Electrochemical Characterization of Intermetallic Compounds in AA2024-T3 and Localized Corrosion Morphology of Al-Cu-Mg at Elevated Temperature

DISTRIBUTION

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

By

Jichao Li

Graduate Program in Materials Science and Engineering

The Ohio State University

2014

Dissertation Committee:

Prof. Rudolph G. Buchheit, Advisor
Prof. Gerald S. Frankel
Prof. Soheil Soghrati
Abstract

The localized corrosion behavior of Al-Cu-Mg alloy AA2024-T3 (Al-4.4Cu-2.5Mg-0.6Mn) at temperatures from 10 to 70 °C was characterized using a range of experimental techniques and approaches. Foremost among these was a characterization of the electrochemical behavior of constituent particles present in the alloys. The range of intermetallic compound particles types found in AA2024-T3 were represented by a proxy subset of intermetallic compounds including: Al$_2$CuMg, Al$_7$Cu$_2$Fe, Al$_{20}$Cu$_2$Mn$_3$, Al$_2$Cu. An Al 4wt.%Cu binary solid solution alloy was examined as a matrix analog. The effect of rare earth metal and vanadate corrosion inhibitors on localized corrosion behaviors was also examined. The electrochemical methods used in this work included collections of polarization curves, open circuit measurements and electrochemical impedance spectroscopy. Data from these electrochemical measurements was compared to the corrosion morphology after exposure to solutions.

In 0.1 M NaCl solution, the corrosion rate of all secondary phases increased with temperature exponentially, and the relationship conformed to an Arrhenius relation. The dealloying corrosion kinetics of Al$_2$CuMg increased with temperature, which was evaluated based on the extent and duration of a period of intense fluctuation of the open circuit potential. Reduction reaction kinetics on Al-Cu-Mg alloys was documented by mass transport-controlled oxygen reduction. This reaction was found to be dependent on
temperature through temperature dependencies on dissolved oxygen concentration and oxygen diffusivity in solution. Above 70 °C, the formation of corrosion products film on the surface was found to be a barrier layer that reduced the corrosion rate.

Rare earth metals (Ce$^{3+}$, Pr$^{3+}$ and La$^{3+}$) were found to be effective cathodic inhibitors, and their inhibition effect was comparable to chromate. Inhibition by REMs arise from formation of hydroxide layer on the noble particles. Hydroxide layer formation occured as a result of localized corrosion process, in which noble particle supported the oxygen reduction reactions (ORR). The ORR produces local increases in pH, which triggered rare earth metal hydroxide precipitation. Since localized corrosion is required to trigger the precipitation, these rare earth metal species are classified as slow corrosion inhibitors. This slow inhibition nature is more obvious at high temperature as indicated by the severity of corrosion induced.

The inhibition mechanism of the vanadate on the AA2024-T3 at elevated temperature was also studied by second electron microscopy (SEM), focused ion beam (FIB), Raman, and X-ray photoelectron spectroscopy (XPS). Trenching corrosion around AlCuMnFe is strongly inhibited and dealloying corrosion of S phase is also effectively suppressed. This inhibition is attributed to the vanadate film formed at high temperatures. Vanadate could be reduced by Al or Mg at elevated temperature (>50 °C), and this reduction reaction promoted the subsequent polymerization of vanadate species. The vanadium oxidation states in vanadate film comprised mainly V$^{5+}$ and V$^{4+}$. V$^{4+}$ is oxidized to V$^{5+}$ by reaction with oxygen from the air. Samples treated in vanadate solution at high temperature showed residual protection in NaCl solution without any inhibitor.
Dedication

This document is dedicated to my family.
Acknowledgments

I would like to acknowledge my advisor, Dr. Rudy Buchheit, for giving this opportunity to pursue Ph.D degree in Fontana Corrosion Center. I really appreciate that he allows enough time for me to learn the basic corrosion science and get used to the new life here. His feedback and encouragement help me get through the difficult time in the research as well as daily study. I am also grateful for his trust and support on developing some new ideas. Without his guidance and encouragement, it is difficult for me to fulfill this thesis. I would also like to thank Dr. Jerry Frankel for the kind discussion and suggestions on my research. I also thank Dr. Soheil Soghrati and Dr. Michael Dunn for being the committee members of my final exam and for the suggestions on my thesis.

I would also like to thank group members of the Fontana Corrosion Center who helps me during the graduate study, namely Dr. Xiaoji Li, Dr. Meng Tong, Dr. Huang Lin, Dr. Liu Cao, Dr. Anusha Chilukuri, Dr. Brendy Carolina Rincon Troconis, Dr. Severine Cambier, Jiheon Jun, Pitichon Klomjit, Jinwook Seong, Zhicao Feng, Evan Huang, Xiaolei Guo, Xi Wang and the rest of the group. I also thank Dr. Hurley Belinda for the kind help on the vanadate work, and Dr. Nick Birbilis from Monash University for the assistance on the fast Fourier transformation.

