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It is entitled:
Mechanism of Passivation and Inhibition of Trivalent Chromium Process Coating on Aluminum Alloys

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Mechanism of Passivation and Inhibition of Trivalent Chromium Process Coating on Aluminum Alloys

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Abstract

Chromium conversion coatings (CCC) based on Cr(VI) are widely used to enhance corrosion resistance of aluminum alloys. However, the conventional CCC system consists of various Cr(VI) compounds, which are toxic and carcinogenic, leading to increasingly restricted usage. The Trivalent Chromium Process (TCP), for example, has proven to be a promising alternative to CCC. Although significant research on the application and performance of TCP has been done, questions such as the film microstructure, the nature of the TCP/substrate interface and the evolution of the TCP film in response to different environments have not been answered.

Neutron reflectivity (NR) and x-ray reflectivity (XRR) are used to determine the structure and composition of TCP films on aluminum alloy 2024-T3. A new electro-assisted deposition method was designed. Quantitative NR and XRR analysis confirmed linear film growth. The film composition was determined to be $\text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O}\cdot x(\text{ZrO}_2\cdot j\text{H}_2\text{O})$ ($i = 2.10 \pm 0.55$, $j = 1.60 \pm 0.45$ and $x = 0.85 \pm 0.14$).

*In-situ* neutron reflectivity was used to observe the structure and evolution of a TCP passive film with a simplified formulation on Al in a NaCl-D$_2$O solution. We observed the evolution of the TCP film on the Al anode and compared the degradation of the Al with and without TCP protection.

A dramatic improvement in corrosion resistance of AA2024-T3 is achieved by anodic hardening TCP passive films with Ce(III). The anodic current density is suppressed by the factor of 500 after exposure in the presence of Ce(III) at potentials in metastable pitting region (-580 mV vs. SCE for $4 < \text{pH} < 8$). Dynamic polarization analysis after
step-by-step polarization reveals that Ce(III) increases both the open circuit potential and the pitting potential.

*In-situ* NR is applied to investigate the evolution of structure and composition of a TCP passive film on pure Al under Ce(III) anodic hardening. We observed the formation of a Ce-enriched TCP layer at the film/solution interface during anodic polarization, which extends the pitting potential range and reduces the baseline corrosion current.

Similar to the *in-situ* Ce(III) anodic hardening experiment, *in-situ* NR is used to investigate the evolution of structure and composition of a TCP passive film under cathodic polarization in the presence of Ce(III). We observed a film evolution at Al/TCP interface; while the *in-situ* current between the anode and the cathode process shows significant attenuation over 24 hours. Cathodic inhibition was verified by a separate potentiostatic electrochemical experiment. An evolution model based on the *in-situ* NR data is proposed to explain the cathodic inhibition process.

These experiments are the first to measure the response of a passive film on Al in an active corrosion environment. The results dramatically alter the conventional wisdom regarding passive films. TCP film is not a water barrier. In fact the films rapidly imbibe water. Nevertheless the metal remains passive. Protection is due to a very thin barrier layer right at the metal/film interface. The presence of the water in the bulk film actually facilitates Ce(III) penetration, which leads to further improvement in corrosion protection.
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# Table of Contents

Abstract ........................................................................................................................................ i
Acknowledgements ........................................................................................................................ iv
List of Figures ................................................................................................................................ ix
List of Acronyms ........................................................................................................................... xiv

Chapter 1 General introduction ....................................................................................................... 1
  1.1 RESEARCH SIGNIFICANCE ....................................................................................... 1
  1.2 TECHNICAL BACKGROUND ................................................................................. 1
    1.2.1 Metal dissolution and pH increase ................................................................. 1
    1.2.2 Precipitation and deposition of TCP film ..................................................... 2
    1.2.3 Dehydration-condensation of TCP ............................................................... 2
    1.2.4 Structure and morphology of TCP .............................................................. 3
    1.2.5 Surface defects ............................................................................................ 4
    1.2.6 Mechanisms of active inhibition ................................................................. 4
    1.2.7 Specular reflection of neutron (or x-ray) ..................................................... 6
  1.3 SCOPE OF THE RESEARCH ................................................................................ 8
  1.4 STATEMENT OF OBJECTIVES ........................................................................ 9
  REFERENCES .............................................................................................................. 10

Chapter 2 Structure and composition of electro-assisted trivalent chromium process (EA-TCP) films on Al alloy ................................................................................................. 13
  2.1 INTRODUCTION ...................................................................................................... 13
  2.2 MATERIALS AND METHODS ............................................................................. 14
    2.2.1 Silicon wafer substrates ............................................................................. 14
    2.2.2 Deposition Methods .................................................................................. 14
    2.2.3 Drying and baking .................................................................................... 15
    2.2.4 NR and XRR ............................................................................................. 16
    2.2.5 Time-of-flight secondary ion mass spectrometry ...................................... 17
  2.3 RESULTS .................................................................................................................. 17
    2.3.1 Structure of AA 2024-coated wafer substrate ........................................... 17
    2.3.2 Film structure of as-prepared immersion-TCP film ................................... 19
    2.3.3 Film structure of as-prepared electro-assisted (EA) TCP film ................. 19
    2.3.4 RT drying and vacuum baking .................................................................... 19
    2.3.5 Speciation of EA-TCP deposition film by XRR and NR ......................... 20
  2.4 DISCUSSION ............................................................................................................. 20
    2.4.1 Immersion films ......................................................................................... 20
    2.4.2 EA deposition ............................................................................................. 22
    2.4.3 Transition from hydroxide complex to crystal ......................................... 24
    2.4.4 EA-TCP film structure after vacuum baking ........................................... 24
    2.4.5 Speciation of TCP film ............................................................................. 27
    2.4.6 SIMS of EA-TCP film .............................................................................. 28
  2.5 CONCLUSION ............................................................................................................ 28
  REFERENCES .............................................................................................................. 30

Chapter 3 In-situ evolution of Trivalent Chromium Process (TCP) passive film on Al in a corrosive aqueous environment ...................................................................................................... 43


<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 INTRODUCTION</td>
<td>44</td>
</tr>
<tr>
<td>3.2 EXPERIMENTAL DETAILS</td>
<td>46</td>
</tr>
<tr>
<td>3.2.1 Silicon wafer substrates</td>
<td>46</td>
</tr>
<tr>
<td>3.2.2 TCP deposition</td>
<td>46</td>
</tr>
<tr>
<td>3.2.3 Neutron reflectivity (NR)</td>
<td>47</td>
</tr>
<tr>
<td>3.2.4 In-situ split liquid cell</td>
<td>47</td>
</tr>
<tr>
<td>3.3 DATA AND RESULTS</td>
<td>49</td>
</tr>
<tr>
<td>3.3.1 Electro-assisted (EA) TCP deposition</td>
<td>49</td>
</tr>
<tr>
<td>3.3.2 Comparison between METALAST® and simplified NAVAIR EA-TCP films</td>
<td>50</td>
</tr>
<tr>
<td>3.3.3 In-situ NR of bare Al</td>
<td>51</td>
</tr>
<tr>
<td>3.3.4 In-situ NR study of TCP passivity</td>
<td>52</td>
</tr>
<tr>
<td>3.4 DISCUSSION</td>
<td>53</td>
</tr>
<tr>
<td>3.4.1 TCP passivation and corrosion rate on Al-coated wafer</td>
<td>54</td>
</tr>
<tr>
<td>3.4.2 TCP passive structure and water penetration</td>
<td>55</td>
</tr>
<tr>
<td>3.5 CONCLUSIONS</td>
<td>59</td>
</tr>
</tbody>
</table>

REFERENCES | 61 |

Chapter 4 Ce(III) Inhibition of Passivated Aluminum Alloy AA2024-T3 by Ce(III)

Anodic Hardening | 75 |

4.1 INTRODUCTION | 75 |
4.2 EXPERIMENTAL METHODS | 77 |
4.2.1 Substrate | 77 |
4.2.2 Simplified TCP formulation | 77 |
4.2.3 Electro-assisted (EA) deposition | 77 |
4.2.4 Ce(III) anodic hardening | 78 |
4.3 DATA AND RESULTS | 78 |
4.3.1 Optimization of EA deposition | 78 |
4.3.2 Ce(III) inhibition and anodic hardening | 79 |
4.3.3 Effect of pH | 81 |
4.4 DISCUSSION | 81 |
4.4.1 EA deposition of TCP on AA 2024-T3 | 81 |
4.4.2 EA-TCP passivation on AA 2024-T3 | 83 |
4.4.3 Ce(III) anodic hardening | 84 |
4.5 CONCLUSIONS | 85 |

REFERENCES | 87 |

Chapter 5 In-situ Evolution of Trivalent Chromium Process Passive Film on Al under Ce(III) Anodic Hardening | 98 |

5.1 INTRODUCTION | 98 |
5.2 EXPERIMENTAL DETAILS | 99 |
5.2.1 Silicon wafer substrates | 99 |
5.2.2 TCP deposition | 99 |
5.2.3 Neutron reflectivity (NR) | 100 |
5.2.4 In-situ split liquid cell | 100 |
5.2.5 Inductively coupled plasma atomic emission spectroscopy | 102 |
5.3 DATA AND RESULTS | 102 |
5.4 DISCUSSION | 104 |
5.4.1. The content of Ce(III) in TCP film – Ce(III) anodic inhibition.............. 104
5.4.2. Inductively coupled plasma atomic emission spectroscopy Ce leaching and
Cr exchanging........................................................................................................... 107
5.5. CONCLUSIONS............................................................................................ 108
REFERENCE............................................................................................................ 110
Chapter 6 In-situ Evolution of Trivalent Chromium Process Passive Film on Al under
Ce(III) Cathodic Inhibition ..................................................................................... 117
6.1. INTRUDUCTION.......................................................................................... 117
6.2. EXPERIMENTAL DETAILS......................................................................... 118
6.2.1. TCP-passivated Al / Si wafer electrode .................................................. 118
6.2.2. Neutron reflectivity (NR)......................................................................... 118
6.2.3. In-situ split liquid cell .......................................................................... 118
6.3. DATA AND RESULTS................................................................................ 119
6.3.1. Evolution of the cathode at the pitting transition under Ce(III) inhibition 119
6.3.2. Current profile of a cathodically polarized TCP-passivated pure Al /Si
wafer ..................................................................................................................... 121
6.4. DISCUSSION............................................................................................... 122
6.5. CONCLUSIONS.......................................................................................... 123
REFERENCE............................................................................................................ 125
Chapter 7 General Summary and Technical implications ............................................. 130
REFERENCES........................................................................................................... 131
List of Figures

Figure 1.1 A roadmap of the experimental strategy to reach the objective. .......................... 12

Figure 2.1 (a) The alloy-coated wafer is anodically activated in 25 vol% TCP solution. The native oxide and part of the Al alloy layer dissolve while the proton reduction reaction occurs on the graphite cathode. (b) The alloy-coated wafer is then cathodically polarized. Proton reduction occurs on the wafer surface. The pH rise triggers Cr(III) compound precipitation on the wafer surface. ................................................................. 31

Figure 2.2 (a) SPEAR NR data collected from as-prepared alloy-coated silicon substrate. (b) best-fit SLD profile corresponding to the solid line through the data points in (a). ................................................................. 32

Figure 2.3 (a) XRR data collected from as-prepared AA 2024 alloy-coated silicon substrate. (b) Best-fit SLD profile corresponding to the solid line through the data points in (a). ................................................................................. 33

Figure 2.4 (a) XRR data collected from 30-s acid-activated AA 2024 alloy-coated silicon substrate measured in air 4 h after activation. (b) Best-fit SLD profile corresponding to the solid line through the data points in (a)................................................................. 34

Figure 2.5 (a) XRR data collected from as-prepared TCP deposition film on AA 2024-coated silicon wafer by the immersion method (3 min) (b) best-fit SLD profile corresponding to the solid line through the data points in (a).................................................................................. 35

Figure 2.6 (a), (b), (c) SNS NR data of as-prepared EA-TCP film after 1, 2, and 4-min EA deposition in 25 vol% TCP solution. (d) Resulting SLD profiles. A dense interfacial layer is observed at the alloy surface. The bulk layer thickness increases with deposition time (Figure 2.7). The peak at 0 Å is the SiO2-covered Si surface. The peak at about 270 Å is the dense EA-TCP interface layer. The data could not be adequately fit without this interfacial layer. ................................................................................................................ 36

Figure 2.7 As-prepared EA-TCP deposition film thickness and SLD as a function of EA deposition time. A constant film growth rate and minimal change in SLD are observed. 37

Figure 2.8 SPEAR NR data for three identical EA-TCP films (A, B, C) after 4-days drying at ambient conditions. (d) SLD profiles based on the solid lines in (a), (b), (c).... 38

Figure 2.9 SPEAR NR data before and after vacuum baking of samples A and B in Figure 2.8. ......................................................................................................................... 39

Figure 2.10 XRR and NR data comparison of samples C (RT dried state). NR data are from SPEAR. .................................................................................................................... 40

Figure 2.11 Schematics of EA-TCP deposition via cathodic polarization in the initial state (a), and steady state where a gradient in metal ion concentration exists (b). At high cathodic polarization, the reduction reactions rapidly transition from charge-transfer to diffusion control leading to kinetically-limited, steady-state growth. ........................ 41
Figure 2.12 Positive-ion SIMS surface spectrum of EA-TCP film. Peaks at 50, 52, 53 are from Cr. Peaks at 90, 91, 91 and 94 are from Zr. Peaks between 106 and 111 are signals from the Pd substrate and ZrO₂. Peaks after 120 are due to Cr₂O₃.

Figure 3.1 Schematic diagram of the TCP deposition on Al-coated wafers. (a) The substrate is anodically activated in a 10-vol% TCP bath. The native oxide and part of the Al dissolve. (b) Under cathodic polarization, proton reduction occurs on the Al surface. The pH rise triggers TCP deposition.

Figure 3.2 Design of the split liquid cell. The liquid space in the cell is separated into three cavities, a bulk reservoir in middle and two thin reaction layers on both sides. Neutrons penetrate the Si substrate from above and reflect off the TCP/water interface. The wafer electrodes directly contact the electrolyte in the reaction layer. The thickness of the reaction layer is 3 mm. Holes between the cavities allow NaCl-D₂O solution to flow to the reaction layers to sustain corrosion.

Figure 3.3 Deposition potential and current density during EA process on AA 2024-T3 coupons, a) blue: +0.50 V, 30 s followed by -1.25 V, 180 s (straight line); b) red: +0.50 V, 30 s followed by -1.50 V, 180 s (straight line).

Figure 3.4 Dynamic DC polarization curves of TCP-treated AA 2024-T3 samples and a bare control in (1 g / 100 mL NaCl de-aerated aqueous solution). All samples were conditioned at OCP for 30 min prior to the scan. The scan rate was 1 mV/s.

Figure 3.5 (a) SPEAR NR data ($R-q$ plots) on a simplified TCP sample (blue) and METALAST® TCP sample (red). (b) SLD profiles based on the best fit. Comparison between the two SLD profiles shows similar film structure, including a sharp interface and broad bulk layer. The SLD of the dry film using simplified formulation is $1.84 \times 10^{-6}$ Å⁻², very close to the SLD used for METALAST® TCP film, which is $1.98 \times 10^{-6}$ Å⁻².

Figure 3.6 (a) SPEAR NR data ($R-q$ plots) on a corroding Al layer in a split liquid cell. The data before and after 3-hour exposure at 100 mV noble to the OCP in de-aerated NaCl-D₂O solution show that $q$ spacing between fringes expands, indicating reduced thickness of Al layer. (b) SLD profiles based on the $R-q$ plots. The Al layer thickness changed by ~ 360 Å (from ~ 860 Å before exposure to ~ 500 Å after 3-hour exposure). A color scheme is adopted in the SLD profile to highlight the different layers present.

Figure 3.7 Dynamic DC polarization curves from TCP treated Al-coated wafer anode in the split liquid cell. The liquid cell was filled with NaCl-D₂O solution and stabilized for 30 min prior the measurement. The OCP is indicated at -1.00 × 10³ mV.

Figure 3.8 (a) SPEAR NR data ($R-q$ plots) for In-situ TCP under anodic potentials. Below -800 mV the film is stable. However fringes disappeared after the potential reached -750 mV, indicating TCP coating and Al layer were stripped. (b) SLD profiles based on $R-q$ plots show the disappearance of TCP film as well as the Al layer after the potential exceeded $E_{pit}$. The position of D₂O solution drops from ~ 760 Å to 0 Å.
Figure 3.9 Current density recorded for bare Al in the split cell. The reduction in Al layer thickness is in agreement with the average in current density. The durations of the NR snapshots are marked as vertical bars. The current density was measured during the 3-hour polarization experiment (Figure 3.5)

Figure 3.10 Current density curves of a TCP-coated sample after each potential step. (a) Recorded current densities in the passive region (-975 - -800 mV vs. SCE) were under 10 nA/cm². The red curve (at -800 mV) showed some instability, as indicated by the noise peaks. (b) The current density for potentials more noble than -775 mV jumped to µA/cm² scale, but eventually dropped back after the Al dissolved, leaving a bare silicon wafer. The curve at -725 mV illustrates this behavior within the time window of the experiment.

Figure 3.11 SLD profiles of RT-dried TCP-coated Al samples before polarization (blue curve). A dense interfacial TCP layer is observed between the bulk TCP film and Al. The SLD profile after exposure (red curve, from Figure 3.7b) is plotted for comparison. The dense interfacial layer still exists in the wet state but is overwhelmed by the bulk TCP layer, which has higher SLD.

Figure 3.12 (a) NR data (R - q plots) for the metastable state at -775 mV. (b) SLD profiles of the metastable state compared to the passive and failed states. In the metastable state the Al layer dissolves and TCP film swells. The SLD of the TCP layer is $5.7 \pm 0.1 \times 10^{-6}$ Å⁻² and the thickness is $690 \pm 20$ Å.

Figure 4.1 Step-by-step anodic polarization of an EA-TCP passivated AA 2023-T3 in 1 wt-% NaCl and 0.1 wt-% CeCl₃ de-aerated aqueous solution (blue line). Left axis is applied potential (red curve). The right axis is the current density (blue and black curves). The polarization current density of an EA-TCP sample without Ce(III) inhibition is plotted as the dotted black curve connecting the current expected at each potential step based on the anodic branch of the -1.5V DC polarization curve in Figure 3.4. The degree of current suppression compared to the uninhibited system is the length of the vertical black arrows.

Figure 4.2 The step-by-step polarization data for EA-TCP passivated AA 2024-T3 in 1% NaCl solution without Ce³⁺. The current density reaches 0.1 mA/cm² at -680 mV, indicating that TCP films breakdown. Note that the current scale if 500 times larger than Figure 4.1.

Figure 4.3 Step-by-step anodic polarization of an EA-TCP passivated AA 2024-T3 held in the Ce³⁺ test solution. After the 4-hour exposure at -580 mV the DC polarization curves in Figure 4.4 were measured. At -580 mV the sample is still in the passive state just below the breakdown potential.

Figure 4.4 DC polarization of EA-TCP passivated AA 2024-T3 step-by-step-inhibited by Ce³⁺ (green). A bare control immersed in the same Ce³⁺ solution for 18 hours was also scanned (blue). The bare alloy curves from Figure 3.4 are included for comparison (dashed lines). The combination of a TCP film and Ce³⁺ is required to achieve effective corrosion inhibition.
Figure 4.5 Step-by-step anodic polarization of -1.50 V EA-TCP sample in 1 wt% NaCl and 0.1 wt% CeCl₃ de-aerated aqueous solution. The pH was adjusted to 7.97. The short-term and long-term passivation effects are apparent between 7 and 13 h.

Figure 4.6 Step-by-step anodic polarization of -1.50 V EA-TCP sample in 1 wt% NaCl and 0.1 wt% CeCl₃ de-aerated aqueous solution. The pH was adjusted to 4.03.

Figure 4.7 Comparison of initial EA current (0 ~ 30 s) for two -1.5V samples under 0.5 V polarization. Differences are due to the history-dependent oxide film that is stripped by about 15 s.

