A-2: STEM ADF image (top left) and resulting spectrum image (top right) with component spectra for sample implanted $7 \times 10^{16}$ Cl/cm$^2$. Arrows point to clustered regions of chlorine observed with the higher fluence and not with Al implanted $5 \times 10^{16}$ Cl/cm$^2$. 
A 3 mm punched disk was pursued during the latter stages of this project. High purity Al foil can be heat treated to produce a desired microstructure with a controlled grain size. The Al foils could then be implanted with chloride ions and electrochemically polarized using the same 1 mm capillary set up used with the Al films and centering the exposure area within the 3 mm punched disk.

A disk could then be electropolished from one-side for only a few seconds to produce our initial surface of the Al. The sample could then be electropolished from the back side to thin for electron transparency. The final thinning TEM preparation step could be made at any desired stage of pitting experimentation. For example, a final thinning polish could be made to a disk that had not been subjected to any polarizations or it could be performed to a disk after the front side had been anodically polarized, just below or above the pitting potential. The basis for this sample geometry is to enable TEM investigations of the various stages of pitting corrosion while maintaining pit localization.

Initial TEM results are presented here. High purity rolled aluminum was heat treated at 350 °C for 1 hour, which resulted in a larger (> 1 μ) grain size. A 3mm disk was punched and implanted with 3 x10^{16} Cl/cm^2, a fluence closer to the critical concentration required for pitting in the aluminum films. TEM BF of the unpolarized material is given in Figures B1 and B2. One boundary exhibits diffraction contrast
associated with ion implantation while voids are observed along another boundary. AXSIA results from along this boundary are presented in Figure B-3. The spectrum image from the boundary component is given and rich in oxygen. Chlorine is present in all three resulting components and is not spatially resolved. The STEM dark field image also shows arrows pointing to voids along the boundary which appear to be holes resulting from the electropolish.
Figure B-2: TEM BF of 3 mm punched disk implanted with 3 x 10^{16} Cl/cm² at 35 keV as received (unpolarized). Diffraction contrast from different regions along boundary. Top right image near area scanned for AXSIA in Figure B-3.
Figure B-3: a.) STEM ADF of 3 mm punched disk implanted with $3 \times 10^{16}$ Cl/cm$^2$ at 35 keV as received (unpolarized) with 300 by 300 nm area selected (labeled 1) for AXSIA. Arrows pointing to voids. b.) Spectrum image (2.34 nm/pixel) from boundary (green) resultant component. c.) AXSIA results, individual component spectra and RGB overlay spectrum image.
A similar implanted 3 mm disk was anodically polarized to just below the pitting potential and then thinned using the final backside electropolish. TEM BF results in Figure B-4 show rectangular inclusions along the boundary. AXSIA results are presented in Figures B-5 and B-6. The boundary-rich component spectrum image and EDS spectrum is presented for both data sets and each are predominantly oxygen and also contains chorine. The Cl component is more unique in the polarized material and is present in the boundary component.

![Figure B-4: TEM BF images of 3mm punched disk implanted with 3 x10^{16} Cl/cm^2 at 35 keV and polarized below pitting potential. Rectangular inclusions observed along boundaries.](image)

It is believed that the electrochemical polish the samples undergo caused preferential etching at the grain boundaries. This geometry may still be optimized for future work by adjusting the etching/polishing solution, i.e. concentration, time, temperature. The 3 mm disks have the potential to really benefit this study, especially if a smaller grain size is produced that offers more sites for investigation. The geometry permits easy TEM plan-view sample preparation. FIB cross-sections could also be made from the material before electrochemically polishing to electron transparency allowing
both views of TEM samples to be made from the same material. Initial results deem promising for future work using this geometry to investigate the initiation of pitting corrosion.

**Figure B-5:** a.) STEM ADF of 3 mm punched disk implanted with \(3 \times 10^{16} \text{ Cl/cm}^2\) at 35 keV and polarized with 400 by 400 nm area selected (labeled 1) for AXSIA. b.) Spectrum image (3.125 nm/pixel) and component spectra from boundary (green) resultant component. c.) AXSIA results, component spectra overlay and RGB overlay spectrum image.
Figure B-6: a.) STEM ADF of 3 mm punched disk implanted with $3 \times 10^{16}$ Cl/cm$^2$ at 35 keV and polarized with 400 by 200 nm area selected (labeled 1) for AXSIA. b.) Individual component spectra and spectrum image (1.56 nm/pixel) from boundary (green) resultant component. c.) AXSIA results, component spectra overlay and RGB overlay spectrum image.