Most of all, I would like to thank my parents and brother for all support. Your understanding enables me to focus on the study and research. Lastly, I would like to thank my fiancé, Ying Lu, for all support and encouragement.
Vita

2010 ......................................................... B.S. Metallurgical Engineering, University of Science and Technology Beijing, China

2014 ......................................................... M.S. Materials Science and Engineering, The Ohio State University, Columbus, OH

2011 to present ......................................... Ph.D, Materials Science and Engineering The Ohio State University, Columbus, OH

Fields of Study

Major Field: Materials Science and Engineering
# Table of Contents

Abstract ........................................................................................................................................ ii

Dedication .................................................................................................................................. iv

Acknowledgments ....................................................................................................................... v

Vita ................................................................................................................................................ vi

Table of Contents ......................................................................................................................... vii

List of Tables ................................................................................................................................ xv

List of Figures ............................................................................................................................... xvi

Chapter 1 Introduction .................................................................................................................. 1

References ..................................................................................................................................... 3

Chapter 2 Literature Review ......................................................................................................... 4

2.1 Introduction ............................................................................................................................. 4

2.2 Microstructure of AA2024-T3 and electrochemical characteristics of intermetallic compounds ................................................................................................................................. 6

2.2.1 Microstructure of AA2024-T3.............................................................................................. 6

2.2.2 Electrochemical characteristics of second phase particles in AA2024-T3....... 8

2.3 Electrochemical microcell ...................................................................................................... 14
2.3.1 Electrochemical microcell set up.............................................................. 14
2.3.2 Localized corrosion study using the microcell method................................. 16
2.3.3 Limitations of the microcell .................................................................. 18
2.4 Vanadate and rare earth inhibitors ................................................................ 22
  2.4.1 Rare earth metals inhibitors.................................................................. 23
  2.4.2 Vanadate inhibitors............................................................................. 26
2.5 Critical issues ........................................................................................... 34
2.6 Figures ........................................................................................................ 36
Reference ........................................................................................................ 46

Chapter 3 Effect of Temperature on the Localized Corrosion of 2024-T3 and the
Electrochemistry of Intermetallic Compounds during Exposure to Dilute NaCl Solution
.................................................................................................................................. 55

Abstract .............................................................................................................. 55

3.1 Introduction ................................................................................................. 56
3.2 Experimental ................................................................................................ 59
  3.2.1 Materials and sample preparation.......................................................... 59
  3.2.2 Potentiodynamic polarization measurements......................................... 60
3.3 Results ......................................................................................................... 61
  3.3.1 Potentiodynamic response of IMCs as a function of temperature........... 61
3.3.2 Electrochemical behavior and corrosion morphology of AA2024-T3 at different temperatures................................................................. 67

3.4 Discussion ........................................................................................... 68

3.4.1 Effect of temperature on the anodic response .................................... 68

3.4.2 Effect of temperature on the cathodic response................................. 71

3.4.3 Local corrosion morphology and its relationship to microcell data ....... 73

3.5 Conclusions .......................................................................................... 76

3.6 Figures and Tables .................................................................................. 78

References ..................................................................................................... 97

Chapter 4 Microelectrochemical Characterization of the Effect of Rare Earth Inhibitors on the Localized Corrosion of AA2024-T3 ............................................... 100

Abstract ....................................................................................................... 100

4.1 Introduction ............................................................................................. 101

4.2 Experimental .......................................................................................... 103

4.2.1 Sample and solution preparation ...................................................... 103

4.2.2 Electrochemical measurements ......................................................... 104

4.2.3 Corrosion morphology and cerium precipitation on the S phase and AlCuMnFe particles...................................................................................... 104

4.3 Results .................................................................................................... 105

 ix
4.3.1 Electrochemical response of IMC in 0.1 M NaCl solution with and without inhibitors ................................................................. 105

4.3.2 Localized corrosion morphology of AA2024-T3 after 50 hours immersion in NaCl and inhibitor solutions ................................................................. 109

4.3.3 Cross-section observation of precipitation and S phase after different exposure time in NaCl plus 4mM CeCl₃ ................................................................. 110

4.4 Discussion ............................................................................. 111

4.4.1 Effect of REMs on E_corr, E_pit and i_corr ................................................................. 111

4.4.2 Effect of REM inhibition on cathodic kinetics of IMCs ................................. 113

4.4.3 A model to simulate the pH distribution around dealloyed S phase based on the cathodic current density ................................................................. 114

4.4.4 Quantification of the cerium precipitation on S phase and AlCuMnFe particles, and comparison with their ORR kinetics ............................................. 116

4.4.5 Slowness of inhibition by rare earth metal inhibitors on AA2024-T3 .......... 117

4.4.6 Relation of microcell data with the free corrosion morphology of AA2024-T3 ......................................................................................... 118

4.5 Conclusions ............................................................................ 119

4.6 Figures ................................................................................ 121

References ................................................................................ 138
Chapter 5 The Effect of Temperature on the Inhibition Performance of Cerium on AA2024-T3 ................................................................. 142

Abstract ........................................................................................................ 142

5.1 Introduction ............................................................................................. 143

5.2 Experimental .......................................................................................... 145

5.2.1 Materials and sample preparation ...................................................... 145

5.2.2 Potentiodynamic measurements ......................................................... 146

5.2.3 Corrosion morphology ....................................................................... 146

5.3 Results .................................................................................................... 147

5.3.1 Electrochemical response of IMCs at high temperature in CeCl₃ solutions... 147

5.3.2 Free corrosion morphology after 1 hour exposure in CeCl₃ at 10, 30, 50 and 70 °C ...................................................................................................................... 151

5.4. Discussion ............................................................................................. 152

5.4.1 Effect of temperature on the electrochemical properties of IMCs in CeCl₃ solution ........................................................................................................ 152