Figure 4.8 Current density curves during the deposition stage (30 ~ 210 s). The curve in blue was polarized at -1.25 V, and the curve in red was polarized at -1.50 V. The attenuation of the cathodic current is due proton diffusion limitations in the solution (initial decrease) and in the oxide (gradual decrease after 100 s, as the TCP film grows).

Figure 4.9 Detailed anodic current density in the Ce³⁺ step-by-step inhibition experiment. Potential is -580 mV, sampling period is 2 s. Two time constants are evident as rapid fluctuations (electrochemical noise) superimposed on decreasing background current.

Figure 5.1. DC polarization curves of AA 2024-T3 samples with and without TCP protection and Ce(III) inhibition. The curve (green) measured after step-by-step anodic polarization in Ce(III) shows an increased OCP, while the curve (orange) measured after 24-hour immersion in Ce(III) shows a decreased OCP compared to the bare AA 2024-T3 alloy (black), and TCP passivated AA 2024-T3 (red) without Ce(III) inhibition.

Figure 5.2. Schematic of the split liquid cell set up for observing Ce(III) anodic inhibition. Liquid space is separated into three cavities, a bulk reservoir in middle and two thin reaction layers on both sides. The angle of the incidence is greatly exaggerated. Details are found elsewhere. The neutron beam impinged on the TCP sample for observing the corresponding film evolution.

Figure 5.3. Step-by-step potentiostatic scan of a TCP-passivated Al anode in 0.1 wt% CeCl₃-inhibited 1-wt% NaCl-D₂O solution (red), compared to the case without Ce(III) (blue). The passive region of the TCP-passivated Al anode extends to higher potentials with a lower current baseline during Ce(III) inhibition. A transition region at -725 mV is observed prior to the stable pitting above -700 mV. The counter electrode was a Au-coated wafer. The uninhibited data are from in-situ work described in Chapter 3.

Figure 5.4. SPEAR NR data (R ~ q plots, and SLD profiles) for in-situ TCP film evolution exposed to step-by-step anodic polarization (-825 mV to -725 mV) in Ce(III)-inhibited NaCl solution (0.1 g CeCl₃, 1 g NaCl in 100 ml D₂O, de-aerated). a) R ~ q plots below -725 mV are identical; b) small change in higher q range was observed at the transition potential of -725. c) SLD profiles indicate significant Ce(III) distribution within the TCP layer, compared to the original dry TCP (black), and the TCP film under anodic polarization in passive region (-900 mV to -800 mV) without Ce(III) inhibition (green), which is corresponding to the blue current profile in passive state in Figure 5.4. The
difference in SLD between the uninhibited and inhibited curves is attributed to Ce penetration. Details regarding the uninhibited TCP data can be found in Chapter 3.1...

Figure 5.5. ICP data on the Ce, Cr, Zr atomic concentration in NaCl (1 wt %) water solution over 20 days. A TCP-passivated AA 2024-T3 sample and a TCP-passivated AA 2024-T3 sample after Ce(III) anodic hardening were immersed in NaCl (1 wt %) water solution for 20 days. Solution samples were taken every 3 ~ 4 days, to track the concentration of Ce (purple), Cr (green) and Zr (blue) released from TCP-passivated AA 2024-T3 samples without hardening (dashes) and after anodic hardening. Substantial amount of Ce is measured, and the concentration of Cr from both samples are also considerable, while the Zr curve is almost 0...

Figure 6.1. Schematic of the cell setup for investigating Ce(III) cathodic inhibition. The cell is flipped compared to Figure 5.2, presenting the TCP counter electrode (cathode) on top for NR interrogation. The working TCP anode is polarized at -730 mV for 24 hours.

Figure 6.2. Anodic current density profile when the TCP-coated Al anode was controlled at transition stage at -730 mV. The current drops to 0 at 23 hour. The origin of the noise is uncertain; it may be due to mechanical vibrations or metastable pitting.

Figure 6.3. SPEAR NR data $R - q$ plots (a), SLD profiles (b) and layered model as a function of time (c) for in-situ TCP-coated Al cathode under Ce(III) inhibition during constant polarization of the anode at -730 mV. The evolution of the structure and composition of the TCP bulk layer in the SLD (b) profiles reflect the continuous change as observed in $R - q$ plots (a). A peak at Al/TCP interface forms after 18 hours, at which point the TCP film thickness increased significantly. c) Illustration of the structural and chemical composition evolution in TCP layer showing build of Ce at the metal-film interface.

Figure 6.4. Current density profile at constant cathodic polarization as a function of time. The TCP-coated Al cathode was polarized at -50 mV vs OCP (-850 mV vs SCE) for 36 hours in de-areated CeCl$_3$ (0.1 wt %) NaCl (1 wt %) water solution. The current attenuation is an valid indication of Ce(III) cathodic inhibition.
**List of Acronyms**

AMCC: Advanced Materials Characterization Center, University of Cincinnati;

DCP: direct current polarization;

EA: electro-assisted;

EIS: electrochemical impedance spectroscopy;

LANL: Los Alamos National Laboratory

LANSCE: Los Alamos Neutron Science Center

NR: neutron reflectivity;

OCP: open circuit potential.

ORNL: Oak Ridge National Laboratory

PVD: physical vapor deposition;

RT: room temperature

SEM: scanning electron microscopy;

SPEAR: The Surface Profile Analysis Reflectometer

TCP: Trivalent Chromium Process;

XRR: x-ray reflectivity;
Chapter 1 General introduction

1.1 RESEARCH SIGNIFICANCE

Chromate conversion coatings (CCC) based on Cr(VI) are widely used surface pretreatments to enhance corrosion resistance of Al alloys and to improve the adhesion of organic primers and top coats. Because of the low cost and superior performance, conventional CCC has been used for decades. However, the conventional CCC system consists of various hexavalent chromium compounds, which are toxic and carcinogenic. Toxicity has led to increasingly restricted usage.\textsuperscript{1, 2} Consequently, recent research has focused on the development of various non-chromate replacements.\textsuperscript{3-5} For example, Trivalent Chromium Process (TCP) developed by NAVAIR\textsuperscript{6} has proven to be a promising alternative.\textsuperscript{6-8} Although significant research on the application and performance of TCP has been done, questions regarding the micro-structure, the nature of the TCP/substrate interface and the evolution of the TCP film in response to different environments have not been answered. Even the mechanism by which TCP systems inhibit corrosion has not been firmly established.\textsuperscript{5}

1.2 TECHNICAL BACKGROUND

1.2.1 Metal dissolution and pH increase

It has been popularly accepted that the formation of TCP passive film on Al alloys takes place in two stages. The first stage involves the dissolution of the aluminum substrate. The TCP precursor solution has a surface etching agent (HF) or acidic oxidants, which promote the dissolution of both the surface oxide and Al underneath, exposing the noble intermetallic phases that strengthen the alloy. Proton reduction reactions on the
intermetallics occur simultaneously, and H₂ bubbles are observed on the substrate surface during TCP immersion. As a result of the consumption of protons, the pH of the TCP solution near the substrate surface increases.

1.2.2 Precipitation and deposition of TCP film

The increase of pH triggers the precipitation of TCP compounds such as Cr(OH)₃, and Zr(OH)₄. These compounds deposit on the substrate forming a new layer. It has been claimed that the corrosion resistance by this hydroxide layer can be as good as that provided by hexavalent CCC.⁹ Details are vague, however. Understanding on the mechanism of deposition is limited, leaving open the following questions. Why and how does the insoluble hydroxide form a layer to provide a physical barrier against corrosion? How does the water content in the film affect the corrosion resistance? In order to address such questions, fundamental research on micro-morphology is necessary.¹⁰

1.2.3 Dehydration-condensation of TCP

Some research indicates that a dehydration-condensation stage occurs during the drying or baking process after TCP deposition. This assumption is reasonable, because dehydration-condensation enables cross-linking to form an -O-Cr(III)-O- network as a passive layer protecting the metal substrate. Otherwise accumulation of individual Cr(III) compounds can hardly account for the observed corrosion resistance.
1.2.4 Structure and morphology of TCP

The thickness of TCP formed by immersion has been often studied. With increasing immersion time, the thickness increases until the metal is passivated and stops consuming hydrogen ions.\textsuperscript{11} In another words, the TCP film growth is self-terminated.

Porosity is also frequently discussed. The TCP film is formed by deposition of insoluble Cr(III) and Zr(IV) compounds, so its porosity is primarily related to the deposition rate and the availability of Cr(III) and Zr(IV) in the solution. Due to the lack of Cr(VI), which is a strong oxidant, the dissolution rate of Al in TCP precursor solution is less vigorous and deposition of TCP film is slower than conventional CCCs. Accordingly the TCP film is less condensed than conventional CCCs. The coating system parameters such as formulation, concentration, and application conditions, can also affect the film porosity.

A multi-layer structure in the TCP passive film on Al alloys has been reported recently.\textsuperscript{12, 13} Usually a dense inner layer is observed above the substrate, with an outer layer that is thicker but less dense on top. The inner, layer can be attributed to the initial high film deposition rate. Once this dense layer forms, it passivates the metal substrate as a thin barrier that slows the proton reduction process and reduces the local pH gradient. Thus further precipitation and deposition of Cr(III) and Zr(IV) compounds are retarded, leading to a slower deposition rate, hence a looser outer layer. In some cases the film surface can even re-dissolve.\textsuperscript{11} According to this explanation, the film density, porosity and thickness is controlled by the concentration of protons near the substrate surface, i.e.
the local pH gradient. So if a constant pH gradient can be sustained, a uniform and controllable TCP deposition process will ensure.

### 1.2.5 Surface defects

Both conventional CCCs and TCP coatings have micro-cracks. Micro-cracking on CCC surface is due to the tensile stress developed during the drying or dehydration stage. But contradictory conclusions on surface defects on TCP surfaces are often reported regarding the solution formulation, pH value, and conditions of application. For example, it is believed thicker TCP film involves tensile stress, which increases the chance of cracking; however it is also reported that increasing the immersion time can significantly decrease the density of micro-cracks. It was even found that the Cr(III)-treated surface only has preferentially etched zones with smooth appearance after drying at 70°C but that crack networks form in circular regions on the scale of about 8 μm before baking and 2 μm after baking. Backing leads to surface shrinking. Nevertheless drying at elevated temperature can improve the surface appearance. Neither the nature of the film nor the film formation mechanism are clear at this point.

### 1.2.6 Mechanisms of active inhibition

In conventional CCCs, both Cr(VI) and Cr(III) exist. The commonly accepted theory states that Cr(VI) plays an active role in corrosion protection, which is found mainly in the outermost layer of the CCC film. Cr(III) compounds form a physical barrier between the metal substrate and the corrosive environment. Cr(VI) is believed to leach out where the CCC film is damaged. Free Cr(VI) forms O-Cr(VI) species that diffuse to
damaged region, and inhibit the corrosion process by excluding the corrosive anions such as Cl\(^-\) from the surface.

Compared to CCC, TCP coatings are assumed to be free of Cr(VI). Thus TCP does not possess active inhibition character unless additional non-chromate inhibitor is added. However comparable corrosion resistance to CCC has been reported repeatedly. Therefore TCP passivation needs to be carefully investigated.

Another uncharted area is the mechanisms behind the corrosion protection of TCP films. Different ideas are proposed continuously. For example,\(^\text{17}\) it has been claimed that Cr(III) compounds oxidize to Cr(VI) under certain conditions, leading to active protection. In order to understand the mechanism of corrosion, passivation and inhibition, there is still a lot of work to be done.

As regards inhibitor additives, it has been reported that cerium, molybdate, and phosphate enhance active inhibition in TCP systems. Although a general inhibition mechanism of these additional inhibitors is well-accepted,\(^\text{18}\) methods to determine the response of TCP films in their presence are not well-established. The problem is that methods to determine the inhibition mechanism are neither quantitative nor definitive. Moreover the results are often compromised by the intermingling of redox process on the alloy surface. This report presents the first data on the action of inhibitors on TCP films in a well-defined system.

Two issues must be clarified prior to establish the TCP passivation and inhibition mechanism, 1) the structure and composition the TCP film itself; 2) the response of TCP film to a corrosive environment with or without additional inhibitors. To address these
issues, 1) we applied a commercial TCP film on an AA 2024 coated silicon wafer and investigated structure of this prototype by neutron reflectivity (NR) and x-ray reflectivity (XRR); 2) we developed an electro-assisted (EA) method for deposition of well-defined TCP film. We interpreted the film structure and composition through quantitative NR and XRR analysis and theoretical calculations; 3) we simplified the commercial TCP system and developed in-situ monitoring techniques by combining NR and electrochemical control through an innovative liquid split cell; 4) we verified the TCP passivity by NR in an active corrosion process; 5) we invented anodic hardening technique to enhance TCP performance by recovery of passivity in the presence of inhibitor and tracked film response during post-hardening via an in-situ monitoring techniques; 6) we verified TCP inhibition during anodic hardening by NR, and formulated a model for both anodic and cathodic inhibition processes.

1.2.7 Specular reflection of neutron (or x-ray)

Neutron (or x-ray) reflectivity has been extensively used to elucidate interfacial structure in a variety of disciplines but is not widely known in corrosion science. The most important advantages of NR for corrosion research are a greater range of sample environments (e.g. vacuum and aqueous) and quantitative characterization of interfacial properties. Tun et al., 19-22 for example, combined electrochemical impedance spectroscopy and NR. We applied their methods of quantitative NR analysis to TCP-Al systems. 23, 24

The NR experiments were performed on the Surface Profile Analysis Reflectometer (SPEAR) at the Lujan Neutron Scattering Center, Los Alamos National Laboratory, and
at the Liquids Reflectometer (LR) at Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL). The incident neutron beam has a broad spectrum of wavelengths, $\lambda$, typically from 1.5 Å to 16 Å. The wavelength of any particular neutron is determined by time-of-flight, because neutrons with different wavelengths have different velocities. The polychromatic character of the incident beam allows a range of scattering vectors, $q$, to be probed simultaneously at a fixed angle of incidence, $\theta$. The relationship between $\lambda$ and $q$ is:

$$q = \frac{4\pi \sin \theta}{\lambda}$$

(1.1)

For a NR measurements, $q$ typically extends from 0 to 0.2 Å$^{-1}$, which is achieved using multiple fixed angles of incidence. A typical NR measurement at SPEAR requires a low-angle and a high-angle setting. For our in-situ NR measurements, however, only low-angle data were measured because we require a rapid measurement with sufficient time resolution to monitor an evolving surface.

The ratio of the reflected flux to the incident flux, $R$, is plotted as a function of $q$. The data are normalized to one at low $q$ where the beam is 100% reflected. The $R - q$ plot typically shows fringes resulting from the superposition of waves scattered by different layers. The amplitude and attenuation of each wave are determined by the thickness, roughness, and scattering length density (SLD) of the layers. Thickness and roughness represent structural information while the SLD reveals the chemical composition:

$$\text{SLD} = \rho \frac{N_A}{M} \sum_{\text{molecule}} b_i$$

(1.2)
where $\rho$ is the mass density; $N_A$ is Avogadro number; $M$ is molecular weight; $b_i$ is the neutron scattering length of atom $i$; and $\rho \frac{N_A}{M}$ is molecular number density. $\sum_{\text{molecule}} b_i$ is the sum over neutron scattering lengths of all atoms present in one molecule. The $b$ values are tabulated for all elements.\textsuperscript{25}

The analytical tool used for the NR data reduction is Irena\textsuperscript{26} 2.35 for Igor Pro 6.10, which inverts the $R - q$ plot (reciprocal space) to the SLD profile (real space). The SLD profile is the SLD as a function of the perpendicular distance from the Si substrate. For the TCP system further analysis of these SLD profiles enables us to determine the evolution of the TCP passive film, in the presence of Ce(III), as the potential is raised from the passive to the stable pitting regime.

1.3 STATEMENT OF OBJECTIVES

The objective of this project is to understand the mechanism and inhibition of TCP passivity by starting from a well-defined metal layer, and finishing with a multi-layered system in an aqueous corrosion environment. The strategy is to utilize a combined \textit{in-situ} methodology for interface characterization using NR and electrochemistry, and to correlate the film evolution with the electrochemical current response. The results of the \textit{in-situ} research will bridge the gap between current knowledge on TCP systems based on conventional electrochemical evaluation and the interfacial and morphological evolution observed by NR in response to corrosion environment.
SCOPE OF THE RESEARCH.

A roadmap of the experimental strategy to reach the objective is presented in Figure 1.1.
REFERENCES

Figure 1.1 A roadmap of the experimental strategy to reach the objective.
Chapter 2 Structure and composition of electro-assisted trivalent chromium process (EA-TCP) films on Al alloy

**SUMMARY:** Neutron reflectivity (NR) and x-ray reflectivity (XRR) were used to determine the structure and composition of trivalent chromium process (TCP) films on aluminum alloy AA-2024. Two deposition methods were developed, immersion and electro-assisted (EA) deposition. EA deposition method was designed to guarantee a well-defined EA-TCP film with a uniform structure and minimum contamination from Al and additives in the precursor solution. Quantitative NR and XRR analysis of the EA-TCP film confirmed linear growth as a function of deposition time. By analyzing both NR and XRR data on as-prepared and dried films, the film composition was determined to be Cr$_2$O$_3$·iH$_2$O$_{·x}$ZrO$_2$·jH$_2$O (i =2.10 ± 0.55, j = 1.60 ± 0.45 and x = 0.85 ± 0.14).

2.1 INTRODUCTION

Neutron reflectivity (NR) and x-ray reflectivity (XRR) offer new approaches to elucidate film microstructure and film growth processes. In this chapter, the NAVAIR TCP$^1$ system was applied on AA 2024-coated silicon wafers to form a well-defined system suitable for NR and XRR. Two methods were perfected for film deposition: simple immersion, and electro-assisted (EA) deposition. NR and XRR show that samples prepared by EA-deposition form a uniform layer whose thickness increases linearly with deposition time. Based on comparison of the room-temperature-dried and vacuum-baked films, the dry EA-TCP film is a hydrous oxide of composition Cr$_2$O$_3$·iH$_2$O$_{·x}$ZrO$_2$·jH$_2$O (i =2.10 ± 0.55, j = 1.60 ± 0.45 and x = 0.85 ± 0.14). To our knowledge, the results
reported here are the first measurements of the structure and composition of EA-TCP films.

2.2 MATERIALS AND METHODS

2.2.1 Silicon wafer substrates

AA 2024-coated silicon wafers were used as the substrate. Both NR and XRR require smooth substrates, accounting for the choice of Si wafers. One-side-polished single crystal (111) wafers (1 or 5 mm thickness) were obtained from Wafer World, Inc. (West Palm Beach, FL, USA). AA 2024 films were physically deposited on silicon wafers by e-beam evaporation from a bulk alloy ingot in vacuum. The AA 2024 ingot was purchased from McMaster-Carr Supply Company (Aurora, OH, USA). The composition of ingot is 3.8-4.9 Cu, 1.2-1.8 Mg, 0.3-0.9 Mn, 0.5 Si and Fe, 0.15 Zn and Ti, and 0.1 Cr on a wt% basis. The thickness of AA 2024 film was controlled at about 400 Å, which is thick enough to assure the film is not stripped in the deposition process, but thin enough to assure the required smoothness (± 5 Å). The deposited AA 2024 layer was not annealed. The scattering length density (SLD) of the deposited layer equals calculated SLD for AA 2024, assuring that the AA 2024 layer has the same average composition as the ingot. The TCP solution, METALAST® TCP-HF, was purchased from Chemetall. (2241 Park Place, Suite C, Minden, NV).

2.2.2 Deposition Methods

We developed two methods to deposit the TCP film: 1) immersion and 2) electro-assisted (EA) deposition. For immersion method, AA 2024-coated wafers were first activated in 40-vol% H₂SO₄ at room temperature. XRR analysis as a function of
activation time revealed an optimum exposure time of 30 s at 25 °C. After 30-second activation, the substrates were immediately rinsed in deionized (DI) water and then immersed in 25 vol % TCP solution (25 ml METALAST® TCP-HF in 75 ml DI water, pH = 3.75 ± 0.40). To minimize re-oxidation of the fresh surface, the transition time from DI water to 25 vol % TCP solution was less than 5 s. The immersion time was fixed at 3 min, after which a TCP layer was visually noticeable. Samples were rinsed in DI water again and air-blown to dry.

A DC power supply was used for EA deposition. Acid-activation step in conventional immersion process was replaced by anodic polarization. AA 2024-coated wafers were connected as the anode against a graphite cathode, and immersed in 25 vol % TCP solution. The anodic polarization was optimal at 2 V for 30 s (Figure 2.1a). After 30-s anodic polarization the potential was switched from 2V to -3 V (Figure 2.1b); the wafer became a cathode (measured to be -1.55 V SCE). Three different coating times under cathodic polarization were chosen: 1 min, 2 min and 4 min. The coated samples were rinsed and air-blown to dry.

2.2.3 Drying and baking

Since the EA samples show a uniform-layered morphology, the EA method was chosen to prepare samples for the observation of the effect of drying and baking. Specifically 4-min samples (cathodically polarized for 4 min) were aged at room temperature for more than 4 days before NR measurements. The same samples were re-measured again after baking in an oven at 150 °C, 3×10⁻³ Torr, for 6 hours, so as to verify the presence of
hydration water. In a practical service scenario, TCP conversion coating films may undergo a transition from hydroxide complex to hydrous oxide crystal.²

2.2.4 NR and XRR

Neutron reflectivity on untreated alloy-wafer substrates, immersed samples, EA-deposited samples and baked samples was carried out at Surface Profile Analysis Reflectometer (SPEAR), Lujan Neutron Scattering Center, Los Alamos National Laboratory and the Liquids Reflectometer at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory.

Access to NR facilities however is limited. XRR, on the other hand, is readily available, so it is used in concert with NR. XRR is also very rapid and useful to observe time-dependent processes. For parts of the analysis presented below both methods are required. XRR was done using the PANalytical X’Pert Pro x-ray diffractometer at the Advanced Materials Characterization Center at the University of Cincinnati.

Like all diffraction analyses, interpretation of the NR data involves the inversion from reciprocal space \((R – q)\) plot to real space (scattering length density, SLD profile), which is usually not unique. Since more than one SLD profile may fit the \(R – q\) plot, physical insight and consistency between NR and XRR data analyses are required to assure credible SLD profiles. Since most parameters in the SLD profile are known, such as the SLD of silica, the SLD of AA 2024 and the thickness of the substrate layer, this information eliminates unrealistic profiles, leaving little freedom in fitting. Furthermore the profile that we accept evolves reasonably in different conditioning processes. Further analysis of these SLD profiles enables us to determine the film composition, the film
growth mechanism and the impact of drying on film morphology. Errors in the fitting parameters were estimated by repeating the complete deposition-measurement-analysis protocol.

2.2.5 Time-of-flight secondary ion mass spectrometry

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) data were obtained using the IonToF SIMS IV at the Advanced Materials Characterization Center, University of Cincinnati (http://www.eng.uc.edu/amcc). ToF-SIMS reveals elements and simple compounds by plotting the secondary ion count rate vs. ion mass. The count rate is calibrated using standards of known density (CrK(SO₄)₂·12H₂O and K₂ZrF₆). The static SIMS analysis was done at energy of 25 keV with a liquid-metal primary Ga ion gun. Since the samples were moderately non-conductive, a tungsten-based electron flood gun was used to compensate for the charging.

2.3 RESULTS

2.3.1 Structure of AA 2024-coated wafer substrate

NR data for an AA 2024-coated wafer substrate are shown in Figure 2.2. The SLD profile (b) shows a layered structure based on the best fit to the measured reflectivity data (a). The thickness of the bulk alloy layer is 350 ± 5 Å. An amorphous Al₂O₃ layer 25 ± 5 Å is detected on the top surface. The SLD of the bulk alloy metal is 2.13 ± 0.03 × 10⁻⁶ Å⁻², which is consistent with the calculated SLD based on the density and atomic composition of the alloy. The SLD of the amorphous oxide layer is 3.5 ± 0.03 × 10⁻⁶ Å⁻², which is 60% of crystalline Al₂O₃.
The XRR data collected from alloy-coated wafer (Figure 2.3) show the same structure as observed with NR. The alloy thickness is $350 \pm 5$ Å. An Al$_2$O$_3$ layer ($25 \pm 5$ Å) is also detected. The x-ray SLD of bulk alloy is $23.0 \pm 0.3 \times 10^{-6}$ Å$^{-2}$, consistent with the density and atomic composition of the alloy. The SLD of the amorphous oxide layer is $26.0 \pm 0.3 \times 10^{-6}$ Å$^{-2}$, which is very close to the value of amorphous Al$_2$O$_3$ ($26.4 \times 10^{-6}$ Å$^{-2}$, assuming a mass density of 2.4 g/cm$^3$) and close to the value calculated from the NR data. Although the oxide dissolves in 25 vol % TCP solution, we chose to remove this oxide by acid activation before deposition. XRR data (Figure 2.4) shows the results after an optimized acid-activation of 30-s exposure to 40 vol % H$_2$SO$_4$ at 25°C.

The XRR SLD profile observed 4 hours after acid activation (Figure 2.4b) shows that the oxide layer “disappears” with minimal change of the AA 2024 layer ($350 \pm 5$ Å) underneath. The apparent absence of an oxide layer may be due a near match of the re-formed oxide to aluminum. Amorphous boehmite (AlOOH) for example has and SLD of 25.8, only 12% larger than that of the alloy. In addition, the fresh oxide after activation may be of lower density and thinner than initial oxide layer leading to the broadened interface observed in Figure 2.4b.

TCP films deposited by immersion were prepared on AA 2024-coated wafers after acid-activation. As the activated wafers were immediately rinsed and transferred to TCP solution, the immersed TCP film is determined mainly by the AA 2024 layer and is minimally compromised by the thin oxide surface.
2.3.2 Film structure of as-prepared immersion-TCP film

XRR data for all samples prepared by immersion show a two-layer structure on a thinned Al-alloy layer (Figure 2.5). As shown in Figure 2.5b, starting from the SiO$_2$-covered-Si substrate, the layers are: a) an AA 2024 layer ($180 \pm 5$ Å), which is thinner than the native alloy layer, b) a middle film layer 1 ($340 \pm 5$ Å, SLD = $19.7 \pm 0.2 \times 10^{-6}$ Å$^{-2}$), and c) a top layer 2 ($120 \pm 5$ Å, SLD = $10 \pm 2 \times 10^{-6}$ Å$^{-2}$) with the lowest SLD. As seen from Figure 2.5b, layer 2 is not a constant SLD region even though this “layer” is required to adequately fit the reflectivity data. As the observed structure is quite complex, compromising further quantitative analysis, electro-assisted films were used for further study.

2.3.3 Film structure of as-prepared electro-assisted (EA) TCP film

In contrast to the immersion samples, NR data for the as-prepared samples of different EA deposition time (1 min, 2 min, 4 min) all show a single-layer structure with a thin, high-SLD interfacial layer (Figure 2.6) at the alloy surface. The thickness of the bulk deposition layer increases in proportion to the polarization time with minimal change in SLD (Figure 2.7).

2.3.4 RT drying and vacuum baking

The 4-min EA samples were dried at room temperature. To check the consistency of the protocol, three identically prepared samples were examined. After exposure to the ambient environment for more than 4 days, NR data (Figure 2.8) show a significant change in SLD profile compared to Figure 2.6. The average thickness of bulk film is 730
± 20 Å and the average SLD is $1.98 \pm 0.06 \times 10^{-6}$ Å$^{-2}$. This change could be due to dehydration and/or structural re-organization of the film.

Samples A and B in Figure 2.8 were further baked at 150 °C at $3 \times 10^{-3}$ Torr for 6 hours to dehydrate the film fully. The dehydrated films showed further decrease in layer thickness with corresponding SLD increase (Figure 2.9). The thickness changes from 730 ± 20 Å to 620 ± 20 Å. The SLD increases from $1.98 \pm 0.06 \times 10^{-6}$ Å$^{-2}$ to $2.72 \pm 0.06 \times 10^{-6}$ Å$^{-2}$.

2.3.5 Speciation of EA-TCP deposition film by XRR and NR

XRR data for 4-min film (sample C) were also collected (Figure 2.10). The SLDs of the layers are different due to differences in scattering lengths of the atoms for x-rays and neutrons but the layer structure and thicknesses are the same. This consistency justifies layered-structure model.

2.4 DISCUSSION

2.4.1 Immersion films

The observed structure of the immersed samples (Figure 2.5, b) is consistent with the film-formation mechanism postulated by Wen et al. for Cr(III) conversion coatings. The driving force for Cr(III) deposition comes from the rise in pH near the metal surface caused by redox reactions on the heterogeneous heat-treated alloy. The oxidation reaction occurs on Al-rich regions (similar to our alloy substrates) accompanied by proton reduction on Cu-rich inclusions, which are absent in our films. Cu inclusions are absent because the films are deliberately not heat treated.
Oxidation and dissolution of the alloy surface are confirmed by the XRR SLD profiles (Figure 2.4, b and Figure 2.5, b), which show reduction of layer thickness 350 ± 5 Å to 180 ± 5 Å in 3 minutes, which is equivalent to a corrosion current of 270 μA/cm². This rapid rate is promoted by the presence of F⁻ ions in the TCP solution (based on the METALAST composition, TCP solution contains BF₄⁻, Zr⁴⁺, F⁻, besides Cr³⁺.) F⁻ ions increase the solubility of Al³⁺, and impede the formation of Al₂O₃.² The proton reduction reaction, on the other hand, increases the solution pH, triggering the precipitation of Cr(III) and Zr(IV) hydroxides at the alloy surface.

The two-layer structure can be accounted for within the Wen mechanism. Layer 1 forms during the initial rapid pH rise. The high availability of Cr(III) and Zr(IV) leads to Cr(OH)ₓ⁽³⁻ₓ⁾⁺ and Zr(OH)ₓ⁽⁴⁺ₓ⁾⁺ cations, which migrate to cathodic regions on the metal surface, forming a dense layer. Once formed, however, layer 1 retards both oxidation of the alloy and the reduction of protons. Proton reduction is favored at certain transient cathodic sites causing an increase in the local pH. Since Zr hydroxide precipitates at lower pH than Cr hydroxide, precipitation of Zr occurs before precipitation of Cr, leading to Zr enrichment on transient cathodic spots. Once a fresh passivation layer covers these spots, however, proton reduction transfers to other places, thus activating new precipitation sites. This fluctuating localized precipitation leads to a rough, defective surface, which we observe in Figure 2.5b as a broadened interfacial region (“layer 2”) of lower SLD.

Immersion-TCP films are not particularly desirable for further NR and XRR study. Desirable films are simple, uniform and thick enough to be measured precisely. Immersion films are not simple because dissolution of Al and deposition of TCP occur
simultaneously. Al(III) compound inevitably remains in the deposited film, compromising determination of film speciation. Also immersion film has a rough and defective surface. The interpretation of this non-uniform structure is more difficult than for a single-layer structure. Moreover, the thicknesses of layer 1, and the AA 2024 layer are comparable, which makes it more difficult to sort out the true profile. Finally, film growth quickly ceases leading to rather thin films whose thickness cannot be measured with sufficient accuracy to assess the effect of drying and baking. These considerations motivated us to restrict further analysis to EA films.

2.4.2 EA deposition

In the EA method proton reduction is controlled electrochemically; film deposition, therefore, is controllable and sustainable over a long period of time. The resulting film is uniform and arbitrarily thick. In addition the film is not contaminated by Al.

For EA deposition, the oxide layer and part of the alloy are removed via anodic polarization in 25 vol% TCP solution (Figure 2.1a). The wafer is then cathodically polarized in 25-vol.% TCP solution, causing the deposition a hydroxide film on the bare alloy surface. Although TCP solution contains BF$_4^{-}$, Zr$^{4+}$, F$^-$, besides Cr$^{3+}$, the alloy-coated wafer is under cathodic polarization during deposition process. As a result Al dissolution is suppressed and BF$_4^{-}$, F$^-$ anions are excluded from the cathode. Under these conditions the EA-TCP film should be a Zr(IV)-Cr(III) hybrid with no contamination from F, B or Al.

In contrast to the immersion method, the alloy layer is not dissolved during film deposition, since the anodic reaction is water oxidation, which occurs on the graphite
counter electrode. Although oxygen bubbles were observed, it is possible that \( \text{Cr}^{3+} \) oxidation also occurs. The water reduction potential is about 1.2 V (SHE), whereas \( \text{Cr}_2\text{O}_7^{2-}/ \text{Cr}^{3+} \) is roughly 1.3 V (SHE). The proton reduction reaction proceeds on the wafer surface at a constant rate because the driving force for this reaction (electrons) comes from the external power supply. Thus, in contrast to the immersion case, the pH gradient near metal surface is maintained. The EA-TCP deposition rate is only affected by the availability of the Cr(III) and Zr(IV) in the solution.

The single-layer structure with a thin, dense interface (Figure 2.6) in all as-prepared EA samples can be explained by a two-stage deposition (Figure 2.11): a fleeting initial state followed by continuous film growth. In the initial state the pH increases rapidly due to cathodic polarization leading to proton reduction and pH rise. \( \text{Cr}^{3+} \) and \( \text{Zr}^{4+} \) form hydroxy-cations that precipitate at the metal surface. Since the initial local concentration of \( \text{Cr}^{3+} \) and \( \text{Zr}^{4+} \) is high, a dense layer results. After a short period, these cations are quickly depleted so further deposition is limited by diffusion of \( \text{Cr}^{3+} \) and \( \text{Zr}^{4+} \) from bulk solution, leading to kinetically limited steady-state growth (Figure 2.11b). Kinetic growth typically produces porous, rough interfaces.\(^{10}\) During steady-state growth, electrons, protons, and \( \text{Cr}^{3+} \), \( \text{Zr}^{4+} \) cations are all maintained at constant gradient. Therefore the EA-TCP film grows linearly with deposition time with little change in the film density or composition as shown in Figure 2.7.

Accelerator additives\(^2, 11\) typically found in Cr(VI) and vanadate conversion coating systems such as \( \text{F}^- \) and \( \text{Fe(CN)}_6^{3-} \) are not needed for EA deposition. Typically \( \text{F}^- \) is required for Al dissolution, and \( \text{Fe(CN)}_6^{3-} \) serves as a red-ox mediator to promote the Al
oxidation and Cr(VI) reduction as discussed Xia and McCreery. In the EA scheme these species are excluded during the cathodic polarization.

2.4.3 Transition from hydroxide complex to crystal

Since the as-prepared EA-TCP film is a Zr(IV)/Cr(III) hydroxide complex, further evolution is inevitable. NR data in Figure 2.8d, confirm this change. Comparing the 4-min film (1680 ± 10 Å, SLD = 0.90 ± 0.02 × 10^{-6} Å^{-2}), and RT-dried film (730 ± 20 Å, SLD = 1.98 ± 0.06 × 10^{-6} Å^{-2}), the scattering lengths per unit area (SLD × thickness) are 1500 ± 40 × 10^{-6} Å^{-1}, and 1450 ± 80 × 10^{-6} Å^{-1} respectively. Additional water could be lost, but the large difference in film thickness mainly implies a structural change from amorphous to crystalline, perhaps from amorphous Zr(IV)/Cr(III) hydroxide to crystalline Zr(IV)/Cr(III) oxide (Cr_{2}O_{3}·xZrO_{2}·nH_{2}O). This transition partially occurred before the data in Figure 2.6 were collected.

2.4.4 EA-TCP film structure after vacuum baking

The neutron SLD profiles of EA-TCP film before and after vacuum baking (Figure 9, b & d) show not only film compression but also dehydration (loss of crystal water). Comparing the bulk EA-TCP film before baking (730 ± 20 Å, SLD = 1.98 ± 0.06 × 10^{-6} Å^{-2}) and after baking (620 ± 20 Å, SLD = 2.72 ± 0.06 × 10^{-6} Å^{-2}), the scattering lengths per unit area are 1450 ± 80 × 10^{-6} Å^{-1}, and 1690 ± 90 × 10^{-6} Å^{-1} respectively. The increase is due to the loss of water during baking, as water has a negative scattering length.

The film hydration fraction can be determined from the assumed film composition Cr_{2}O_{3}·xZrO_{2}·nH_{2}O. The ratio x will be discussed later. Another assumption is that the
EA-TCP film is totally dehydrated after 6 hours baking at 150 °C, 3×10^{-3} Torr, leaving anhydrous oxide, Cr_2O_3·xZrO_2. The hydrate number of crystalline hydrous oxide (n in Cr_2O_3·xZrO_2·nH_2O) before baking is calculated as follows.

Equation 2.1 and 2.2 are the SLD of the EA-TCP layer before (hydrous, h) and after baking (anhydrous, a).

\[
\text{SLD}_h = \rho_h \frac{N_A}{M_h} b_h 
\]

(2.1)

\[
\text{SLD}_a = \rho_a \frac{N_A}{M_a} b_a 
\]

(2.2)

Where \(\rho_h\) is density of hydrated film and \(\rho_a\) is the density of the anhydrous film; \(N_A\) is Avogadro’s number; \(b\) is the corresponding molecular scattering length, \(M_a\) and \(M_h\) are the molecular weight of anhydrous and hydrous coating species.

Define the SLD of “anhydrous part” of hydrous metal oxide crystal in the deposition layer before baking as SLD_{h-H_2O}. (i.e. SLD_{h-H_2O} is the SLD of MO_m in the MO_m·nH_2O species)

\[
\text{SLD}_{h-H_2O} = \rho_h \frac{N_A}{M_h} (b_h - n \times b_{H_2O}) 
\]

(2.3)

Based on metal-atom conservation (i.e., no Cr and Zr atoms are lost after vacuum baking) the number of hydrous oxide molecules (Cr_2O_3·xZrO_2·nH_2O) is equal to the number of anhydrous oxide molecules (Cr_2O_3·xZrO_2). Then the total scattering length from the dry part of hydrous oxide layer (Cr_2O_3·xZrO_2 species in Cr_2O_3·xZrO_2·nH_2O) is
equal to the total scattering length from the anhydrous oxide layer (\(\text{Cr}_2\text{O}_3\cdot x\text{ZrO}_2\) species in \(\text{Cr}_2\text{O}_3\cdot x\text{ZrO}_2\)), as number of \(\text{Cr}_2\text{O}_3\cdot x\text{ZrO}_2\) species is constant, and scattering length of \(\text{Cr}_2\text{O}_3\cdot x\text{ZrO}_2\) is unchanged. Additionally the total scattering length is scattering length density times total volume. Therefore:

\[
(SLD_{h-H_2O}) \times V_h = (SLD_a) \times V_a
\]  

(2.4)

where \(V\) is the volume of bulk layer. \(V\) is proportional to layer thickness (730 ± 20 Å and 620 ± 20 Å) since area is conserved.

The neutron scattering lengths of the relevant compounds are listed below:

\[
b_a = b_{\text{Cr}_2\text{O}_3 \cdot x\text{ZrO}_2} = b_{\text{Cr}_2\text{O}_3} + x \cdot b_{\text{ZrO}_2}
\]

\[
b_h = b_{\text{Cr}_2\text{O}_3 \cdot x\text{ZrO}_2 \cdot nH_2O} = b_{\text{Cr}_2\text{O}_3} + x \cdot b_{\text{ZrO}_2} + n \cdot b_{\text{H}_2\text{O}}
\]

\[
b_{\text{Cr}_2\text{O}_3} = 2.46 \times 10^{-4} \text{Å} 
\]

\[
b_{\text{ZrO}_2} = 1.876 \times 10^{-4} \text{Å}
\]

\[
b_{\text{H}_2\text{O}} = -0.167 \times 10^{-4} \text{Å}
\]

\[
SLD_h = (1.98 \pm 0.06) \times 10^{-6} \text{Å}^{-2} = \rho_h \frac{N_A}{M_h} (2.46 + 1.876x - 0.167n) \times 10^{-4} \text{Å}
\]  

(2.5)

\[
SLD_a = (2.72 \pm 0.06) \times 10^{-6} \text{Å}^{-2} = \rho_a \frac{N_A}{M_a} (2.46 + 1.876x) \times 10^{-4} \text{Å}
\]  

(2.6)

\[
\rho_h \frac{N_A}{M_h} (2.46 + 1.876x) \times 10^{-4} \text{Å} \times (730 \pm 20) \text{Å}
\]

\[
= (2.72 \pm 0.06) \times 10^{-6} \text{Å}^{-2} \times (620 \pm 20) \text{Å}
\]  

(2.7)
Multiplying Equation 2.5 and Equation 2.7, \( \frac{N_A}{M_b} \) can be canceled, leaving \( x \) and \( n \) in the equation. After simplification, the hydrate number, \( n \), is expressed as a function of \( x \), and can be split into two parts: \( n = i + jx \), \( i = 2.10 \pm 0.55 \), and \( j = 1.60 \pm 0.45 \).