5.4.2 Inhibition performance of cerium on S phase particles at elevated temperature ........................................................................................................... 154

5.4.3 Inhibition performance of cerium on AlCuMnFe particles and matrix at elevated temperatures ......................................................................................... 156

5.5 Conclusions ........................................................................................... 157
Chapter 6 Inhibition Performance Study of Vanadate on AA2024-T3 at High Temperature by SEM, FIB, Raman and XPS ................................................................. 170

Abstract .................................................................................................................. 170

6.1 Introduction ........................................................................................................ 171

6.2 Experimental ....................................................................................................... 173

6.2.1 Materials and Sample Preparation ................................................................. 173

6.2.2 Instrumental .................................................................................................... 174

6.3 Results .................................................................................................................. 176

6.3.1 NMR Analysis ............................................................................................... 176

6.3.2 Raman Analysis ............................................................................................. 176

6.3.3 XPS Analysis .................................................................................................. 177

6.3.4 SEM/EDS Analysis ......................................................................................... 178

6.3.5 FIB Analysis .................................................................................................. 180

6.3.6 EIS analysis ................................................................................................... 180

6.4 Discussion ............................................................................................................ 181

6.5 Conclusions ........................................................................................................ 193

6.6 Figures ............................................................................................................... 195
Chapter 7 Fast Fourier Transform of Potential Transients to Interfacial Characteristics of Intermetallic Phases Present in AA2024-T3

7.1 Introduction

7.2 Experimental

7.2.1 Sample and solution preparation

7.2.2 Fast Fourier transformation of potential transient, and data analysis procedure

7.2.3 Electrochemical polarization measurements

7.3 Results

7.4 Discussion

7.4.1 Comparison of electrochemical characteristics (polarization resistance and capacitance) of passive film on IMCs in NaCl and chromate solution

7.4.2 Relationship between polarization resistance and corrosion rate of IMCs in NaCl and chromate solution

7.4.3 Evaluation of dealloying corrosion of S phase and alloy using single frequency EIS

7.5 Conclusions

7.6 Figures and Tables

References
<table>
<thead>
<tr>
<th>Chapter 8 Conclusions and Future Work</th>
<th>243</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.1 Conclusions</td>
<td>243</td>
</tr>
<tr>
<td>8.2 Future work</td>
<td>245</td>
</tr>
<tr>
<td>Bibliography</td>
<td>247</td>
</tr>
</tbody>
</table>
List of Tables

Table 3.1 Composition changes of S phase particles in Fig. 3.13 a after 1 hour exposure in 0.1 M NaCl at 70 °C ................................................................. 95

Table 3.2 Composition changes of AlCuMnFe particles in Fig. 3.14 a after 1 hour exposure in 0.1 M NaCl at 70 °C ................................................................. 96

Table 6.1 Binding energy constraints used for Gaussian-Lorentzian fitting of XPS peaks. ........................................................................................................ 205

Table 6.2 Values of Gaussian-Lorentzian fit (binding energy) for samples exposed at 80 °C and subsequently stored in either an argon environment or a dry air environment. Fit is shown in Fig. 6.3 B and C. *V$_2$O$_3$ and VO$_2$ literature values were used to establish the presence of V$^{5+}$ and V$^{4+}$, respectively[35]. ................................................................. 206

Table 7.1 Summary of the typical fit parameters obtained for IMCs and Al 4wt.Cu% in 0.1M NaCl and chromate solution ................................................................................................................................. 238
List of Figures

Fig. 2.1 Porous structure of S phase after free corrosion in 0.1M NaCl with pH 3 for 90mins[77].................................................................36

Fig. 2.2 Schematic redistribution of copper from the corrosion of S phase[36].........37

Fig. 2.3 Capillary microcells with different address area : a, b by free droplet, c by silicon rubber gasket[65]. ...........................................................................................................38

Fig. 2.4 Capillary with silicone sealant without deformation (a) and with deformation (b) [50]......................................................................................................................................39

Fig. 2.5 Schematic set up of the microcell.................................................................40

Fig. 2.6 a, Schematic set up of microscope with microcell and electrochemical equipment; b, Microcell assembled on the microscope[50]. ........................................41

Fig. 2.7 Modified microcell set up[50]. .......................................................................42

Fig. 2.8 Commonly used equivalent circuit and the impedance spectrum (Bode plot)[64]. ......................................................................................................................................43

Fig. 2.9 Two stages proposed for the cerium oxide conversion coating formation[92]. 44

Fig. 2.10 Equilibrium species ions of V^{5+}--OH^- as function of pH and concentration (adapted from reference[94]). .................................................................45

Fig. 3.1 Sectional view of the copper stage and the water flow path ......................78

Fig. 3.2 Anodic polarization curves of Al4%Cu (a), Al2Cu (b), Al7Cu2Fe (c) and Al20Cu2Mn3 (d) in 0.1 M NaCl at 10, 30, 50 and 70 °C (continued) .......................79
Fig. 3.3 Corrosion potential of IMCs in 0.1 M NaCl at 10, 30, 50 and 70 °C (The corrosion potential of S phase was obtained from the open circuit potential curves at 80 seconds).