Therefore \( \text{Cr}_2\text{O}_3\cdot x\text{ZrO}_2\cdot n\text{H}_2\text{O} \) is rewritten as Equation 2.8:

\[
\text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O}\cdot x(\text{ZrO}_2\cdot j\text{H}_2\text{O}) \text{ with } i = 2.10 \pm 0.55, j = 1.60 \pm 0.45
\]

(2.8)

Note that the hydrate number for chromium, \( i \), is independent of the ratio, \( x \), which specifies the zirconium oxide fraction.

2.4.5 Speciation of TCP film

The ratio \( x \) between \( \text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O} \) and \( \text{ZrO}_2\cdot j\text{H}_2\text{O} \) is calculated based on comparison of neutron SLD and x-ray SLD of the bulk EA layer in Figure 2.10b.

\[
\frac{\text{SLD}_{\text{x-ray}}}{\text{SLD}_{\text{Neutron}}} = \frac{23.0 \pm 0.5}{1.85 \pm 0.02} = 12.43 \pm 0.40
\]

(2.9)

\[
\frac{\text{SLD}_{\text{x-ray}}}{\text{SLD}_{\text{Neutron}}} = 12.43 \pm 0.40 = \frac{b_{\text{h,x-ray}}}{b_{\text{h,neutron}}} = \frac{26.05 + x \cdot 20.17}{2.10 + x \cdot 1.60}
\]

(2.10)

where \( b_{\text{h,x-ray}} \) is x-ray scattering length of \( \text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O}\cdot x(\text{ZrO}_2\cdot j\text{H}_2\text{O}) \), and \( b_{\text{h,neutron}} \) is neutron scattering length of \( \text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O}\cdot x(\text{ZrO}_2\cdot j\text{H}_2\text{O}) \). From Equation 2.10 the ratio, \( x \), between \( \text{ZrO}_2\cdot j\text{H}_2\text{O} \) and \( \text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O} \) is \( 0.85 \pm 0.14 \), so the as-deposited film composition is:

\[
\text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O}\cdot x(\text{ZrO}_2\cdot j\text{H}_2\text{O}); \ i = 2.10 \pm 0.55, j = 1.60 \pm 0.45 \text{ and } x = 0.85 \pm 0.14
\]

(2.11)
In contrast to Equation 2.11, one unpublished reported TCP film contains little Cr. The lower Cr content in conventional films is consistent with Pourbaix diagrams, which show that Zr(IV) precipitates at a lower pH than Cr(III). In conventional deposition, the pH gradient is determined by Al dissolution rate, which decreases once the passivation film forms. The resulting shallow pH gradient favors Zr precipitation, eventually reaching the point where only Zr will precipitate. In EA deposition, by contrast, the pH gradient is steeper and is maintained by polarization. As a result, Zr and Cr are more likely to co-precipitate, as we observe.

2.4.6 SIMS of EA-TCP film

SIMS data on EA-TCP film (Figure 2.12) confirm co-precipitation of Cr and Zr. The normalized peak intensities of $^{52}$Cr and $^{90}$Zr are $5.5 \times 10^5$ and $1.0 \times 10^5$ counts, after calibration by standards CrK(SO$_4$)$_2$·12H$_2$O (1.83 g/cm$^3$, $^{52}$Cr = $3.5 \times 10^5$ counts) and K$_2$ZrF$_6$ (3.48 g/cm$^3$ $^{90}$Zr = $5.7 \times 10^5$ counts). The $^{90}$Zr/$^{52}$Cr atomic ratio is calculated to be $0.74 \pm 0.16$, confirming that the films contain comparable amounts of Zr and Cr.

2.5 CONCLUSION

The structure of TCP deposition films depends on how the films are deposited. Immersion films are different from EA films in that the latter grow linearly with cathodic polarization time after a thin dense layer forms at the metal interface. In the immersion experiment, proton consumption is driven by the metal dissolution. Metal dissolution, however, is inevitably restricted by the film itself. Metal-ion diffusion though the film becomes increasingly difficult as the film grows. Thus dissolution is retarded and proton
consumption is replenished by ions from the bulk solution. The pH gradient decreases, leading to a Zr-rich surface, which is rough and defective.

EA deposition produces a denser, thicker EA-TCP film compared to immersion. The dense interfacial layer between the metal and the bulk TCP deposition film is extremely thin due to rapid deposition in the initial state. Consumption of hydrogen ions is controlled by the applied potential, leading to diffusion-controlled, steady-state growth after the interfacial layer forms. Film thickness then depends on the time under cathodic polarization. The composition of the film is Cr$_2$O$_3$·$i$H$_2$O·$x$(ZrO$_2$·$j$H$_2$O) ($i$ =2.10 ± 0.55, $j$ = 1.60 ± 0.45 and $x$ = 0.85 ± 0.14) as determined by comparing the SLD before and after driving off the water of hydration by vacuum baking, and by comparing the neutron and x-ray SLDs. SIMS data from the EA-TCP film confirm co-deposition of Cr and Zr compounds.

These experiments represent the first measurements of the structure and composition of EA-TCP films. The new data provide the opportunity to learn how TCP films form and what the optimum structure is for corrosion protection. At this point it is not clear which film is most protective. The immersion film is thin, less dense (lower SLD) and rich in Zr(IV). The EA-TCP films, on the other hand, have an extremely thin dense layer, and are overall thicker and denser. The EA-TCP film also has more Cr(III), which could affect corrosion protective properties. Further investigation of Cr(III) and Zr(IV) precipitation on a polarized substrate is needed to optimize the Zr/Cr ratio.
REFERENCES

Figure 2.1 (a) The alloy-coated wafer is anodically activated in 25 vol% TCP solution. The native oxide and part of the Al alloy layer dissolve while the proton reduction reaction occurs on the graphite cathode. (b) The alloy-coated wafer is then cathodically polarized. Proton reduction occurs on the wafer surface. The pH rise triggers Cr(III) compound precipitation on the wafer surface.
Figure 2.2 (a) SPEAR NR data collected from as-prepared alloy-coated silicon substrate. (b) best-fit SLD profile corresponding to the solid line through the data points in (a).
Figure 2.3 (a) XRR data collected from as-prepared AA 2024 alloy-coated silicon substrate. (b) Best-fit SLD profile corresponding to the solid line through the data points in (a).
Figure 2.4 (a) XRR data collected from 30-s acid-activated AA 2024 alloy-coated silicon substrate measured in air 4 h after activation. (b) Best-fit SLD profile corresponding to the solid line through the data points in (a).
Figure 2.5 (a) XRR data collected from as-prepared TCP deposition film on AA 2024-coated silicon wafer by the immersion method (3 min) (b) best-fit SLD profile corresponding to the solid line through the data points in (a).
Figure 2.6 (a), (b), (c) SNS NR data of as-prepared EA-TCP film after 1, 2, and 4-min EA deposition in 25 vol% TCP solution. (d) Resulting SLD profiles. A dense interfacial layer is observed at the alloy surface. The bulk layer thickness increases with deposition time (Figure 2.7). The peak at 0 Å is the SiO₂-covered Si surface. The peak at about 270 Å is the dense EA-TCP interface layer. The data could not be adequately fit without this interfacial layer.
Figure 2.7 As-prepared EA-TCP deposition film thickness and SLD as a function of EA deposition time. A constant film growth rate and minimal change in SLD are observed.
Figure 2.8 SPEAR NR data for three identical EA-TCP films (A, B, C) after 4-days drying at ambient conditions. (d) SLD profiles based on the solid lines in (a), (b), (c).
Figure 2.9 SPEAR NR data before and after vacuum baking of samples A and B in Figure 2.8.
Figure 2.10 XRR and NR data comparison of samples C (RT dried state). NR data are from SPEAR.
Figure 2.11 Schematics of EA-TCP deposition via cathodic polarization in the initial state (a), and steady state where a gradient in metal ion concentration exists (b). At high cathodic polarization, the reduction reactions rapidly transition from charge-transfer to diffusion control leading to kinetically-limited, steady-state growth.
Figure 2.12 Positive-ion SIMS surface spectrum of EA-TCP film. Peaks at 50, 52, 53 are from Cr. Peaks at 90, 91, 91 and 94 are from Zr. Peaks between 106 and 111 are signals from the Pd substrate and ZrO$_2$. Peaks after 120 are due to Cr$_2$O$_3$. 
Chapter 3 *In-situ* evolution of Trivalent Chromium Process (TCP) passive film on Al in a corrosive aqueous environment

**SUMMARY.** *In-situ* neutron reflectivity (NR) is used to observe the structure and evolution of a Trivalent Chromium Process (TCP) passive film with a simplified formulation on Al in a NaCl-D$_2$O solution. Using a split liquid reflectivity cell we mimicked the corrosion process on the anodic sites in alloy AA 2024-T3 in a pitting scenario. The split cell separates the anodic and cathodic reactions, allowing NR observation of the corroding anodic surface under potential control. We observed the evolution of the TCP film on the Al anode and compared the degradation of the Al with and without TCP protection. When held at 100 mV above the open-circuit potential (OCP), unprotected aluminum dissolves at a rate of 120 Å/h. By contrast TCP-passivated Al is stable up to the pitting potential (200 mV above OCP). In the passive state D$_2$O molecules penetrate the bulk TCP film by partially replacing the hydrate water. In spite of exchange of hydration water, the TCP film is stable and the underlying pure Al is fully protected. The passive character of the TCP film is due to a dense layer at the Al/TCP interface and/or to suppressions of ion transport in the bulk film. As the pitting potential is approached the film swells and NaCl-D$_2$O solution penetrates the TCP film. At this point 50 vol % of the TCP film is occupied by bulk NaCl-D$_2$O solution. Failure occurs by aluminum dissolution under the swollen TCP film as the imbibed solution contacts the Al metal. Further increase in potential leads to complete stripping of the TCP film.
3.1 INTRODUCTION

AA 2024-T3 is susceptible to pitting corrosion in chloride-containing environments due to its high Cu content (3.8 – 4.9 wt%). Heterogeneous precipitation of Cu and other minor elements during heat treatment results in Cu-rich inclusions. As the native oxide layer on the alloy surface breaks down, preferential dissolution of light metals occurs from Cu-rich inclusions (for example, Al and Mg from Al2CuMg). The porous Cu remnants that result from this de-alloying process act as cathodes on the alloy surface and promote further dissolution of surrounding Al matrix – hence the propagation of the pits.

NAVAIR TCP pretreatments are used to mitigate pitting corrosion. Extensive evaluation of non-chromate aluminum pretreatments by Environmental Security Technology Certification Program (ESTCP) finds that among the potential chromate replacements, the NAVAIR TCP performs best on AA 2024-T3 alloy.

Previous chapter has clarified the TCP deposition mechanism. The core components of the formulation include Cr2(SO4)3, K2ZrF6, and HF. Cr(III) and Zr(IV) form hydroxides near substrate surface where pH increases due to the cathodic proton reduction reaction. F− ions in the TCP precursor solution promote activation of the aluminum alloy surface. The native Al2O3 passive film dissolves as [AlF6]3−, exposing the bare metal. It is believed that the native aluminum oxide is stripped before TCP deposition proceeds.

The deposited TCP layer undoubtedly acts as physical barrier of some type that isolates the underlining metal from the aqueous environment. The interfacial morphology and its
response to an active corrosion environment, however, are not known. Additionally, pitting corrosion still compromises TCP-coated AA 2024-T3, which motivates our focus on anodically polarized surfaces, where pitting initiates.

We introduce an *in-situ* method to quantify this uncharted area using neutron reflectivity (NR) in a potential-controlled split liquid cell. We address four questions: 1) does *in-situ* NR data correlate with the electrochemical response; 2) what is the morphology of the TCP film in the potential range where the film is electrochemically passive; 3) what is the response of the passive TCP film as a function of potential in a corrosive environment; 4) how does the TCP film fail?

We investigated the electrochemical and morphological response of TCP film in a pitting scenario by combining electrochemistry and NR. This combined approach employs a liquid-filled cell that holds two wafer electrodes (anode working electrode and cathode counter electrode) as well as a reference electrode used to monitor the potential of the working electrode. The cell allows us to track the evolution of the anode surface in an aqueous corrosion environment by NR. This approach circumvents the limitations of conventional electrochemical investigations, which are inevitably compromised by the intermetallic structure where anodes and cathodes are intermingled. The information derived from the split liquid reflectivity cell regarding the TCP response on a well-defined Al anode is unique in corrosion science.
3.2 EXPERIMENTAL DETAILS

3.2.1 Silicon wafer substrates

Silicon wafers from Wafer World, Inc. (West Palm Beach, FL, USA) were cleaned according to the standard process (Piranha etching). The e-beam metal deposition on both anode and cathode wafers was performed in a vacuum deposition chamber at a pressure of $10^{-4}$ Torr. The material to be evaporation for forming a metal coating is in the form of an ingot. The thickness of metal coating is controlled by deposition time. The e-beam depositions were performed at Advanced Materials Characterization Center at the University of Cincinnati. The instrument is a FC1800 e-Beam Evaporator from Airco Temescal, USA. An Al ingot was used to prepare the Al-coated anode wafer. We used a pure Al coating to represent Al matrix anode in AA 2024-T3. The thickness of Al layer was controlled at 400 – 800 Å, which gives good smoothness and adequate thickness. We tested Cu and Au as noble-metal cathodes on Si wafers. The choice of Cu originated from AA 2024-T3 alloy composition. However the lifetime and degradation rate of Cu layer were not compatible with the requirements of the split liquid cell. We eventually settled on Au with a Cr buffer layer to enhance adhesion to the wafer substrate.

3.2.2 TCP deposition

The TCP passive film on Al-coated wafer substrates was deposited under cathodic polarization by an electro-assisted (EA) method. The EA deposition developed in the previous chapter was further improved. A potentiostat (Gamry PCI4 300) was used to control the EA process. The two-step EA deposition process was optimized as a brief anodic polarization (+0.50 V vs. SCE, 30 s) to strip the native oxide (Figure 3.1a),
followed by cathodic deposition for 3 minutes (Figure 3.1b). We investigated two different cathodic potentials (-1.50 V vs. SCE, and -1.25 vs. SCE) on AA 2024-T3 first, but eventually settled on -1.50 V as standard for preparing Al-coated wafer substrates.

The TCP system studied in this chapter is a simplified version of the original NAVAIR formulation. The TCP system in the following chapters (Chapter 4, 5, 6) is also the simplified version of NAVAIR formulation. The simplified formulation was chosen based on the film composition reported in our previous work. In cathodic deposition step oxidation of Al is suppressed and negative ions, including most of the additives in commercial TCP formulations, are repelled from the Al-coated wafer and excluded from the deposited film. A Cr(III) / Zr(IV) oxide film forms on Al during the cathodic step with little contamination by aluminum oxide and other substances. Therefore we simplified the formulation to a Cr(III) / Zr(IV) system with an atomic ratio of Cr : Zr = 3 : 5. To make solutions of this ratio, 6 g KCr(SO₄)₂ and 8 g K₂ZrF₆ were first dissolved in 1 L of distilled water, then diluted to 10 vol % (pH = 3.5 ± 0.2) and aged for 24 hours before EA deposition.

3.2.3 Neutron reflectivity (NR)

The in-situ NR experiments were performed on Surface Profile Analysis Reflectometer (SPEAR) at the Lujan Neutron Scattering Center, Los Alamos National Laboratory.

3.2.4 In-situ split liquid cell

A key goal of this research was to observe the evolution of the TCP film on anodic sites in AA 2024-T3 when exposed to a chloride-containing aqueous environment. This objective was achieved by building a NR split liquid cell. The split liquid cell isolates the
relevant galvanic couple on two separate silicon wafers and allows a reference electrode to be inserted in the liquid cavity between them (Figure 3.2). The upper wafer is the working electrode, which is interrogated by the neutron beam. The cathodic proton reduction reaction proceeds on the lower wafer, which serves as the counter electrode. A D₂O-based NaCl solution (1 g / 100 mL) was injected into the cell. Heavy water (D₂O) is used to minimize incoherent scattering. The cell is made of Macor® ceramic (Ceramic Products, Inc., 32 MacArthur Ave, Hasbrouck Heights, NJ), which was also chosen to minimize incoherent scattering.

The working electrode is a 5-mm thick, 75-mm diameter Si wafer coated with a thin layer (< 1000 Å) of Al. A similar Au-coated wafer is used for the counter electrode. Under anodic polarization of the working electrode the two wafers mimic the microscopic galvanic couple between the Al matrix and the noble intermetallic inclusions in AA 2024-T3.

Using the split liquid cell, we performed two in-situ corrosion experiments on two different working electrodes: 1) the original Al-coated wafer, which serves as a control; and 2) a TCP-coated, Al-coated wafer for the TCP passivity study. The TCP-coated Al working electrode mimics the pitting prone anodic areas on a TCP treated Al alloy when exposed to a chloride-containing aqueous environment. The TCP morphology and the interface between TCP and Al were investigated by NR under a sequence of potentials starting at the open circuit potential (OCP) and increasing up to the pitting potential where the anodic current rises dramatically.
The D₂O electrolyte is de-aerated to ensure that the cathodic process is dominated by the proton reduction reaction. De-aeration also reduces open circuit potential (OCP), leaving a wider passive potential range, which facilitates elucidation of the response of TCP film to varied anodic conditions. Also, in a pitting scenario, the anodic pit is oxygen depleted so de-aeration is appropriate.

Using a potentiostat we established an active corrosion environment within the cell, and tracked the applied potential and resulting current during the corrosion process. Meanwhile a neutron beam impinges on the wafer from above and is reflected at the interface between coating surface and electrolyte in the liquid cavity, revealing the evolution of the interface of the TCP film and underlying Al during active corrosion.

### 3.3 DATA AND RESULTS

#### 3.3.1 Electro-assisted (EA) TCP deposition

The *in-situ* study of TCP film requires a well-defined film, which we achieved using the EA deposition method. Two different cathodic potentials were tested on AA 2024-T3 coupons, -1.50V vs. SCE and -1.25 V vs. SCE. During deposition both the applied potential and the current density profiles were recorded as shown in Figure 3.3.

During initial anodic stage (0 s – 30 s), the current density curves are quite different, but reach the same level (0.35 ± 0.05 mA/cm²) after 30 s. In cathodic deposition phase, the current density curves are almost identical (30 s – 210 s). For example, all current density curves of the -1.50 V group (red) show a slight decrease from -0.30 ± 0.02 mA/cm² to -0.24 ± 0.02 mA/cm² during the time period from 30 s to 90 s. After this period, the cathodic current density continues to attenuate slowly (30 s – 90 s), finally
reaching at -0.2 ± 0.01 mA/cm². Similar behavior was observed for the -1.25-V group with the current stabilizing at -0.1 ± 0.02 mA/cm².

After 24 h of room-temperature drying, the TCP-treated AA 2024-T3 and a bare control were compared by dynamic DC polarization (Figure 3.4). In the presence of the TCP passivation film, the OCP shifted from -950 mV to -770 ± 25 mV (-1.50 V TCP samples) and -870 ± 25 mV (-1.25 V TCP samples), leading to a significant decrease in the anodic current. Compared to the bare control, suppression of the cathodic branch was not obvious.

Since the TCP film deposited at -1.50 V performed better than -1.25 V film, so -1.50 V was chosen as a standard for TCP deposition.