Fig. 3.4 Pitting potential of IMCs in 0.1 M NaCl at 10, 30, 50 and 70 °C

Fig. 3.5 Corrosion rate (lgi_corr) of IMCs in 0.1 M NaCl as function of 1/T

Fig. 3.6 Cathodic polarization curves of Al4%Cu (a), Al2Cu (b), Al7Cu2Fe (c) and Al20Cu2Mn3 (d) in 0.1 M NaCl at 10, 30, 50 and 70 °C (continued)

Fig. 3.7 Cathodic current density of each sample at -1 V_SCE as a function of temperature in aerated 0.1 M NaCl

Fig. 3.8 The anodic polarization curves of Al2CuMg after different delay time in 0.1 M NaCl at 10 °C

Fig. 3.9 OCP changes of Al2CuMg as a function of time in 0.1 M NaCl at different temperatures

Fig. 3.10 OCP transient of AA2024-T3 bulk sheet at different temperature in 0.1 M NaCl

Fig. 3.11 The localized corrosion morphology of AA2024-T3 bulk sheet after 1 hour exposure in the 0.1M NaCl at each temperature (continued)

Fig. 3.12 Theoretical limiting current density of diffusion-limited oxygen reduction reactions in DI water based on the data (D from [26], C from [27], δ from [28])

Fig. 3.13 Corrosion morphology of a region rich in S phase particles before (a) and after (b) 1 hour exposure in 0.1 M NaCl at 70 °C, and its BSE image (c)
Fig. 3.14 Corrosion morphology of a region rich in AlCuMnFe particles before and after 1 hour exposure in 0.1 M NaCl at 70 °C……………………………………………………………………… 94

Fig. 4.1 Anodic polarization curves of IMCs in AA2024-T3 in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) +NaCl solutions and chromate solution (continued)…………………………………… 121

Fig. 4.2 Cathodic polarization curves of IMCs in AA2024-T3 in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) + NaCl solutions and chromate solution (for Al$_2$CuMg, it is initiated after 1000s OCP) (continued) ………………………………………………………………………………… 124

Fig. 4.3 Corrosion potential distribution (a) and pitting potential distribution (b) of IMCs in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$)+NaCl solutions and chromate solution……… 127

Fig. 4.4 OCP of S phase in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) +NaCl solution and chromate solution……………………………………………………………………………… 128

Fig. 4.5 corrosion morphology of AA2024-T3: a. after polishing (The insert is magnified S phase); b, after 6 hours exposure in 0.1 M NaCl; c, 50 hours in 0.1M NaCl+ 4mM CeCl$_3$; d, 50 hours in 0.1M NaCl+ 4mM LaCl$_3$; e, 50 hours in 0.1M NaCl+ 4mM PrCl$_3$; f, 50 hours in 0.1M NaCl+ 1mM K$_2$CrO$_4$……………………………………………………………………………… 129

Fig. 4.6 EDS spectra of point 1 on S phase Fig. 4.5 (a), of point 2 on AlCuMnFe(Si) in Fig. 4.5 (b); c, EDS line scanning across an S phase particle; d, magnified SEM image of the crack in c ………………………………………………………………………………… 130

Fig. 4.7 Cross-section SEM of S phase after different exposure time to 0.1 M NaCl solution plus 4mM Ce$^{3+}$………………………………………………………………………………………… 131

Fig. 4.8 Relationship between the pitting potential and corrosion potential of IMC in each test solution………………………………………………………………………………………… 132
Fig. 4.9 Comparison of corrosion rate in 0.1 M NaCl with and without inhibitors (The black horizontal line represented the corrosion rate in 0.1 M NaCl) ....................... 133
Fig. 4.10 Cathodic current density comparison in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) +NaCl solution and chromate solution ........................................................................ 134
Fig. 4.11 Modeling used to calculate the pH distribution around the dealloyed S phase 135
Fig. 4.12 pH distribution around the dealloyed S phase in 0.1M NaCl basing on the model in Fig.4.11 ......................................................................................................................... 136
Fig. 4.13 EDS of Ce element after 52.5 hour exposure in CeCl$_3$ on S phase and AlCuMnFe particles: a and b: corrosion morphology (a is BSE image); c and d: Ce mapping data obtained by EDS on the corresponding particles in a and b; e and f: replotted Ce distribution only on particle based on the extracted data by Matlab........ 137
Fig. 5.1 Anodic polarization curves of IMCs in 0.1 M NaCl with 4 mM CeCl$_3$ at 30, 50 and 70 °C (continued) ................................................................................................................................. 159
Fig. 5.2 Corrosion potential of IMCs as a function temperature in 0.1 M NaCl with 4 mM CeCl$_3$ ................................................................................................................................................. 161
Fig. 5.3 Pitting potential of IMCs as a function temperature in 0.1 M NaCl with 4 mM CeCl$_3$ ................................................................................................................................................. 162
Fig. 5.4 Corrosion rate of IMCs as a function temperature in 0.1 M NaCl with 4 mM CeCl$_3$ ................................................................................................................................................. 163
Fig. 5.5 Cathodic polarization curves of IMCs in 0.1 M NaCl with 4 mM CeCl$_3$ at 30, 50 and 70 °C (continued) ................................................................................................................................. 164
Fig. 5.6 Open circuit potential of S phase in 0.1 M NaCl with 4 mM CeCl₃ at 30, 50 and 70 °C.............................. 166

Fig. 5.7 Corrosion morphology of second phase particles after 1 hour exposure in 0.1 M NaCl+4 mM CeCl₃.............................................. 167