3.3.2 Comparison between METALAST® and simplified NAVAIR EA-TCP films

METALAST® formulation was used for prepare EA-TCP film for the research work described in Chapter 1. Since this chapter, a simplified TCP system based on NAVAIR’s formulation has been adopted. SPEAR NR date on the dry EA-TCP film based on METALAST® formulation and simplified formulation are shown in Figure 3.5.

The film structure of the METALAST® TCP and simplified NAVAIR TCP are very similar according to the SLD profiles (Figure 3.5 b). both have sharp interface and a broad bulk layer. The SLD of the dry bulk layer of simplified TCP film is measured to be $1.84 \times 10^{-6} \text{ Å}^{-2}$, very close to the SLD used for METALAST® TCP film, which is $1.98 \times 10^{-6} \text{ Å}^{-2}$ METALAST® TCP. The similarity between the two systems verifies our simplified formulation. And the structure model and film composition based on the
measured SLD profiles in Chapter 1 are still valid for the future calculation in Chapter 3, 4, 5, 6.

### 3.3.3 *In-situ* NR of bare Al

A bare Al-coated wafer was tested first in the split liquid cell. The NR data yielded information on the change in thickness of the Al layer when a constant potential of -930 mV vs. SCE was applied, which is an overpotential of +100 mV. This bare-metal study mimicked the pitting area on un-protected AA 2024-T3.

Figure 3.6 shows the evolution of Al without TCP protection at a constant anodic potential in NaCl-D2O solution in the split cell. We obtained NR curves (Figure 3.6 a) at the beginning of polarization (blue), and after 3 hour exposure (red). We measured low-angle $R - q$ snapshots at 0 – 20 min and 180 – 200 min. The 20-min snapshots provide sufficient time resolution to capture the film thickness change during the active dissolution process.

The 3-h reflectivity curve (red in Figure 3.6 a) flattened after 3-h polarization, indicating a major structural change in the Al coating. Figure 3.6 b gives the SLD profiles, which reveal the change in Al coating thickness. The 0-Å position on abscissa marks the surface of Si wafer. A native SiO$_2$ layer forms on Si with a thickness of 10 Å – 20 Å. Since SiO$_2$ has a higher SLD than Si, a sharp peak is observed at the wafer surface. The SLD observed at large distances from the surface is the value expected for the NaCl-D$_2$O environment ($6.37 \times 10^{-6}$ Å$^{-2}$). The region between SiO$_2$ peak and NaCl-D$_2$O environment is the Al layer with a constant SLD of $2.14 \times 10^{-6}$ Å$^{-2}$. Comparing the SLD
profiles before (blue curve) and after 3-hour polarization (red curve), the thickness of Al changes from 860 ± 10 Å to 500 ± 10 Å.

The bare Al-coated wafer mimics the unprotected anodic sites on AA 2024-T3 when exposed to a corrosive environment. Also this experiment shows that the corrosion rate is matched to the time-resolution of the NR instrument. Below we show consistency between Al dissolution measured by NR and by the measured anodic current.

3.3.4 In-situ NR study of TCP passivity

To quantify TCP protection of the pitting-prone anodic sites in the alloy, we observed the evolution of the TCP-covered Al anode exposed to progressively increasing anodic potentials in NaCl-D$_2$O solution. The DC polarization data in the split liquid cell were measured prior to the in-situ NR in order to find the OCP (Figure 3.7). A sequence of NR snapshots revealed the TCP structure at different potentials above the OCP, which occurs at -1.00 × 10$^3$ mV. Each potential was applied for 1 hour. Each low-angle snapshot took 20 minutes, which is suitable for observation of film evolution.

Figure 3.8 a shows a sequence of $R - q$ plots from the TCP-coated sample at different potentials. No significant change was observed during the first 12 hours when potential was below -800 mV (red curves), indicating passivity. When the potential was nobler than the pitting potential ($E_{pit} = \sim -800$ mV), however, the TCP film started to degrade (Figure 3.8 a, blue). Eventually the TCP film and entire Al layer dissolved as revealed by the disappearance of NR fringes (Figure 3.8 a, black).

The structural change in the TCP passive films under anodic conditions is revealed by the SLD profiles in the passive state (Figure 3.8 b, red), and after the film disrupted
(Figure 3.8 b, black). The red SLD profile in Figure 3.8 b shows a stable TCP film between ~ 150 Å and ~ 760 Å. Below 150 Å is the Al layer, whose thickness decreased from ~ 400 Å to ~ 150 Å due to the anodic step of EA-TCP deposition process. When the applied potential is more noble than -800 mV, however, both the TCP layer and the Al layer disappear (black profile), leaving wafer substrate directly exposed to D₂O solution (marked by the sharp SLD drop at 0 Å).

These experiments reveal that TCP has a dramatic effect on anodic polarization behavior of Al. The bare metal film uniformly degrades over several hours under slight anodic polarization. With TCP protection, however, the Al layer is completely stable to an overpotential of +200 mV, after which Al starts to oxidize.

3.4 DISCUSSION

The In-situ NR data and corresponding electrochemical records harbor insights into the protection and failure of TCP-coated Al. Here we discuss:

1. The difference in the corrosion rate of the bare and TCP-protected Al anode based on NR and electrochemical data;

2. The passive TCP structure in a pitting scenario;

3. The penetration of aqueous phase into the passive TCP film under a sequence of potentials;

4. The failure mode when the applied potential compromises TCP protection.
3.4.1 TCP passivation and corrosion rate on Al-coated wafer

First of all, the in-situ 3-hour polarization on the bare Al layer at an overpotential of +100 mV validates the correlation between the in-situ electrochemical data and simultaneous NR SLD profiles. The current density collected indicates dissolution of the Al layer (Figure 3.9). Assuming the anodic current is due to Al oxidation, the dissolved Al per unit area can be calculated based on integration of the measured current density between 0 and 180 minutes according to Faraday’s Law.

\[
F \times Z \times \frac{V \times \rho_{Al}}{A \times M_{Al}} = \int_{0}^{180min} i(t) \times dt = 14600 \mu C
\]

(3.1)

where \( F \) is the Faraday’s constant \( (96,485 \text{ C/mol}) \); \( Z \) is the valence of \( Al^{3+} \); \( V \) is the volume of dissolved Al; \( A \) in is total area of the corroding surface; \( \rho_{Al} \) is the mass density of Al; \( M_{Al} \) is the atomic weight of Al, \( i \) is the current density; and \( t \) is time. The dissolved Al in units of volume per unit area, \( \frac{V}{A} \), is calculated to be \( 380 \pm 20 \text{ Å} \).

Based on the measured current density, the native oxide layer showed little resistance against anodic attack. The NR SLD profiles indicate the same behavior. Two NR In-situ snapshots on the anode (Figure 3.6) were taken at 0 – 20 minutes and 180 – 200 minutes. The SLD profiles give an Al thickness change of \( 360 \pm 10 \text{ Å} \), consistent with the thickness change based on the integration of the recorded current density in Figure 3.9. Consistency also assures that the electrochemistry is not compromised by the design of the split cell.
The evolution of current density for the TCP-protected sample shows radically different behavior compared to the bare Al. The protected system shows significant passive character even when applied the potential is +200 mV noble to the OCP.

The measured current density curves corresponding to each applied anodic potential are plotted in Figure 3.9 a (-975 mV to -800 mV) and Figure 3.9 b (-975 mV to -725 mV). In Figure 3.9 a, the measured current density remained below 10 nA / cm² at each polarization step. The TCP film effectively protects the underlying Al layer, indicating a passive state. The current density curve at -800 mV (red) however showed some peculiarities. Large “noise” peaks continuously popped up during the 1-hour step. Although the average current declined, these peaks imply some local breakdown in the TCP film that is immediately re-passivated. The cause of re-passivation is not clear. Perhaps Al corrosion product blocks the newly formed ion channels in TCP film. The current density curves for subsequent steps (-775 mV, -750 mV, and -725 mV) are included in Figure 3.9 b. The current at -775 mV rapidly increased from nA / cm² to μA / cm². The TCP film loses its passivity at this potential and Al layer starts to dissolve. At -750 mV and -725 mV dissolution continues until there is no Al left on the silicon wafer.

3.4.2 TCP passive structure and water penetration

The passive film structure and failure mechanism in a pitting scenario are revealed by analysis of the NR data in Figure 3.8 for TCP-protected Al wafer. When in passive range (below -800 mV), the TCP film is stable as indicated by the identical red $R - q$ plots in Figure 3.8 a and SLD profile in Figure 3.8 b. The thickness of the Al layer did not change during these steps. Above the -800 mV TCP no longer suppresses the dissolution of Al
layer. The entire system (Al and TCP) strips, leaving the oxide-covered silicon substrate directly in contact with the D₂O electrolyte (Figure 3.8 b). The metastable state (-775 mV) will be discussed later after we examine the water content of the TCP layer in the passive state.

To quantify the D₂O penetration into the passive TCP film, we compared the SLD profile of the TCP film before and after D₂O exposure (Figure 3.11) below -800 mV. The SLD profile of the dry sample shows that a thin, dense interfacial layer exists between the metal and the bulk TCP film. In the wet state, this layer is masked in the high SLD wet film. We determined the composition of the bulk film in the dry state previously by a combination of neutron reflectivity and x-ray reflectivity: \( \text{Cr}_2\text{O}_3 \cdot i\text{H}_2\text{O} \cdot x(\text{ZrO}_2 \cdot j\text{H}_2\text{O}) \) \((i = 2.10 \pm 0.55, j = 1.60 \pm 0.45 \text{ and } x = 0.85 \pm 0.14)\).¹⁵

Comparing the SLD profiles of TCP films in the room-temperature dried state (Figure 3.11, blue curve), and in the split liquid cell (Figure 3.11, red curve), the SLD of the TCP film increases from \(1.98 \pm 0.06 \times 10^{-6} \text{ Å}^{-2}\) to \(3.6 \pm 0.1 \times 10^{-6} \text{ Å}^{-2}\), while the thickness did not change significantly. The SLD increase can be explained by exchange of D₂O for the H₂O in Cr and Zr oxide hydrates that constitute the TCP film.

The molecular fraction, \(f\), converted from hydrate to deuterated is calculated as:

\[
\frac{3.6 \times 10^{-6} \text{ Å}^{-2}}{1.98 \times 10^{-6} \text{ Å}^{-2}} = \frac{b_{\text{Cr}_2\text{O}_3 \cdot i\text{ZrO}_2 \cdot ((1-f)\text{H}_2\text{O}+f\text{D}_2\text{O})}}{b_{\text{Cr}_2\text{O}_3 \cdot i\text{ZrO}_2 \cdot \text{H}_2\text{O}}} \quad (3.2)
\]

where \(i = 2.10 \pm 0.55, j = 1.60 \pm 0.45 \text{ and } x = 0.85 \pm 0.14\).¹⁵
Given the neutron scattering lengths of the relevant compounds:

\[ b_{\text{Cr}_2\text{O}_3} = 2.46 \times 10^{-4} \text{Å} \]
\[ b_{\text{ZrO}_2} = 1.876 \times 10^{-4} \text{Å} \]
\[ b_{\text{H}_2\text{O}} = -0.167 \times 10^{-4} \text{Å} \]
\[ b_{\text{D}_2\text{O}} = 1.915 \times 10^{-4} \text{Å} \]

Equation 3.2 yields \( f = 40 \pm 5 \% \), which means 40 % of H\(_2\)O molecules in the Cr(III)/Zr(IV) oxide hydrate is exchanged, while the TCP film remains protective. This result shows that the bulk TCP film is not chemically inert when exposed to an aqueous environment, although it remains passive. Water molecules from the salt solution penetrate the bulk TCP layer by replacing the original water of hydration.

TCP passivity is attributed to the suppression of NaCl-D\(_2\)O solution penetration, hence acting as barrier against ion transport. Since the TCP bulk film retains its original dry-state structure with no swelling, the Cr\(_2\)O\(_3\)/ZrO\(_2\) matrix is not altered by exchange of hydrate water. If bulk salt solution penetrated the film it would swell. In the absence of such swelling, transport of Na\(^+\), Cl\(^-\) and Al\(^{3+}\) is suppressed, as there is no bulk water to stabilize these ions. Suppression of ionic transport precludes Al dissolution. In addition, the dense interfacial layer is immune to both deuterate-hydrate exchange and bulk water penetration, so this layer also blocks ion transport.

Failure of the TCP film is attributed to penetration of bulk salt solution, which facilitates ion transport. Evidence for this failure mechanism comes from examination of the NR data in the metastable state at -775 mV. According electrochemical data (Figure 3.10) the TCP film loses protective character at this potential.
The \( R - q \) plot in the metastable state is shown in Figure 3.12 a. Figure 3.12 b compares the SLD profiles in the passive, metastable and failed states. In the metastable state the Al layer thins while the TCP film swells significantly, as indicated by both increased thickness and higher SLD. Compared to passive state the SLD increases from \( 3.6 \pm 0.1 \times 10^{-6} \text{ Å}^{-2} \) to \( 5.7 \pm 0.1 \times 10^{-6} \text{ Å}^{-2} \). The higher SLD can be explained by complete conversion of crystal hydrate water plus physical invasion of bulk salt solution.

Given the SLD of D\(_2\)O \((6.37 \times 10^{-6} \text{ Å}^{-2})\), and \( SLD_{\text{swollen TCP}} \(5.7 \times 10^{-6} \text{ Å}^{-2}\), the volume fraction, \( \phi \), occupied by NaCl-D\(_2\)O bulk solution in the metastable film can be estimated if we assume complete exchange of crystal hydration water plus penetration of bulk D\(_2\)O:

\[
SLD_{\text{swollen TCP}} = (1 - \phi)SLD_{\text{Cr2O3:}i\text{D2O-x(ZrO2:jD2O)}} + \phi \times SLD_{\text{D2O}}
\]

(3.3)

where \( SLD_{\text{Cr2O3:}i\text{D2O-x(ZrO2:jD2O)}} \) can be calculated from the known scattering lengths.

\[
\frac{SLD_{\text{Cr2O3:}i\text{D2O-x(ZrO2:jD2O)}}}{SLD_{\text{Cr2O3:iH2O-x(ZrO2:jH2O)}}} = \frac{b_{\text{Cr2O3:}i\text{D2O-x(ZrO2:jD2O)}}}{b_{\text{Cr2O3:iH2O-x(ZrO2:jH2O)}}}
\]

(3.4)

Substitution yields:

\[
\phi = \frac{5.7 \times 10^{-6} \text{ Å}^{-2} - 4.84 \times 10^{-6} \text{ Å}^{-2}}{6.37 \times 10^{-6} \text{ Å}^{-2} - 4.84 \times 10^{-6} \text{ Å}^{-2}} = 50 \pm 10 \text{ vol \%}
\]

(3.5)

The chloride-containing aqueous phase occupies approximately 50 vol % of the swollen TCP film. Both bulk and interfacial TCP layers are penetrated by salt solution.
The aqueous environment now directly contacts the Al. Both Cl- and Al$^{3+}$ ions diffuse through the film. The entire passivation system fails and Al oxidizes as indicated by the recorded current density curves (Figure 3.10 b).

3.5 CONCLUSIONS

The techniques developed here give corrosion researchers their first quantitative look at the composition and physical structure of passive films in an active corrosion environment. These NR data reveal the corrosion process of bare and TCP-coated Al and, for the first time, the structure and morphology of TCP film in aqueous solution under pitting conditions.

The *in-situ* experiment on bare Al anode, first of all, verifies the correlation of NR SLD profiles with the electrochemical response. In chloride-containing aqueous environment, a uniform Faradaic corrosion process was observed near the OCP on a bare Al surface as supported by the recorded corrosion current density and thickness change in the Al layer measured by NR.

Secondly, a stable TCP film is observed by NR when the film remains protective in a chloride-containing aqueous environment. Neither the TCP film nor the underlying Al show any change when the applied anodic potential increases from OCP to +200 mV vs. OCP over a 12 h period. This passive character is proven by both current density, which remains in the nA / cm$^2$ range, and NR data, which show identical $R - q$ plots and SLD profiles.

Thirdly, based on SLD profiles of the TCP film under stable conditions, approximately 40 % of the solid hydrate water in the bulk TCP layer is exchangeable when exposed to
an aqueous environment. In spite of exchange of hydration water, however, the 
Cr$_2$O$_3$/ZrO$_2$ matrix retains its original dry-state structure with no swelling. In the absence 
of bulk solution in the film, transport of Na$^+$, Cl$^-$ and Al$^{3+}$ is suppressed and the 
underlying aluminum remains fully protected. Passivity is attributed to suppression of ion 
transport by both the bulk and interfacial layers.

Finally, when the potential reaches pitting potential, the TCP film swells and loses 
passivity. The underlying aluminum dissolves as indicated by the current density in $\mu$A / 
cm$^2$ scale. The TCP film swells, but does not dissolve. In this swollen state the chloride-
containing aqueous phase penetrates the entire TCP film including the dense layer at the 
Al/TCP interface. Ion transport is no longer suppressed so the aluminum under the 
swollen TCP film oxidizes. The TCP film itself disappears with a 25 mV increase in 
applied potential.
REFERENCES


Figure 3.1 Schematic diagram of the TCP deposition on Al-coated wafers. (a) The substrate is anodically activated in a 10-vol% TCP bath. The native oxide and part of the Al dissolve. (b) Under cathodic polarization, proton reduction occurs on the Al surface. The pH rise triggers TCP deposition.
Figure 3.2 Design of the split liquid cell. The liquid space in the cell is separated into three cavities, a bulk reservoir in middle and two thin reaction layers on both sides. Neutrons penetrate the Si substrate from above and reflect off the TCP/water interface. The wafer electrodes directly contact the electrolyte in the reaction layer. The thickness of the reaction layer is 3 mm. Holes between the cavities allow NaCl-D₂O solution to flow to the reaction layers to sustain corrosion.
Figure 3.3 Deposition potential and current density during EA process on AA 2024-T3 coupons, a) blue: +0.50 V, 30 s followed by -1.25 V, 180 s (straight line); b) red: +0.50 V, 30 s followed by -1.50 V, 180 s (straight line).
Figure 3.4 Dynamic DC polarization curves of TCP-treated AA 2024-T3 samples and a bare control in (1 g / 100 mL NaCl de-aerated aqueous solution). All samples were conditioned at OCP for 30 min prior to the scan. The scan rate was 1 mV/s.
Figure 3.5 (a) SPEAR NR data ($R - q$ plots) on a simplified TCP sample (blue) and METALAST® TCP sample (red). (b) SLD profiles based on the best fit. Comparison between the two SLD profiles shows similar film structure, including a sharp interface and broad bulk layer. The SLD of the dry film using simplified formulation is $1.84 \times 10^{-6}$ Å$^{-2}$, very close to the SLD used for METALAST® TCP film, which is $1.98 \times 10^{-6}$ Å$^{-2}$ METALAST® TCP.
Figure 3.6 (a) SPEAR NR data \((R - q\) plots\) on a corroding Al layer in a split liquid cell. The data before and after 3-hour exposure at 100 mV noble to the OCP in de-aerated NaCl-D\(_2\)O solution show that \(q\) spacing between fringes expands, indicating reduced thickness of Al layer. (b) SLD profiles based on the \(R - q\) plots. The Al layer thickness changed by \(~ 360 \, \text{Å}\) (from \(~ 860 \, \text{Å}\) before exposure to \(~ 500 \, \text{Å}\) after 3-hour exposure). A color scheme is adopted in the SLD profile to highlight the different layers present.
Figure 3.7 Dynamic DC polarization curves from TCP treated Al-coated wafer anode in the split liquid cell. The liquid cell was filled with NaCl-D$_2$O solution and stabilized for 30 min prior the measurement. The OCP is indicated at $-1.00 \times 10^3$ mV.
Figure 3.8 (a) SPEAR NR data ($R - q$ plots) for In-situ TCP under anodic potentials. Below -800 mV the film is stable. However fringes disappeared after the potential reached -750 mV, indicating TCP coating and Al layer were stripped. (b) SLD profiles based on $R - q$ plots show the disappearance of TCP film as well as the Al layer after the potential exceeded $E_{pit}$. The position of D$_2$O solution drops from ~ 760 Å to 0 Å.
Figure 3.9 Current density recorded for bare Al in the split cell. The reduction in Al layer thickness is in agreement with the average in current density. The durations of the NR snapshots are marked as vertical bars. The current density was measured during the 3-hour polarization experiment (Figure 3.5).
Figure 3.10 Current density curves of a TCP-coated sample after each potential step. (a) Recorded current densities in the passive region (-975 – -800 mV vs. SCE) were under 10 nA / cm². The red curve (at -800 mV) showed some instability, as indicated by the noise peaks. (b) The current density for potentials more noble than -775 mV jumped to µA / cm² scale, but eventually dropped back after the Al dissolved, leaving a bare silicon wafer. The curve at -725 mV illustrates this behavior within the time window of the experiment.
Figure 3.11 SLD profiles of RT-dried TCP-coated Al samples before polarization (blue curve). A dense interfacial TCP layer is observed between the bulk TCP film and Al. The SLD profile after exposure (red curve, from Figure 3.7b) is plotted for comparison. The dense interfacial layer still exists in the wet state but is overwhelmed by the bulk TCP layer, which has higher SLD.
Figure 3.12 (a) NR data ($R - q$ plots) for the metastable state at -775 mV. (b) SLD profiles of the metastable state compared to the passive and failed states. In the metastable state the Al layer dissolves and TCP film swells. The SLD of the TCP layer is $5.7 \pm 0.1 \times 10^{-6}$ Å$^{-2}$ and the thickness is $690 \pm 20$ Å.
Chapter 4 Ce(III) Inhibition of Passivated Aluminum Alloy AA2024-T3 by Ce(III) Anodic Hardening

SUMMARY: A dramatic improvement in corrosion resistance of aluminum alloy AA2024-T3 was achieved by anodic hardening Trivalent Chromium Process (TCP) passive films with Ce(III). A new step-by-step polarization hardening method shows both a short-term (3 ~ 5 s) and a long-term (hours) anodic inhibition effect. The anodic current density is suppressed by the factor of 500 after exposure in the presence of Ce(III) at potentials in metastable pitting region (-580 mV vs. SCE for 4 < pH < 8). Dynamic polarization analysis after step-by-step polarization reveals that Ce(III) increases both the open circuit potential and the pitting potential. A one-decade improvement in the corrosion resistance is achieved after Ce(III) anodic hardening. Both the TCP film and Ce(III) anodic hardening treatment are required to realize the effect.