Fig. 5.8 SEM images of cross-section of S phase after 1 hour exposure in 0.1M NaCl+4 mM CeCl₃ at 50 and 70 °C........................................ 168

Fig. 6.1 NMR spectra of 4mM NaVO₃ with a pH of 9.2 as a function of temperature. 195

Fig. 6.2 Overlaid Raman spectra of matrix of AA2024 after exposure in 4.0 mM NaVO₃ at: (a) 80 °C, (b) 70 °C, (c) 30 °C, (d) 10 °C, (e) 50 °C. ........................................ 196

Fig. 6.3 XPS spectra and fitting data of two samples after exposure in 4.0 mM NaVO₃ at 80° C: (A) original XPS data; (B) fitting data for sample stored in argon environment; (C) fitting data for sample stored in dried air. Raw data, black; Baseline, gold; Fitting, red. ........................................................................................................... 197

Fig. 6.4 Corrosion morphology after exposure in DI water. (A) AA2024 at 50° C; (B) AA2024 at 70° C; (C) unidentified IMC on AA2024 at 50° C; (D) AlCuFeMn(Si) particle at 70 °C .............................................................. 198

Fig. 6.5 Corrosion morphology of AA2024-T3 after exposure in 4.0 mM NaVO₃. (A) at 10° C; (B) at 30° C; (C) at 50° C; (D) at 70° C; (E) S-phase on AA2024 at 50° C; (F) S-phase on AA2024 at 70 °C. .............................................................. 199

Fig. 6.6 Corrosion morphology and EDS elemental mapping of S phase particle in AA2024 after 60 min exposure in aqueous 4.0 mM NaVO₃ at 80 °C. ........................................... 200
Fig. 6.7 Secondary electron microscopy of FIB cross-sections from AA2024 samples after exposure in 4.0 mM NaVO₃ at 80 °C. (A) S phase particle; (B) AlCuFeMn(Si) particle; ................................................................. 201

Fig. 6.8 EIS in 0.1 M NaCl without any inhibitor at room temperature after 1 h treatment in 4mM NaVO₃ and DI water at 80 °C. ................................................................................... 202

Fig. 6.9 Limiting current density of the ORR in DI water as a function of temperature. 203

Fig. 6.10 Corrosion morphology of IMCs (A, AlCuMnFe particles; B, S phase particle) after 1 hour exposure in 0.1M NaCl+1mM CrO₄²⁻ at 70 °C. ................................................................. 204

Fig. 7.1 Open circuit potential changes of S phase in 0.1 M NaCl solution at 30°C...... 225

Fig. 7.2 Current-time profile used to obtain potential transient: zero current at t₀ and t₂ regions and I₁ at t₁ region........................................................................................................... 226

Fig. 7.3 Potential transient of Al 4wt.%Cu in 0.1M NaCl after an injection of charge equivalent to 143.2 µC/cm² ........................................................................................................... 227

Fig. 7.4 Nyquist plots of a dummy cell (R₁ + R//C) obtained by the FFT of potential transient and tradition EIS ........................................................................................................... 228

Fig. 7.5 Nyquist plots of IMCs and matrix by FFT in 0.1M NaCl and chromate solution obtained: a, Al₃CuMg; b, Al₃Cu; c, Al 4wt.%Cu; d, Al₃Cu₂Fe; e, Al₂₀Cu₂Mn₃; f, equivalent circuit used to fit the impedance spectra ................................................................. 229

Fig. 7.6 Comparisons of equivalent capacitance in 0.1M NaCl and chromate solution: red solid horizontal line represented data in NaCl solution while black solid dots in chromate solution ................................................................................................................... 230
Fig. 7.7 Comparisons of polarization resistance in 0.1M NaCl and chromate solution: red solid horizontal line represented data in NaCl solution while black solid dots in chromate solution

Fig. 7.8 Average pitting potential and distribution of IMCs and Al 4wt.%Cu in 0.1M NaCl and chromate solution

Fig. 7.9 Corrosion rate of IMCs and Al 4wt.%Cu in 0.1M NaCl and chromate solution

Fig. 7.10 Relationship between $R_p$ obtained through fast Fourier transformed of potential transient data and $i_{corr}$ extrapolated from polarization curves in 0.1M NaCl and chromate solution

Fig. 7.11 Optical profilometer of S phase (a, and SEM image (b)) and AlCuMnFe particles after 1 hour exposure in 0.1 M NaCl at 10 °C

Fig. 7.12 capacitance changes determined using single frequency EIS after different delay time: a, 960s; b, 15s.

Fig. 7.13 Dealloyed S phase propagation rate calculated based on the capacitance change of the bulk alloy and the dealloyed S phase
Chapter 1 Introduction

Aluminum alloy AA2024-T3 is widely used in the aerospace industry due to its high strength and low density. Its composition is 3.8-4.9 wt.% Cu, 1.2-1.8 wt.% Mg, 0.3-0.9 wt.% Mn, and small quantities of Si, Fe, Zn, Cr and Ti. The mechanical properties are achieved by alloying addition such as Cu and Mg, heat treatment and processing [1,2]. However, the resulting microstructure is heterogeneous, containing many secondary phase particles with electrochemical properties that are different from the matrix. This makes the alloy susceptible to the localized corrosion [3,4]. The secondary phase particles couple with the surrounding matrix to form localized galvanic couples. Depending on a variety of actors, particles may act as anodes or cathodes. This galvanic interaction leads to localized corrosion, which is strongly dependent on the environmental factors such as temperature, Cl\(^-\) concentration and pH [5–8]. In order to anticipate and control localized corrosion, it is important to understand the electrochemical properties of the second phase particles and the surrounding matrix in different environments. The electrochemical microcell has been adopted to characterize the corrosion properties on the special synthesized intermetallic compounds in different Cl\(^-\) concentration solution and pH for this purpose [4,9]. Temperature is an environmental variable that has not been as thoroughly studied as others. Therefore, this research is focused on the effect of temperature on the corrosion properties of the second phase particles in NaCl solution.
and in the presence of certain environmental inhibitors including rare earth metal and vanadate.

This thesis consists of 8 chapters including this introduction. Chapter 2 is the literature review on the second phase particles in AA2024-T3 and their electrochemical properties, electrochemical microcell, and rare earth metal and vanadate inhibitors. In Chapter 3, the effect of temperature on the corrosion properties of second phase particles is studied using the microcell and the electrochemical data is compared to the actual localized corrosion morphology. Chapter 4 focuses on the inhibition performance of rare earth metals on secondary phases at room temperature, and its inhibition efficiency is also compared with that by chromate. Chapter 5 describes the effect of temperature on the inhibition performance of rare earth metal on the secondary phases. Chapter 6 is about inhibition performance of vanadate on the AA2024-T3 at high temperature, and explores the inhibition mechanism. Chapter 7 describes a fast Fourier transformation method to study the interfacial characteristics of secondary phases. An attempt is also made to explore a way to monitor the dealloying process of the active S phase in certain environments based on the capacitance changes. Chapter 8 summarizes the key points in this thesis and suggests possible future work.
References


Chapter 2 Literature Review

2.1 Introduction

Aluminum alloys are used widely in aircraft because of their high strength/density ratio[1]. The good mechanical properties are achieved by the addition of alloying elements such as Cu and Mg. However, the solubility of these alloying elements are low in aluminum, and many intermetallic compounds (IMCs) will form during solidification or heat treatment with sizes ranging from a few hundred nanometers to a few micrometers[2]. This heterogeneous structure improves the mechanical properties, but also renders the alloys susceptible to corrosion. The main second phases in AA2024-T3 are Al₂Cu, (Al,Cu)₆Mn, Al₂₀(Cu,Mn,Fe) and Al₂CuMg, while the matrix is Al-Cu solid solution. IMCs usually possess different corrosion potential from the matrix and form galvanic couples with matrix, causing localized corrosion[3]. Much work has been done to try to understand the basic electrochemical characteristics of IMCs and the mechanism of localized corrosion. The electrochemical microcell method, which is used initially to study the pitting at MnS inclusions in stainless steel, is adopted to study the corrosion properties of phases commonly in Al alloys[4]. It is found that their electrochemical properties strongly depend on the environmental conditions such as Cl⁻ concentration and pH[5,6].
Measurement approaches based on microcell methods can also provide information on how inhibitors (such as vanadate) interact with the IMCs. Vanadate species in solution are very complex, and strongly depended on the pH and concentration[7]. It is reported that monovanadate is the most effective species and inhibits oxygen reduction reaction by physical adsorption on the cathodic sites[8]. Vanadate also suppresses the corrosion of IMCs, and shifts the corrosion potential of the bulk alloy below the pitting potential of the Al$_2$CuMg (S phase), inhibiting the dealloying corrosion of this compound [9]. The actions of other inhibitors such as Ce(dbp)$_3$ have also studied in detail [10].

Conversion coatings based on vanadate have been shown to provide corrosion protection comparable to chromate conversion coatings [11]. Vanadate conversion coatings, which are formed by immersion of the sample in the chemical bath for a few minutes, increase the corrosion resistance and exhibit self-healing behaviors, releasing vanadate into the solution and inhibiting corrosion at the defects. The Al-Zn-V$_{10}$O$_{28}$-$^{6}$-$^{\text{\textsuperscript{6}}}$ hydrotalcites also show good inhibition, and vanadate leach out into aggressive environment by exchanging with Cl$^{-}$ in solution. What is more, vanadate is not carcinogenic and even not toxic at low concentration[12], making them a potent alternative to toxic chromate-based coatings.

The purpose of this chapter is to provide a background based on the literature about the electrochemical characteristics of IMCs, the inhibition mechanism of vanadate and coatings based on vanadate. It aims to illuminate the research gaps that should be addressed in order to understand the factors that affect the inhibition performance of vanadate-based coatings and selected Cr-free inhibitors. In this chapter, three topics will
be described: Part I, the microstructure of AA2024-T3 and their corrosion characteristics; Part II, description, application and limitation of the electrochemical microcell; Part III, vanadate inhibitors and vanadium-based coating and pigment.

2.2 Microstructure of AA2024-T3 and electrochemical characteristics of intermetallic compounds

2.2.1 Microstructure of AA2024-T3

AA2024-T3 is a naturally aged Al-Cu-Mg alloy with good mechanical properties, which was introduced in aircraft design in the early 1930[1]. The primary alloying element is Cu, whose concentration is about 3.8-4.9wt.%. The other alloying elements are Mg (1.2-1.8 wt.%), Mn (0.3-0.9 wt.%) and some minimal amount of elements such as Si, Fe. These alloying elements can improve the mechanical properties by forming a heterogeneous microstructure[13]. Cu improves the strength by solid solution strengthening and precipitation hardening. Mg is added to further increase the strength and accelerate the natural age hardening. The solubility of Mn in Al is very low, but it improves the strength by finely precipitated particles. Si and Fe are common impurities in Al alloys and form undesirable second phases.