4.1. INTRODUCTION

Self-healing implies corrosion resistance beyond a thickened oxide barrier. For conventional chromate conversion coating (CCC) systems, soluble chromate species remaining within (or adsorbed onto) the coating migrate to local damage and re-passivate the metal.1-3 This active inhibition is critical in situations where the conversion coating is the primary barrier against corrosion.

Use of chromate is restricted or forbidden in most countries due to health hazards.4-6 Without hexavalent chromium TCP films require additional inhibitor additives to exhibit active inhibition character.7 It has been reported that the addition of cerium, molybdate,
and phosphoric acid enhance self-healing on TCP systems.\textsuperscript{8-11} Both Ce(III)-based and Ce(IV)-based inhibitor systems are reported to have active protection properties.\textsuperscript{12-16} To obtain Ce(IV) in aqueous solution, however, requires a strong oxidizing agent such as hydrogen peroxide.

\[
2\text{Ce}^{3+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Ce}^{4+} + 2\text{H}_2\text{O}
\]

Because the effect of H\textsubscript{2}O\textsubscript{2} on the EA-TCP film is unknown, we selected Ce(III). Studies by Hinton and Wilson, for example, show that Ce(III) is as effective as the chromate ion on TCP films.\textsuperscript{17-20} In addition, corrosion protection based solely on cerium conversion coatings can equal that of Cr(VI)-based coatings under certain circumstances.\textsuperscript{13, 21-23}

It is generally accepted that Ce(III) functions as a cathodic inhibitor. We present evidence in this chapter, however, that anodic inhibition can also be achieved when used in conjunction with TCP. Significant Ce(III) distribution in TCP structure in metastable pitting region suppresses the current baseline and raises the pitting potential, where “stable” pitting occurs. Our aim in this study is to develop a method to achieve Ce(III) anodic inhibition on TCP-treated AA2024-T3 alloy, and evaluate TCP passivity in metastable pitting region, just below the pitting potential.

The TCP system we studied is a simplified version (a Cr(III)/Zr(IV) hybrid solution) of the original NAVAIR\textsuperscript{24} formulation. This simplified system was chosen based on the film composition of NAVAIR TCP reported in Chapter 3.\textsuperscript{25} An electro-assisted (EA) deposition method was applied to deposit uniform Cr(III)/Zr(IV) films of controllable thickness from a precursor solution of known composition.
4.2. EXPERIMENTAL METHODS

4.2.1. Substrate

AA 2024-T3 alloy panels from ACT Test Panels LLC (273 Industrial Dr, Hillsdale, MI 49242) were cut into 2 × 2 inch specimens. One side of each specimen was sealed by electric tape. The un-taped side was polished (grit 320, 800, and 1200) and sonicated in ethanol for 15 ~ 30 minutes before EA deposition.

4.2.2. Simplified TCP formulation

We previously showed that chemical composition of films prepared using the NAVAIR formulation are primarily Cr(III) oxide and Zr(IV) oxide. Therefore we simplified the formulation to a Zr(IV)/Cr(III) system with an atomic ratio of Cr: Zr : F = 6 : 10 : 50. To make solutions of this ratio, 10.5 g KCr(SO₄)₂ and 8 g KZrF₆ were first dissolved in 1 L distilled water, diluted to 10 vol % (pH = 3.5 ± 0.2) and aged for 24 hours before EA deposition. In EA deposition the Al substrate is the cathode where the TCP coating is formed. Therefore negative ions, including most of the additives in commercial TCP formulations, are repelled from the cathode and excluded from the coatings.

4.2.3. Electro-assisted (EA) deposition

A potentiostat (Gamry PCI4 300) was used to perform EA deposition and to record deposition the current profile. All potentials are reported vs. the saturated calomel electrode (SCE). The EA deposition process consists of two steps: slight anodic polarization (+0.50 V, 30 s) to clean the alloy surface followed by cathodic deposition at one of two different potentials (-1.25 V and -1.50 V) for 180 s. The coated samples were
rinsed and dried at room temperature for 24 hours. The details of the EA deposition method can be found in Chapter 3.

4.2.4. Ce(III) anodic hardening

The electrolyte for the Ce(III) anodic hardening was a de-aerated aqueous solution with 1 wt % (0.17 M) of NaCl and 0.1 wt % (0.0040 M) of CeCl₃. A flat electrochemical cell with an exposed area of 8.03 cm² was used to hold the 24-hour-dried EA-TCP sample. The sample was stabilized in the test solution for 30 minutes before hardening. The anodic hardening process is composed of several potentiostatic polarization steps. The polarization process started from the original open circuit potential (OCP) of the EA-TCP sample and increased step by step. The potential step was +20 mV until the potential exceeded -650 mV, after which the step was reduced to +10 mV. The step time was initially 30 min and extended to 2 hours as the potential increased. Just below the breakdown potential, where the measured current drastically increases (Eₚᵢᵗₛ, where permanent pits are formed), a normal dynamic polarization scan was carried out. The anodic hardening test was repeated at pH = 4, 6, and 8.

4.3. DATA AND RESULTS

4.3.1. Optimization of EA deposition

AA 2024-T3 substrates were coated with TCP using the EA deposition method. Two different voltages (-1.20 V and -1.50 V) were selected. During deposition both the applied potential and the current density profiles were recorded as shown in Figure 3.3. After 24-h room-temperature drying comparison between EA-TCP-passivated AA 2024-T3 samples and a bare AA 2024-T3 control was carried out by dynamic DC polarization
(Figure 3.4). Since the EA-TCP film deposited at -1.50 V performed better than -1.25 V film, we chose this system to evaluate Ce(III) inhibition.

During initial anodic stage (0 ~ 30 s), the current density curves are quite different (t ~ 0 s), but reach the same level (0.35 ± 0.05 mA/cm²) after 30 s. In cathodic deposition phase, the current density curves are almost identical (30 ~ 210 s). For example, all current density curves of -1.50 V show a slight decrease from -0.30 ± 0.02 mA/cm² to -0.24 ± 0.02 mA/cm² during the time period from 30 s to 90 s. After this period, the cathodic current density continues to attenuate slowly (30 s ~ 90 s), finally reaching at -0.2 ± 0.01 mA/cm². Similar behavior was observed at \( E_{\text{app}} = -1.25 \) V with the current stabilizing at -0.1 ± 0.02 mA/cm².

After 24-h of room-temperature drying comparison between EA-TCP-passivated AA 2024-T3 samples and a bare AA 2024-T3 control was measured by dynamic DC polarization (Figure 3.4). In the presence of the EA-TCP passivation film, the open circuit potential (OCP) shifted from -950 mV to -770 ± 25 mV (-1.50 V EA-TCP samples) and -870 ± 25 mV (-1.25 V EA-TCP samples), leading to a significant decrease in the anodic current.

4.3.2. Ce(III) inhibition and anodic hardening

Although EA-TCP did improve the corrosion protection performance, as indicated by the lower current density in passive region, \( E_{\text{pit}} \) changed little (Figure 3.4). Moreover metastable pitting below \( E_{\text{pit}} \) is still a major concern. Metastable pitting initiates at local defects and reduces the overall passivity. To improve the anodic behavior, we developed Ce(III) anodic hardening via step-by-step polarization in the CeCl₃-NaCl test solution.
The applied potential was held for 1 or 2 hours at each step. The results are plotted in Figure 4.1.

The first step was at -740 mV, 20 mV higher than the original OCP of -760 mV. During subsequent 1-hour steps at -720 mV and -700 mV, the current density was not stable, fluctuating above and below 0 nA/cm². When the potential was further raised, current density gradually stabilized between 0 and 200 nA/cm², substantially below the μA/cm² values observed in Figure 3.4. Some samples stabilized at values below 10 nA/cm², including the one in Figure 4.1. At -590 mV the current started to increase but decayed back after 1.5 hour. At -580 mV current density jumped to μA/cm² scale, implying that the passive film had failed. The limits for Ce(III) inhibition, -580 mV, was repeatedly confirmed with different samples.

The step-by-step experiment was also carried out on an EA-TCP passivated AA 2024-T3 sample in the absence of Ce(III) as shown in Figure 4.2. These samples showed an increase in current density at all potentials typical of a slowly corroding specimen. Note that the currents are 500 times larger in Figure 4.2 compared to Figure 4.1.

A hardening test on a bare AA 2024-T3 substrate was also attempted. No significant inhibition effect was observed. Without an EA-TCP film the current was unstable.

In order to obtain DC polarization curves of the Ce(III)-hardened EA-TCP sample, EA-TCP samples were step-by-step anodically polarized, and stopped at -580 mV (Figure 4.3). At this point dynamic DC polarization curves (anodic and cathodic branches, Figure 4.4) were measured from the new OCP. The two current branches were measured separately on different EA-TCP samples. The OCP of Ce(III)-inhibited EA-TCP sample...
increased to -680 ± 10 mV and the passive current density of anodic part dropped one-decade compared to the uninhibited sample. Cathodic part decreased somewhat. $E_{pit}$ also increased after Ce(III) inhibition.

### 4.3.3. Effect of pH

The pH of the Ce(III) test solution in Figure 4.1 was measured to be 6.02. In order to probe the pH limits of Ce(III) anodic hardening, we performed experiments at pH = 7.97 (Figure 4.5) and pH = 4.03 (Figure 4.6) by adjusting the test solution with NaOH or HCl. Both results show a limit at -580 mV. That value is the upper limit for Ce (III) anodic hardening, which is pH independent in the range from 4 to 8.

### 4.4. DISCUSSION

#### 4.4.1. EA deposition of TCP on AA 2024-T3

The current density during EA deposition (Figure 3.3) is positive in the surface cleaning stage (0 ~ 30 s), and negative in the cathodic deposition stage. At the beginning of the cleaning stage the current density is sample dependent, varying from 0.3 mA/cm$^2$ to 0.7 mA/cm$^2$. The shape of each anodic current density curve varies due to differences in the native oxide. Although all the substrates were polished and sonicated in ethanol prior to deposition, a fresh aluminum oxide inevitably reforms on the sample surface.

Two examples of the anodic current density curves from Figure 3.3 are shown for nominally identical coupons in Figure 4.7. The difference is due to variations in the initial native oxide layer. The anodic current is limited by proton diffusion to cathode (cathodic current) and Al$^{3+}$ ion diffusion through alloy surface oxide layer (anodic current). The
proton diffusion conditions at cathode are the same for both samples A and B so the curves are similar once the native oxide is stripped (> 15 s in Figure 4.7).

Due to sample history A and B differ in the thickness and/or integrity of their native oxide, which leads to differing initial response in Figure 4.7. The initial current density of sample B is controlled by the anode, which restricts Al dissolution. The anodic current gradually increases as the oxide film dissolves and eventually reaches the point that the current is dominated by proton diffusion at the cathode. For sample A, with a thin surface oxide layer, the effect of oxide layer is not significant so its entire behavior is dominated by proton diffusion.

In the second stage of the EA deposition, TCP film starts to form. Since the cleaning process rendered all samples the same, the coating process is less sensitive to sample history. In addition, Al dissolution is suppressed at these potentials. Previously dissolved Al\(^{3+}\) cations are coordinated by F\(^-\), forming \([\text{AlF}_6]^{3-}\), which prevents the Al\(^{3+}\) re-deposition under cathodic polarization. Therefore, the composition of the deposited EA-TCP film is the same Cr(III)/Zr(IV) hydrous oxide for all samples. As a result, the current densities for the four samples at the same deposition potential are comparable (Figure 3.3).

The cathodic current density curves reveal two states in the TCP deposition: an initial transient state (30 ~ 90 s) followed by a state of continuous film growth (90 ~ 210 s). The current density curves for two representative samples are plotted in Figure 4.8 to illustrate these two states. In the initial state the current density attenuated substantially (30 < t < 100 s). The pH increases due to proton reduction. Free Cr\(^{3+}\) and Zr\(^{4+}\) ions form hydroxy-cations that precipitate at the bare alloy surface, resulting in current attenuation. Because
of initial higher local concentration of Cr\textsuperscript{3+} and Zr\textsuperscript{4+}, and higher cathodic current density, a dense TCP layer deposits in the initial stage. In the succeeding continuous-film-growth state, the current density is attenuated by proton diffusion, but is also affected by the presence of the Cr(III)/Zr(IV) hydroxide layer. The growth of hydroxide retards proton diffusion to the alloy surface and hydrogen diffusion to bulk solution, which could be the reason for a slight decrease of the current density throughout the second stage.

The cathodic current density is nearly independent of sample history, which indicates that EA deposition produces well-defined EA-TCP films, uncompromised by differences in the native oxide.

4.4.2. EA-TCP passivation on AA 2024-T3

We chose different potentials to deposit EA-TCP film, -1.50 V, and -1.25 V. After drying at RT for 24 hour, both groups showed increased OCP and decreased anodic current density (Figure 3.4), which is different from typical TCP film formed by immersion.\textsuperscript{7, 26} The immersed TCP film usually provides little anodic protection against oxidation due to localized deposition on the Cu-rich cathodic sites. As a result, the Al matrix is less protected. By contrast the entire alloy surface is cathodically polarized in EA, so there is no preference for Cr(III)/Zr(IV) species to deposit on Cu-rich inclusions compared to the Al matrix. The EA-TCP film uniformly covers the alloy. As a result, the film acts as a physical barrier against both cathodic and anodic reactions.

Figure 3.4 shows that EA-TCP films formed at -1.50 V performed better than films formed at -1.25 V. This difference can be attributed to more aggressive deposition conditions. The deposition of Cr(III)/Zr(IV) species is primarily controlled by local pH.
Protons are consumed more rapidly at -1.50 V than at -1.25 V, leading to more aggressive deposition. If the potential is too active, however, the films structure could be damaged. Hydrogen bubbles disrupt the film, leaving a loose porous film structure.

According to the DC polarization curves (Figure 4.4), the EA-TCP passivation in the absence of Ce(III) did not change $E_{\text{pit}}$. If pit initiation occurs under anodic conditions, the EA-film itself is unable to suppress pitting due to the non-healing character of Cr$_2$O$_3$ and ZrO$_2$. From this prospective, an active inhibitor species must be added to improve $E_{\text{pit}}$.

4.4.3. **Ce(III) anodic hardening**

The Ce(III) anodic hardening process was developed to improve the corrosion resistance of TCP under anodic conditions. At the beginning the applied potential was close to the original OCP and increased step-by-step approaching the pitting potential (Figure 4.1, red lines). At each step the potential was maintained for a certain period of time to confirm the inhibition effect. As plotted in Figure 4.1, the measured current density was nearly independent of potential and remained below 100 nA/cm$^2$ until the potential reached -580 mV. Details of the current density curve are plotted in Figure 4.9. Peaks continuously pop up and drop back, which indicates metastable pitting. The pits or local defects on the EA-TCP film form and immediately re-passivate. Another feature is that the base line of the current density curve shows a decreasing trend. This trend is also be attributed to the Ce(III) inhibition. As pits continuously initiate and re-passivate, the surface condition of the EA-TCP film gradually improves. This initiation and re-passivation process makes the EA-TCP film more resistant to anodic reactions. Both current arrest and decreasing baseline indicate Ce(III) inhibition.
The limit for Ce(III) inhibition is -580 mV, above which pitting can be no longer suppressed by Ce(III). This limitation is independent of pH in the range from 4 ~ 8 (Figures 4.3, 4.5, and 4.7).

In order to evaluate the improvement by Ce(III) inhibition on EA-TCP film, a DC polarization curve was obtained after the sample was polarized at -580 mV for 4 hours (Figure 4.4). The improvement is significant in that: 1) OCP was shifted 100 mV noble for the -1.50 V EA-TCP sample, 2) the anodic current density decreased by a factor of ten and 3) E_{pit} increased by 50 mV.

4.5. CONCLUSIONS

We developed EA deposition method that produces well-controlled TCP films suitable for systematic inhibition studies. Examination of the current vs. time profiles during the deposition sequence shows that the final films are uncompromised by differences in native oxide on alloy surface.

Step-by-step anodic polarization is shown to be a straightforward assessment tool to evaluate self-healing potential and determine the upper limit of Ce(III) inhibition on TCP films. The observed upper limit is -580 mV in aqueous solution (4 < pH < 8). According to the step-by-step current density profile Ce(III) inhibition takes time to activate, particularly near the upper potential limit.

Inhibition is revealed by short-term (3 ~ 5 s) electrochemical noise (rapid passivation of incipient pits) and long-term (hours) current suppression, both of which are consistent with anodic inhibition. At potentials approaching the pitting potential current reductions by the factor of 500 are observed. After long-term anodic exposure in the presence of
Ce(III) the polarization resistance increases by one decade. The observed excellent passivation with self-healing character requires both TCP film and Ce(III).