Due to their low solubility, alloying elements usually form intermetallic compounds during solidification[13]. Buchheit examined second phase particles in AA2024-T3 that are larger than about 0.5~0.7 μm, and divided them into four categories[14]. The largest category includes small and round Al$_2$CuMg (S phase), which constitutes about 66.2% of the particles by number and about 2.7% of the total area. The irregular Al-Cu-Mn-Fe is the second largest category and is assigned as Al$_6$(Cu, Fe, Mn), which is followed by Al-
Cu-Fe type particles (Al$_7$Cu$_2$Fe). The last one is Al-Cu-Mn, which is expressed as (Al, Cu)$_6$Mn. Al$_2$Cu that is bigger than 0.5~0.7 µm is essentially not observed due to the Cu:Mg ratio (4:1~2:1) in AA2024-T3[15]. However, a recent study showed that Al$_2$Cu made up about 5.4% of the particles, and usually clustered with Al$_2$CuMg, which made it indiscernible[16,17].

IMCs possess different corrosion potentials from the matrix, and galvanic couples can form and induce localized corrosion. Particles except the S phase usually show more positive corrosion potential than the surrounding matrix, acting as cathode, while S phase initially is an anode, and then switches to cathode as dealloying enriches the particle with Cu. Among the particles, the area densities of cathode and anode region are equal[17]. In neutral aerated solution, the cathodic reaction is usually oxygen reduction, while the anodic reaction is the oxidation of active metals. The reactions are expressed by the following equations:

Anodic reaction: \( \text{Al} - 3\text{e}^- \leftrightarrow \text{Al}^{3+} \)  \hspace{1cm} (Equation 2.1)

Cathodic reaction: \( \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^- \) \hspace{1cm} (Equation 2.2)

The local pH decrease at anodic sites due to hydration further accelerates the localized corrosion. This galvanic corrosion induces localized corrosion such as peripheral trenching, which can be crack initiation sites and finally lead to failure of the structural components. Almost all the localized corrosion is associated with the second phase particles. The measurement of electrochemical properties of these particles will lead to better understanding of the IMCs’ roles in the localized corrosion.
2.2.2 Electrochemical characteristics of second phase particles in AA2024-T3

The particles commonly found in AA2024-T3 possess different electrochemical characteristics than the matrix[3], making the alloy susceptible to localized corrosion. There are generally two kinds of pit morphologies[5]. Circumferential pits or ‘trenches’ around the particles are due to dissolution of matrix adjacent to a particle. This is attributed to the noble characteristics of particles, which act as cathodes in the galvanic couple and induced the corrosion of the matrix. The other morphology observed is dissolution of the particles. These particles are more active than the matrix and would preferentially dissolve. For some particles such as S phase, noble remnants are left after selective dissolution of active elements. It is reported that both cathodes and anodes are necessary to initiate localized corrosion in Al alloy[18]. Hence, it is very important to learn the electrochemical properties of each particle type in order to have a better understanding about the mechanism of localized corrosion. What is more, these basic corrosion data can be used to simulate the pit initiation and propagation. In this section, the electrochemical characteristics of IMCs as well as the matrix in AA2024-T3 are reviewed.

2.2.2.1 Matrix

The matrix of AA2024-T3 is an Al-Cu-Mg solid solution with about 1.9-2wt.% Cu[16]. The maximum solubility of Cu in Al is about 5.65 wt.% at 548 °C. Pure Al is very active with a corrosion potential around -1.2 V_{SCE} in 0.1M NaCl[19], but is protected by an oxide film formed in the air or water. The dissolved copper in Al confers beneficial effects on corrosion properties of Al. The corrosion potential of Al in 0.1M
NaCl solution increases from -1.2 to -0.9 V$_{SCE}$ by the addition of 4 wt.% Cu [19]. The dissolved copper also shifts the pitting potential, about 200mV by addition of 5.2wt.%Cu. However, aging for a certain time when θ” precipitation predominates, decreases the pitting potential[20]. Kim and Buchheit also reported the pitting potential is elevated by copper dissolved in the alloy and attributed this to inhibition of metastable pitting by copper[21]. Cu enrichment on the surface through potentiostatic and cyclic polarization without damaging the passive film enhance the noble behavior[22]. However, Ramgopal thought the addition of copper has greater effect on the dissolution kinetics[23]. It was found that the exchange current density slightly increased with copper, but Tafel slope is increased more. This resulted in higher surface overpotential, shifting up the pitting potential. Cu also showed inhibition effects on metastable pitting by reducing its initiation and growth rates[21]. It is found that the copper did not affect the first stage of repassivation of metastable pitting but tended to extend the second stage due to the slower mass transportation rate. This phenomenon is caused by copper accumulation on the surface.

The dissolved Cu in the matrix increases the corrosion resistance of Al. However, the matrix is susceptible to localized corrosion due to its low corrosion potential compared to the particles in AA2024 except S phase. Oxygen reduction on these cathodic particles increases the local pH, which induces selective dissolution of Al in the adjacent matrix and induces formation of Cu nanoparticles[24]. Then, the matrix with these Cu particles will become noble than the remote matrix, and induces corrosion of matrix remote from
the original particles. Hence, Cu existing in IMC particles is detrimental to the corrosion resistance, while that dissolved in the matrix is beneficial.