Although the above work is not a technology at this point, it does illustrate that there is opportunity for dramatic improvement in corrosion protection compared to what is achievable using through native passive films and conversion coatings.
REFERENCES


Figure 4.1 Step-by-step anodic polarization of an EA-TCP passivated AA 2023-T3 in 1 wt-% NaCl and 0.1 wt-% CeCl₃ de-aerated aqueous solution (blue line). Left axis is applied potential (red curve). The right axis is the current density (blue and black curves). The polarization current density of an EA-TCP sample without Ce(III) inhibition is plotted as the dotted black curve connecting the current expected at each potential step based on the anodic branch of the -1.5V DC polarization curve in Figure 3.4. The degree of current suppression compared to the uninhibited system is the length of the vertical black arrows.
Figure 4.2 The step-by-step polarization data for EA-TCP passivated AA 2024-T3 in 1% NaCl solution without Ce$^{3+}$. The current density reaches 0.1 mA/cm$^2$ at -680 mV, indicating that TCP films breakdown. Note that the current scale is 500 times larger than Figure 4.1.
Figure 4.3 Step-by-step anodic polarization of an EA-TCP passivated AA 2024-T3 held in the Ce$^{3+}$ test solution. After the 4-hour exposure at -580 mV the DC polarization curves in Figure 4.4 were measured. At -580 mV the sample is still in the passive state just below the breakdown potential.
Figure 4.4 DC polarization of EA-TCP passivated AA 2024-T3 step-by-step-inhibited by Ce$^{3+}$ (green). A bare control immersed in the same Ce$^{3+}$ solution for 18 hours was also scanned (blue). The bare alloy curves from Figure 3.4 are included for comparison (dashed lines). The combination of a TCP film and Ce$^{3+}$ is required to achieve effective corrosion inhibition.
Figure 4.5 Step-by-step anodic polarization of -1.50 V EA-TCP sample in 1 wt% NaCl and 0.1 wt% CeCl₃ de-aerated aqueous solution. The pH was adjusted to 7.97. The short-term and long-term passivation effects are apparent between 7 and 13 h.
Figure 4.6 Step-by-step anodic polarization of -1.50 V EA-TCP sample in 1 wt% NaCl and 0.1 wt% CeCl₃ de-aerated aqueous solution. The pH was adjusted to 4.03.
Figure 4.7 Comparison of initial EA current (0 ~ 30 s) for two -1.5V samples under 0.5 V polarization. Differences are due to the history-dependent oxide film that is stripped by about 15 s.
Figure 4.8 Current density curves during the deposition stage (30 ~ 210 s). The curve in blue was polarized at -1.25 V, and the curve in red was polarized at -1.50 V. The attenuation of the cathodic current is due proton diffusion limitations in the solution (initial decrease) and in the oxide (gradual decrease after 100 s, as the TCP film grows).
Figure 4.9 Detailed anodic current density in the Ce\textsuperscript{3+} step-by-step inhibition experiment. Potential is -580 mV, sampling period is 2 s. Two time constants are evident as rapid fluctuations (electrochemical noise) superimposed on decreasing background current.
Chapter 5 *In-situ* Evolution of Trivalent Chromium Process

Passive Film on Al under Ce(III) Anodic Hardening

**SUMMARY:** *In-situ* NR is applied to investigate the evolution of structure and composition of a TCP passive film on pure Al under Ce(III) anodic hardening. Using a split liquid reflectivity cell and potentiostatic technique, we observed the evolution of TCP film on Al in a Ce(III)-containing solution. The NR data reveal the formation of a Ce-enriched TCP layer at the film/solution interface during anodic polarization, which increases the pitting potential and reduces the baseline corrosion current.

5.1. INTRUDUCTION

In spite of its robust passive nature, low pitting resistance is a weakness TCP passivated aluminum. Chapter 3 discusses water penetration into TCP films on Al in an uninhibited aqueous corrosion environment.\(^1\) The TCP layer remains on the Al as pits stabilize and propagate. Stable pitting is coincident with bulk water penetration and swelling of film. Recent research has been focused on improving the pitting resistance by adding non-chromate inhibitors.\(^2-8\) Chapter 4 discusses the electrochemistry of anodic hardening of TCP passive films by Ce(III) inhibition. How the morphology of the TCP film evolves under Ce(III) inhibition, however, is unknown. Verifying the presence of Ce(III) in the TCP film after anodic hardening is the objective of this chapter.

We combine neutron reflectivity\(^9-16\) (NR) and potentiostatic methods to probe the response of the TCP layer to an increasingly aggressive aqueous environment under step-by-step anodic polarization in the presence of Ce(III). Using this combined *in-situ*
methodology, the evolution of morphology and composition in TCP film under Ce(III) inhibition is established, providing insight into the mechanism Ce(III) anodic hardening of TCP film.

5.2. EXPERIMENTAL DETAILS

5.2.1. Silicon wafer substrates

Silicon wafers are chosen as substrates for in-situ NR because they are readily available and ideally smooth. The wafers are one-side-polished single crystal (111) substrates, 3 inch diameter, and 5 mm thickness, from Wafer World, Inc. (West Palm Beach, FL. USA). A standard cleaning process (Piranha etching followed by ethanol rinsing) was applied to each wafer prior to the electron beam (e-beam) deposition of the metal coating.

The e-beam deposition was used to prepare pure Al layer on the wafers in anticipation of the TCP coating. A nominally pure Al ingot was used as the metal source. The thickness of metal coating is controlled at 400 Å, which ensures smooth films. Using the same procedures, we also prepared Au-coated wafers with a Cr buffer layer to serve as counter electrodes for in-situ anodic polarization in a liquid NR cell.

5.2.2. TCP deposition

The TCP film was deposited on Al-coated wafer substrates under cathodic polarization by an electro-assisted (EA) method. The TCP system used for EA deposition is a simplified version of the original NAVAIR formulation. 6 g KCr(SO₄)₂ and 8 g K₂ZrF₆ were first dissolved in 1 L of distilled water, then diluted to 10 vol % (pH = 3.5 ± 0.2) and aged for 24 hours before EA deposition. The EA method includes a short anodic
polarization for oxide thinning and surface cleaning and a longer cathodic polarization for film deposition (See Chapters 3 and 4 for details). The EA method guarantees a uniform potential distribution and controlled film growth over the Al-coated wafer, forming a well-defined TCP film (primarily Cr(III)/Zr(IV) oxide) with little contamination by aluminum oxide or other substances. A potentiostat (Gamry PCI4 300) was used to control the EA process. The two-step EA deposition was optimized as a brief anodic polarization (+0.50 V vs. SCE, 30 s) to strip the native oxide followed by cathodic deposition (-1.50 V vs. SCE) for 3 minutes. The EA-TCP samples were dried under ambient conditions for 24 hours and stored in sealed container.

5.2.3. Neutron reflectivity (NR)

The in-situ NR experiments were performed on Surface Profile Analysis Reflectometer (SPEAR) at the Lujan Neutron Scattering Center, Los Alamos National Laboratory.

5.2.4. In-situ split liquid cell

It has been reported that the addition of Ce(III) enhances TCP systems against pitting on Al alloys. Due to the fact that Ce(III) has both anodic and cathodic inhibition character, conventional electrochemical methods on Al alloys may be compromised by the intermingled intermetallic structure on alloy surface, resulting in contradictory data depending on electrochemical history. For example, Figure 5.1 shows the open circuit potential (OCP) shifts in opposite directions: 1) after step-by-step anodic hardening in Ce(III) (green), implying anodic inhibition and 2) after simple immersion in Ce(III) (orange), which implies a strong cathodic inhibition effect.
This chapter is devoted to exploring morphological evolution of TCP films under anodic conditions. Ce(III) cathodic inhibition will be discussed in the next chapter. Understanding the evolution of the TCP film under Ce(III) anodic hardening requires a well-defined TCP-passivated Al anode for step-by-step polarization so the evolution of the TCP film can be interrogated by NR. The step-by-step anodic hardening method is described in Chapter 4 and below.

Our NR split cell holds two wafer electrodes (a working electrode and a counter electrode) as well as a saturated calomel electrode (SCE) for performing electrochemical experiment during NR. Potentials reported in this work are all vs. SCE. Figure 5.2 depicts the design the in-situ cell for observation of the anode surface. The TCP sample on Al-coated silicon wafer on the top is the working electrode (anode), while the Au-coated wafer at the bottom is the counter electrode. The Ce(III) NaCl-D$_2$O electrolyte (0.1 g CeCl$_3$ and 1 g NaCl per 100 ml D$_2$O) in the cell reservoir chamber was de-aerated prior to the experiment to reduce open circuit potential (OCP), leaving a wider passive potential range to observe TCP swelling and Ce(III) anodic inhibition, which facilitated elucidation of the response of TCP film to increasingly aggressive anodic conditions.

In the step-by-step method, a sequence of constant potentials was imposed ranging from the open circuit potential (OCP) of the TCP-passivated Al, which was measured to be ~ -850 mV vs. SCE, to the point of failure ($E_{pit}$). Each potential step was maintained for 1 hour, during which the current density was recorded. Meanwhile a neutron beam impinged on the TCP-coated Al anode from above and was reflected at the interface between coating surface and electrolyte. NR measurements were conducted as function of imposed potential. A series of scattering length density (SLD) profiles was generated by
inversion of the $R$-$q$ data, revealing the evolution of the TCP film and underlying Al in response to the increasing potential.

5.2.5. **Inductively coupled plasma atomic emission spectroscopy**

The atomic concentration of Ce, Cr, Zr released from TCP-passivated AA 2024-T3 samples with and without anodic hardening were traced for 20 days using inductively coupled plasma atomic emission spectroscopy, which is available at ICPMS service center, University of Cincinnati (http://plasmachem.weebly.com/icpms-service-center.html). A TCP-passivated AA 2024-T3 sample and a TCP-passivated AA 2024-T3 sample after Ce(III) anodic hardening were immersed in NaCl (1 wt %) water solution for 20 days. Solution samples were taken every 3 ~ 4 days for chemical trace element analysis.

5.3. **DATA AND RESULTS**

The Ce(III) anodic hardening experiment on TCP-passivated AA 2024-T3 alloy (Chapter 4) indicates improved pitting resistance compared to the results in un-inhibited NaCl electrolyte. In Figure 5.3 the current density curves at a sequence of constant anodic potentials are compared to the system without Ce(III). Both curves show a corrosion current $< 10$ nA/cm$^2$, indicating a passive state. The passive range of Ce(III)-inhibited TCP, however, is expanded to nobler potentials (-800 mV to -750 mV), followed by a transition stage at -725 mV, where current rises to ~100 nA/cm$^2$. The current baseline in the passive state is also substantially lower than the un-inhibited case. These observations imply anodic inhibition following step-by-step polarization in the presence of Ce(III). We refer to this effect as “anodic hardening.”
For the inhibited coupon at the transition potential of -725 mV the baseline increases to ~ 100 nA/cm$^2$, but the film remains passive. Even in the stable pitting regime at -675 mV there is modest passivation with current density reaching only ~ 1 μA/cm$^2$.

NR snapshots and corresponding SLD profiles of the Ce(III) inhibited system at -825, -800, -775, -750 and -725 mV are displayed in Figure 5.4. The sample in the cell was exposed to the solution for 30 minutes, resulting in a stable OCP (~ -850 mV) before the step-by-step polarization was started. The snapshot at -825 mV was finished 45 minutes after the initial polarization. The NR snapshots and SLD profiles between – 825 mV and -750 mV are essentially identical. A small change at high q is observed in the -725 mV scan.

The distribution of Ce(III) species in TCP film changes little after initial penetration. The plateau with an SLD = (7.5 ± 0.1) x 10$^{-6}$ indicates that Ce(III) is enriched at the film/solution interface. For comparison, Figure 5.4 b also shows the SLD profile for the dry state before polarization and the profile for the uninhibited state in 1 wt % NaCl solution and polarized at a potential within passive region (from -900 mV to -800 mV). These data are taken from Figure 3.10.

The SLD profile shows that D$_2$O and Ce(OD)$_3$ have fully penetrated the TCP film by 1 hour and that further polarization has minimal impact on the film morphology. The Ce(OD)$_3$ species is indicated because of its large scattering length, which is required to explain the observation that the film SLD is larger than D$_2$O. The film thickness does not change significantly, so the amount of Ce(III) in the TCP structure can be estimated from
the increase in the SLD from the passive green curve to the Ce(III) enriched state in Figure 5.4, as is done below.

5.4. DISCUSSION

5.4.1. The content of Ce(III) in TCP film – Ce(III) anodic inhibition

SLD profiles of Ce(III)-inhibited TCP (Figure 5.4) indicate a distribution of Ce species within the bulk TCP layer. The distribution is not uniform, as the SLD value measured near the sample surface is $(7.5 \pm 0.1) \times 10^{-6} \text{Å}^{-2}$, compared to $(5.5 \pm 0.1) \times 10^{-6} \text{Å}^{-2}$ close to TCP/Al interface. The concentration of Ce species in the inhibited TCP layer can be estimated from these values.

The first analysis is based on the observed SLD value of the Ce(III) inhibited TCP layer and the assumption that the content of D$_2$O, H$_2$O, Cr and Zr in the TCP layer does not change with potential. The SLD value of the Ce(III) inhibited TCP layer can then be expressed as the sum of the SLD of the D$_2$O-penetrated TCP (as discussed elsewhere and in Chapter 3) and the SLD due to the content of the relevant Ce(III) compound (Equation 5.1). The SLD value of water-penetrated TCP (SLD$_{D2O-bulk\ film}$) is obtained from the green curve in Figure 5.4b. The Ce species is assumed to be Ce(OD)$_3$ of unknown density.

\[
\text{SLD}_{\text{total}} = \text{SLD}_{D2O-bulk\ film} + \rho_{\text{Ce(OD)$_3$}} \cdot b_{\text{Ce(OD)$_3$}}
\]

where SLD$_{D2O-bulk\ film} = 3.6 \pm 0.1 \times 10^{-6} \text{Å}^{-2}$, and \( \rho \) is the molecular number density of Ce(OD)$_3$. At the TCP sample surface, where the SLD$_{\text{total}}$ is $7.5 \pm 0.1 \times 10^{-6} \text{Å}^{-2}$, and concentration of Ce is high,
\[ \rho_{\text{Ce(OD)}_3} b_{\text{Ce(OD)}_3} = 3.9 \pm 0.1 \times 10^{-6} \text{Å}^{-2} \]  

(5.2)

Close to the TCP/Al interface, where the SLD\text{total} is 5.5 ± 0.1 \times 10^{-6} \text{Å}^{-2} content of Ce(OD)_3 is less

\[ \rho_{\text{Ce(OD)}_3} b_{\text{Ce(OD)}_3} = 1.9 \pm 0.1 \times 10^{-6} \text{Å}^{-2} \]  

(5.3)

The major components of the TCP layer are Cr(III) oxide and Zr(IV) oxide. Previous work found the Cr/Zr ratio to be 2:0.85 (Chapter 2). We use this ration to calculate atomic ratio between Cr and Ce to estimate the relative concentration range of Ce(III) in the inhibited TCP film.

The calculated neutron scattering lengths of the relevant compounds,

\[ b_{\text{Ce(OD)}_3} = 4.226 \times 10^{-4} \text{Å} \]
\[ b_{\text{Cr}_2\text{O}_3} = 2.46 \times 10^{-4} \text{Å} \]
\[ b_{\text{Zr}_2\text{O}_2} = 1.876 \times 10^{-4} \text{Å} \]
\[ b_{\text{H}_2\text{O}} = -0.167 \times 10^{-4} \text{Å} \]
\[ b_{\text{D}_2\text{O}} = 1.915 \times 10^{-4} \text{Å} \]

The measured SLD of the dry film is, SLD\text{Dry}_{TCP} = 1.98 \times 10^{-6} \text{Å}^{-2}.

The Cr number density is calculated from the dry data (Equation 5.4) and the Ce number density is calculated from the \[ \rho_{\text{Ce(OD)}_3} b_{\text{Ce(OD)}_3} \] (Equation 5.5)
\[ \rho_{\text{Cr}} = 2 \times \frac{\text{SLD}_{\text{dry TCP}} \rho_{\text{Ce}}} \]

\[ \rho_{\text{Ce}} = \frac{\text{SLD}_{\text{dry TCP}}}{b_{\text{Ce(OD)}3}} \]

(5.4)

\[ \frac{\rho_{\text{Cr}}}{N_A} = 1.9 \times 10^{-2} \text{mol/cm}^3 \quad \text{and} \quad \frac{\rho_{\text{Ce}}}{N_A} = 7.5 \times 10^{-3} \sim 1.5 \times 10^{-2} \text{mol/cm}^3 \]

therefore the atomic ratio of Cr/Ce is estimated to be.

\[ \text{Cr:Ce} = \frac{\rho_{\text{Cr}}}{N_A} : \frac{\rho_{\text{Ce}}}{N_A} \]

(5.5)

For the upper limit, Cr:Ce = 2:1.6; for the lower limit the ratio is 2:0.8. So the ratio of Cr:Zr:Ce in the TCP bulk layer after Ce(III) anodic hardening (step-by-step polarization from -825 to -725 mV) is expressed as Equation 5.7.

\[ \text{Cr : Zr : Ce} = 2 : x : y = 2 : 0.85 \pm 0.14 : 1.2 \pm 0.4 \]

(5.6)

where the error of y value for Ce is due to its distribution range in TCP layer from the surface to Al interface; the x = 0.85 value is the ratio between Cr and Zr previously measured in the TCP films.\(^3\)

The Cr number density at the original dry film/Al interface is also calculated for comparison.
\[
\rho_{\text{Cr-interfac}/N_A} = \left( 2 \times \frac{\text{SLD}_{\text{dry interface}}}{b_{\text{Cr}_2\text{O}_3 \cdot i\text{H}_2\text{O} \cdot x(\text{ZrO}_2 \cdot j\text{H}_2\text{O})}} \right) / N_A = 3.5 \pm 0.5 \times 10^{-2} \text{mol/cm}^3
\] (5.8)

The Ce concentration of about \( \sim 1 \times 10^{-2} \) mol/cm\(^3\) is comparable to the Cr concentration in the film but three orders of magnitude large then that in solution, which seems unreasonable. This result implies that the relevant Ce compound has a higher scattering length, perhaps CeCl\(_3\) hepta-deutero-hydrate for which \( b = 10.3 \times 10^{-4} \) Å. The SLD of the crystal is \( 10.3 \times 10^{-6} \) Å\(^{-2}\).

We also explored a model where Ce(III) exchanges with Cr(III). The exchange model assumes the SLD increase is due to the conversion of TCP film from Cr(III)/Zr(IV) mixture to Ce(III)/Zr(IV). However neutron scattering length of Ce\(_2\)O\(_3\) is \( 2.70 \times 10^{-4} \) Å, which is close to Cr\(_2\)O\(_3\) (\( 2.46 \times 10^{-4} \) Å). The total SLD of the TCP layer is not sensitive to this conversion.

5.4.2. Inductively coupled plasma atomic emission spectroscopy Ce leaching and Cr exchanging

Although the second model in the previous section does not lead to reasonable numerical results, the TCP film is still susceptible to exchange after anodic hardening. This suspicion is supported by an element trace analysis on Ce, Cr, and Zr.

Figure 5.5 shows atomic concentration of Ce, Cr, Zr in NaCl (1 wt %) water solution over 20 days. Substantial amount of Ce leached out from the anodically hardened TCP sample, which is reasonable since the NR data indicate a Ce(III) enriched layer after the
step-by-step polarization. Cr released from the TCP film with and without anodic hardening are also considerable, while the Zr curve is almost 0. The amount of Cr indicates the relative instability compared to Zr in the TCP layer, and the possibility of replacement by Ce during anodic hardening. If we include this fact into the previous calculation the content of Ce(III) will be somewhat higher.

The significant amount of Ce(III) is important for understanding Ce(III) anodic hardening as described in Chapter 4. Besides the improved pitting resistance of the anodically hardened TCP film the Ce(III)-enriched layer could serve as a reservoir, which sustains active healing over long term usage in realistic field scenario.

5.5. CONCLUSIONS

The combined electrochemical and NR data reveal the structural and chemical information in TCP layer under both anodic and cathodic conditions. We draw the following conclusions:

Firstly, Ce(III) is identified in the TCP layer under anodic polarization. The Ce(III)-extends the passive potential range and reduces the passive current baseline. In other words, Ce(III) in the film “delays” the occurrence of pitting failure. NR data reveal significant amount of Ce throughout the film, but more concentrated at the film/aqueous environment interface.

Assuming a stable TCP matrix with constant Cr and Zr content the estimated concentration ratio of Ce(III) in the film after anodic hardening is $\text{Cr} : \text{Zr} : \text{Ce} = 2 : \text{...}$. 

108
0.85 ± 0.14 : 1.2 ± 0.4. The concentration of Ce could be even higher, if the calculation includes the partial conversion of the TCP matrix from Cr(III) to Ce(III).

Finally the Ce(III)-enriched TCP layer implies that the anodically hardened TCP film could serve as a leaching reservoir for long term active healing. Moreover the ICP data imply a possible exchange between Cr and Ce during anodic hardening.


Figure 5.1. DC polarization curves of AA 2024-T3 samples with and without TCP protection and Ce(III) inhibition. The green curve measured after step-by-step anodic polarization in Ce(III) shows an increased OCP, while the orange curve measured after 24-hour immersion in Ce(III) shows a decreased OCP compared to the bare AA 2024-T3 alloy (black), and TCP passivated AA 2024-T3 (red) without Ce(III) inhibition.
Figure 5.2. Schematic of the split liquid cell set up for observing Ce(III) anodic inhibition. The liquid space is separated into three cavities, a bulk reservoir in middle and two thin reaction layers on both sides. The angle of the incidence is greatly exaggerated. Details are found elsewhere. The neutron beam impinges on the TCP sample for observing the corresponding film evolution.
Figure 5.3. Step-by-step potentiostatic scan of a TCP-passivated pure Al anode in 0.1 wt% CeCl$_3$-inhibited 1-wt% NaCl-D$_2$O solution (red), compared to the case without Ce(III) (blue). The passive region of the TCP-passivated Al anode extends to higher potentials with a lower current baseline during Ce(III) inhibition. A transition region at -725 mV is observed prior to the stable pitting above -700 mV. The counter electrode was a Au-coated wafer. The uninhibited data are from in-situ work described in Chapter 3.\(^1\)
Figure 5.4. SPEAR NR data ($R-q$ plots, and SLD profiles) for in-situ evolution of TCP-coated pure Al exposed to step-by-step anodic polarization (-825 mV to -725 mV) in Ce(III)-inhibited NaCl solution (0.1 g CeCl$_3$, 1 g NaCl in 100 ml D$_2$O, de-aerated). a) $R-q$ plots below -725 mV are identical; b) small change in higher $q$ range was observed at the transition potential of -725. c) SLD profiles indicate significant Ce(III) distribution within the TCP layer, compared to the original dry TCP (black), and the TCP film under anodic polarization in passive region (-900 mV to -800 mV) without Ce(III) inhibition (green), which is corresponds to the blue current profile in the passive state in Figure 5.4. The difference in SLD between the uninhibited and inhibited curves is attributed to Ce penetration. Details regarding the uninhibited TCP data can be found in Chapter 3.
Figure 5.5. ICP data on the Ce, Cr, Zr atomic concentration in NaCl (1 wt %) water solution. A TCP-passivated AA 2024-T3 sample and a TCP-passivated AA 2024-T3 sample after Ce(III) anodic hardening were immersed in NaCl (1 wt %) water solution for 20 days. Solution samples were taken every 3 ~ 4 days, to track the concentration of Ce (purple), Cr (green) and Zr (blue) released from TCP-passivated AA 2024-T3 samples without hardening (dashes) and after anodic hardening. Substantial amount of Ce is measured, and the concentration of Cr from both samples are also considerable, while the Zr curve is almost 0.
Chapter 6 *In-situ* Evolution of Trivalent Chromium Process

Passive Film on Al under Ce(III) Cathodic Inhibition

**SUMMARY:** Similar to the *in-situ* Ce(III) anodic hardening experiment, the NR split liquid reflectivity cell was used to investigate the evolution of structure and composition of a TCP passive film under cathodic polarization in the presence of Ce(III). The liquid cell has two nominally identical pure Al-coated Si wafer electrodes, both of which are covered by a TCP passive film. One wafer serves as an anode while the other is a counter cathode. Using a potentiostatic technique to maintain a constant potential on the anode, a cathodic condition was generated on the TCP-passivated Al counter cathode. NR data on the cathode reveals film evolution at Al/TCP interface; while the *in-situ* anodic corrosion current shows significant attenuation over 24 hours. Cathodic inhibition by Ce(III) was verified by a separate potentiostatic electrochemical experiment. An evolution model based on the *in-situ* NR data is proposed to explain cathodic inhibition.

6.1. **INTRODUCTION**

Chapter 4 discusses an step-by-step anodic hardening process on TCP passive films by Ce(III) inhibition. Chapter 5 discusses a Ce(III)-enrichment of the TCP film on Al after the anodic hardening process. The previous work provides important information regarding the morphology and pitting resistance of the TCP films with Ce(III) anodic inhibition.

Ce(III) cathodic inhibition has also been reported in conjunction with TCP coatings. For example, after simple immersion in Ce(III) the orange DCP data in Figure 5.1 show
that the OCP of the TCP-passivated AA 2024-T3 alloy shifts to a lower potential, which implies a strong cathodic inhibition effect that is related to passivation of the intermetallic inclusions on the alloy surface.\textsuperscript{6-8} Typically Cu-rich inclusions provide cathodic sites for proton reduction reaction due to its galvanic effect. We chose TCP-passivated pure Al electrode to represent the cathodic sites and generate a similar or even a more aggressive cathodic condition via potentiostatic control. Measuring the evolution of the TCP film under cathodic inhibition in the presence of Ce(III) is the objective of this chapter.

6.2. EXPERIMENTAL DETAILS

6.2.1. TCP-passivated Al / Si wafer electrode

Both wafer electrodes in the split liquid cell have a TCP-passivated Al surface (Figure 6.1). Detailed sample preparation procedures including wafer cleaning, Al deposition and EA-TCP processing can be found in Chapters 2 and 5.

6.2.2. Neutron reflectivity (NR)

The \textit{in-situ} NR experiments were performed on Surface Profile Analysis Reflectometer (SPEAR) at the Lujan Neutron Scattering Center, Los Alamos National Laboratory.

6.2.3. In-situ split liquid cell

The split cell configured for cathode interrogation is shown in Figure. 6.1. Both the anodic and cathodic wafers have an Al layer covered by a TCP passive film. Because of the fact that Ce(III) is reported to have both anodic and cathodic inhibition character, we sought to minimize the influence by the Ce(III) inhibition on anode surface by controlling the TCP-passivated Al anode at the transition stage (polarized at -730 mV constantly),
which is beyond the effective Ce(III) anodic inhibition range, but still below stable pitting failure. This transition is discussed in Chapter 5 (Figure 5.3). As it turned out, however, the anode still passivated after 24h. The corresponding reduction reaction occurs uniformly on the counter cathode, which is interrogated by the neutron beam. The Ce(III) NaCl-D₂O electrolyte (0.1 g CeCl₃ and 1 g NaCl per 100 ml D₂O) in the cell reservoir chamber was de-aerated prior to the experiment. A sequence of SLD profiles of the cathode reveals the structure and chemical composition of the TCP layer as a function of time. Cathodic inhibition was verified in a separate conventional electrochemical experiment at University of Cincinnati using the Gamry PCI4 300 potentiostat.

6.3. DATA AND RESULTS

6.3.1. Evolution of the cathode at the pitting transition under Ce(III) inhibition

The cell was stabilized for 30 minutes before polarizing the TCP-coated Al anode to -730 mV. This potential results in a transition state condition with current density of 200 nA/cm². For a Au-coated counter wafer (Chapter 5), this transition state is beyond the limit of short-term Ce(III) anodic inhibition; i.e., corrosion current does not decline within one hour. However using the TCP-coated Al cathode, the corrosion current profile over 24 h shows slow attenuation (Figure 6.2). In this experiment the neutron beam impinged on the TCP-coated Al cathode to detect changes due to Ce(III) inhibition. The NR data are displayed in Figure 6.3.

Figure 6.3 shows that the TCP film on the cathode changed continuously during the 24-hour polarization in Ce. Three significant features are found in the SLD profiles (Figure 6.3 b): 1) SLD of the bulk TCP film increases from $(4.4 \pm 0.2) \times 10^{-6} \text{Å}^{-2}$ to $(5.7$
\( \pm 0.1 \times 10^{-6} \text{ Å}^{-2} \) over 24 hours; 2) the bulk film thickness increased from 760 \( \pm 10 \) Å to 1000 \( \pm 10 \) Å between 12 hour and 24 hour; c) a SLD peak formed at the Al/TCP interface after 18 hour, when the current density in Figure 6.2 starts to show a substantial decrease. The initial SLD of the bulk TCP film, \((4.4 \pm 0.2) \times 10^{-6} \text{ Å}^{-2}\), is primarily due to \( \text{H}_2\text{O} \) penetration, which leads to oxide hydrate exchange by \( \text{D}_2\text{O} \). The \( \text{D}_2\text{O}/\text{H}_2\text{O} \) exchange was described in Chapter 3 (Figure 3.10).\(^1\) The SLD increase from \((4.4 \pm 0.2) \times 10^{-6} \text{ Å}^{-2}\) to \((5.7 \pm 0.1) \times 10^{-6} \text{ Å}^{-2}\) during the \textit{in-situ} experiment can be partially attributed to the further \( \text{D}_2\text{O}/\text{H}_2\text{O} \) hydrate exchange, but is dominated by penetration of bulk \( \text{D}_2\text{O} \) electrolyte into the film structure as demonstrated in Chapter 3. Significant swelling occurs after hour 12; the content of water in the swollen structure is consistent with our previous observation on swollen TCP film under anodic polarization without inhibition (Chapter 3, Figure 3.11),\(^1\) which leads us to postulate that it is primarily \( \text{D}_2\text{O} \) solution, not \( \text{Ce(III)} \) that increases the SLD of the bulk TCP layer to \((5.7 \pm 0.1) \times 10^{-6}\). At hour 15, a SLD peak at 250 Å appears, which is assumed to be an indication of a \( \text{Ce(III)} \)-enriched interface, as represented by orange species in Figure 6.3 c.

During the first 12 hours, no significant inhibition is observed as the anodic current density is constant at \( \sim 200 \text{ nA/cm}^2 \). After 15 h the current attenuates and drops to 0 after 24 hours. Nevertheless we cannot determine whether \( \text{Ce(III)} \) cathodic inhibition occurs on the cathode based on the 24-hour \textit{in-situ} current density. The measured current attenuation is consistent with \( \text{Ce(III)} \) anodic hardening on the TCP-passivated Al anode, which eventually suppresses the current to zero as the OCP shifts in the noble direction (Figure 5.1).
6.3.2. Current profile of a cathodically polarized TCP-passivated pure Al/Si wafer

It must be emphasized that the current drop in Figure 6.2 is unrelated to cathodic inhibition since only anodic current is measured. In order to assess cathodic inhibition, and *ex-situ* potentiostatic experiment was carried out at UC on a nominally identical TCP-coated Al wafer in the same Ce-NaCl solution (Figure 6.4). The Gamry PCI4 300 potentiostat was used with a 2-in diameter flat electrochemical cell and a SCE reference. We used a graphite counter electrode for the *ex-situ* potentiostatic experiment.

The OCP of the TCP-passivated Al cathode was measured to be -850 mV vs. SCE after 30 minutes stabilization in the de-areated CeCl₃ (0.1 wt %) NaCl (1 wt %) water solution. The sample was then polarized cathodically to generate a current in the range from ~ -600 to ~ -200 nA/cm² (similar to the *in-situ* experiment condition). Eventually the constant polarization potential was adjusted to – 50 mV vs. OCP or -900 mV vs. SCE. The resulting current profile at -50 mV vs. OCP is plotted in Figure 6.4.

Although the inhibition process (Figure 6.4) takes somewhat longer on the cathode than the *in-situ* experiment (Figure 6.2), the cathodic current drops to zero within 36 h. When the current reaches zero at 36 h, the cathode OCP has shifted -50 mV vs. the original OCP. The shift of the OCP in the active direction is consistent with the OCP shift observed on the alloy in Figure 5.1. This experiment shows that the cathode is undergoing inhibition during the 24 h period when the data in Figures 6.2 and 6.3 were measured. The NR data therefore harbor insights into the cathodic inhibition process.
6.4. DISCUSSION

Generally Ce(III) precipitation is triggered by the pH increase, which usually occurs on random cathodic sites where the proton reduction reaction occurs. Precipitation of Ce(III) on such sites is assumed to be related to the current drop as observed in Figure 6.4. We used NR to track the evolution of the TCP-coated Al cathode to verify the content of Ce(III) in the film as evidence supporting the proposed TCP evolution model under cathodic conditions with the presence of Ce(III). NR interrogation of the cathode reveals a SLD peak at the Al/TCP interface between hour 18 and hour 24. Because the SLD value of the Al/TCP interfacial peak exceeds that due to water imbibition, there is a strong implication that Ce(OD)$_3$ is involved since 1) Al dissolution is suppressed; 2) the formation of AlH$_3$ or AlD$_3$ requires aggressive conditions; 3) The TCP layer itself is compromised by proton reduction, and can hardly further densify at the interface; 4) water has reached the maximum content. Additional Ce(OD)$_3$ precipitation at Al/TCP interface is consistent with the currently accepted mechanism for Ce(III) cathodic inhibition.\textsuperscript{3, 6, 7, 9, 10} Ce(III) precipitation is accompanied by the additional water, which swells the film, allowing Ce(III) to pass through and reach the high pH region at the TCP/Al interface.\textsuperscript{2} The swelling stage triggers Ce(III) to precipitate. This scenario is consistent with the observation that TCP passivated AA 2024-T3 exhibits a reduced OCP after 24 hour immersion (orange curve in Figure 5.1), due to localized cathodic inhibition on noble intermetallic.\textsuperscript{3, 6, 8, 11}

The density of Ce species in the inhibited TCP layer can be estimated based on the same numerical model used in Chapter 5, which assumes that the content of D$_2$O, H$_2$O, Cr and Zr in the TCP layer does not change as the Ce species penetrates the film.
The peak SLD value of the Ce(OD)$_3$ precipitation at Al/TCP interface can then be expressed as the sum of the original SLD of the Al/TCP interface plus the contribution due to the content of the Ce(OD)$_3$, Equation 5.1.

$$\text{SLD}_{\text{peak}} = \text{SLD}_{\text{interface}} + \rho_{\text{Ce(OD)$_3$}} b_{\text{Ce(OD)$_3$}}$$

(6.1)

where $\rho$ is the molecular number density of Ce(OD)$_3$, and SLD$_{\text{peak}}$ is $(6.1 \pm 0.1) \times 10^{-6}$ Å$^{-2}$ (Figure 6.3 b).

Since the SLD$_{\text{interface}}$ is hard to accurately measure due to the sharp boundary, we estimated the minimum and maximum by taking the value of a virgin interface $(3.6 \pm 0.5) \times 10^{-6}$ Å$^{-2}$ (as measured in Chapter 2), and the value of fully-swollen TCP $(5.7 \pm 0.1) \times 10^{-6}$ Å$^{-2}$, as in the bulk layer in Figure 6.3. The molecular density is calculated via Equation 6.2.

$$\frac{\rho_{\text{Ce(OD)$_3$}}}{N_A} = 1.5 \times 10^{-3}\text{mol/cm}^3 \sim 9.8 \times 10^{-3}\text{mol/cm}^3$$

(6.2)

where $N_A$ is Avogadro constant.

This density range is reasonable compared to the Ce(III) concentration in the bulk solution $(4 \times 10^{-6}\text{ mol/cm}^3)$, and TCP original interface (density of Cr is $3.5 \times 10^{-2}$ mol/cm$^3$, density of Cr$_2$O$_7$·H$_2$O·x(ZrO$_2$·yH$_2$O) is $1.72 \times 10^{-2}$ mol/cm$^3$, Chapter 5).

6.5. CONCLUSIONS

The combined electrochemical and NR data reveal structural and chemical information regarding TCP layer under cathodic conditions. We draw the following conclusions:
Based on the 36-hour corrosion current profile (Figure 6.4), the Ce(III) cathodic inhibition on TCP film is confirmed.

The \textit{in-situ} NR data on the TCP-passivated Al cathode show a continuous film evolution over 24 hour. Besides the increasing water content in the TCP bulk layer, a peak forms after 20-h polarization, implying a densified Al/TCP interface. The most likely explanation for new interface is precipitation of Ce(OD)$_3$. Building on the generally accepted mechanism for Ce(III) cathodic inhibition, the precipitation process starts after the TCP layer expands due to water imbibition. Ce(III) ions then pass through the loose structure and precipitate at the TCP/Al interface, where localized pH rises due to the proton reduction reaction. The entire cathodic inhibition process is slow, but eventually suppresses the cathodic reduction reaction according the 36-hour cathodic polarization data. Compared to the SLD value before and after 24-hour polarization, molar concentration of Ce(OD)$_3$ at the peak is calculated to be between $1.5 \times 10^{-3}$ mol/cm$^3$ and $9.8 \times 10^{-3}$ mol/cm$^3$.

The two-TCP-coated Al electrode configuration is not best suited for observation of \textit{in-situ} cathodic Ce(III) inhibition. For future work on \textit{in-situ} Ce(III) cathodic inhibition, it would be ideal to polarize a TCP-passivated Al cathode cathodically vs. a Au-coated wafer anode and measure both NR and the cathodic current as the cathode passivates.
REFERENCES


Figure 6.1. Schematic of the cell setup for investigating Ce(III) cathodic inhibition. The cell is flipped compared to Figure 5.2, presenting the TCP counter electrode (cathode) on top for NR interrogation. The working TCP anode is polarized at -730 mV for 24 hours.

Electrolyte: 0.1 g CeCl₃, 1 g NaCl in 100 mL D₂O

-730 mV
Figure 6.2. Anodic current density profile when the TCP-coated Al anode was controlled at transition stage at -730 mV. The current drops to 0 at 23 hour. The origin of the noise is uncertain; it may be due to mechanical vibrations or metastable pitting.
Figure 6.3. SPEAR NR data $R - q$ plots (a), SLD profiles (b) and layered model as a function of time (c) for in-situ TCP-coated Al cathode under Ce(III) inhibition during constant polarization of the anode at -730 mV. The evolution of the structure and composition of the TCP bulk layer in the SLD (b) profiles reflect the continuous change as observed in $R - q$ plots (a). A peak at Al/TCP interface forms after 18 hours, at which point the TCP film thickness increased significantly. c) Illustration of the structural and chemical composition evolution in TCP layer showing build of Ce at the metal-film interface.
Figure 6.4. Current density profile at constant cathodic polarization as a function of time. The TCP-coated Al cathode was polarized at -50 mV vs OCP (-850 mV vs SCE) for 36 hours in de-areated CeCl₃ (0.1 wt %) NaCl (1 wt %) water solution. The current attenuation is an valid indication of Ce(III) cathodic inhibition.
Chapter 7 General Summary and Technical implications

The most significant part in this research is the combination of NR and electrochemical methods for interrogation the TCP film structure in an aqueous environment. Although the concept of combining NR and electrochemical methods was developed in 1997 by Tun et al., 1, 2 our approach emphasizes management film evolution by potentiostatic control and quantitative analysis of the NR data. The information obtained in this research is unique in both corrosion research community and optical thin film research community. The *in-situ* methodology demonstrated in this work opens a broad window for fundamental corrosion research where understanding the chemical and structural response of substrate/coating and coating/environment interfaces is essential.

Detailed conclusions regarding each specific research objectives are included at the end of each chapter. Here we summarize some common aspects regarding the mechanism of passivation, inhibition and failure of trivalent chromium passive coatings on Al and Al alloys.

Using electro-assisted deposition method, a dense TCP interface is generated between the Al and the bulk TCP coating. When exposed to aqueous environment, water penetrates into the bulk TCP coating in minutes either by exchanging the hydrate \( \text{H}_2\text{O} \) in the \( \text{Cr}_2\text{O}_3\cdot i\text{H}_2\text{O} \cdot x(\text{ZrO}_2\cdot j\text{H}_2\text{O}) \) structure or by physically swelling the film. “Jelly” is an apt term for describing the water-penetrated TCP bulk layer. In spite of water imbibition both Al and Al alloy remain passive regardless of whether inhibitor is present. It can be concluded that the dense TCP interface plays a critical role as the sole physical barrier isolating the Al from the aqueous environment.
If Ce(III) inhibitor is present in the aqueous environment, the TCP jelly absorbs the Ce and serves as inhibitor reservoir. The *in-situ* NR data detects substantial Ce(III) in the bulk structure under both anodic and cathodic conditions, leading to improved pitting resistance and an extended passivation window.

The above aspects of the EA-TCP system imply that a more robust and passive TCP system would be achieved, if a multi-dense layered structure could be generated by an improved electro-control method, for example pulse-wave technique. Moreover, inhibitors could be loaded into the relatively looser part between each dense interface.

**REFERENCES**