2.2.2.2 \textbf{Al}_7\text{Cu}_2\text{Fe}

\text{Al}_7\text{Cu}_2\text{Fe} is an irregular constituent intermetallic compound and comprises about 6.8\% of the particles by number[17]. The mean equivalent diameter is 1.7 \mu m and the number density is 1651/mm^2. During cold working, these particles often break and align into bands parallel to the rolling direction. \text{Al}_7\text{Cu}_2\text{Fe} has a corrosion potential about -551m\text{V}_{\text{SCE}} in 0.1M \text{NaCl}, which decreases with increasing chloride concentration[5]. The more noble corrosion potential than the matrix indicates its role as a cathode in the localized corrosion. Furthermore, it supports oxygen reduction at a rate higher than \text{Al}_2\text{Cu}\ and \text{Al}_{20}\text{Cu}_2\text{Mn}_3[25]. This behavior is attributed to the presence of Fe, which is effective cathode site for oxygen reduction reactions [26]. It is also found that its ability to support oxygen reduction increases with increasing pH[25]. Circumferential pitting commonly occurs at the matrix adjacent to this particle, giving ‘trench’ morphology. These localized pits are possible stress concentration sites, and initiated cracks[27].

2.2.2.3 \textbf{Al}_{20}\text{Cu}_2\text{Mn}_3

\text{Al}_{20}\text{Cu}_2\text{Mn}_3 is a common fine dispersoid with a rod shape, and homogeneous distribution in the matrix. The corrosion potential of \text{Al}_{20}\text{Cu}_2\text{Mn}_3 in 0.1M \text{Na}_2\text{SO}_4 +0.1M \text{NaCl} is about -0.5 \text{V}_{\text{SCE}}[28], and a little lower in 0.1M \text{NaCl}, about -0.565 \text{V}_{\text{SCE}}[5]. Like \text{Al}_7\text{Cu}_2\text{Fe}, it also acts as a cathode because of higher corrosion potential than the matrix. It shows enhanced oxygen reduction reaction kinetics compared to pure aluminum. This is attributed to copper clusters present in the Al oxide film on the particle surface, which
increases the conduction of electrons through the oxide film[28]. Ilevbare and Scully reported the impedance of Al_{20}Cu_{2}(MnFe)_{3} in NaCl and Na_{2}SO_{4} solution is high, indicating that these compounds are resistant to self-dissolution, while S phase had low impedance, prone to active dissolution[29]. This is also observed by Leblanc and Frankel using atomic force microscopy (AFM) [18], which showed no localized corrosion at Al-Cu-Mn-Fe particles but significant attack at S phase when these particles are exposed to 0.5M NaCl solution.

2.2.2.4 Al_{2}Cu

Al_{2}Cu is a fine hardening phase formed during aging or heat treatment with a fraction about 5.4% in the particle population [17]. Its corrosion potential is about -0.565 V_{SCE} in aerated 0.1M NaCl solution[5], and is slightly higher in the 0.0050M NaCl+ 0.1M Na_{2}SO_{4} solution, about -0.4 V_{SCE}[29]. But its corrosion potential is higher than that of matrix and it is expected to play a role as a cathode in the localized corrosion process. As cathode, Al_{2}Cu is also efficient cathodic site to support oxygen reduction reaction, and reaction kinetics is independent of pH[6,25,28]. But, its efficiency is lower than Al_{7}Cu_{2}Fe and Al_{20}Cu_{2}Mn_{3} due to the absence of Fe and Mn, which facilitate oxygen reaction[30].

Al_{2}Cu corrodes by selective dissolution of Al during exposure to neutral NaCl, and Cu will also dissolve in the anodic polarization, which can be reduced when the applied potential is lower than the equilibrium potential of metallic copper [31]. These Cu ions would deposit on the bulk sample, and they could induce corrosion on the surrounding bare matrix. This kind of galvanic corrosion resulting from noble metal deposition from the solution on active metals is called deposition corrosion. It is suggested that this kind
of copper redistribution and enrichment in the initial time is dominated by Al$_2$Cu (and Al$_2$CuMg) dissolution mechanisms[32]. However, Vukmirovic thought that the deposited Cu ions are from Al$_2$CuMg not Al$_2$Cu[33]. The selective dissolution of Al is also explored to fabricate Cu catalysts with high surface area. For example, porous copper (Raney™ copper) with high surface area can be obtained by immersing the Al$_2$Cu in 6M NaOH at 274K [34].

2.2.2.5 Al$_2$CuMg

Al$_2$CuMg (S phase) is a spherical particle formed during solidification or aging. S phase is very active, and it has been observed that only S phase corrodes when the bulk 2024-T3 alloy is exposed to 0.5 M NaCl for 30mins[18]. Because of its susceptibility to corrosion and detrimental effects, the corrosion characteristics and mechanism have been studied intensively. The open circuit potential of S phase in 0.5 M NaCl is about -0.93 V$_{SCE}$, and is independent of the solution aeration[35]. The low potential indicates S phase is more active than the matrix, and the dissolution reaction is very fast. However, the free corrosion morphology also shows pitting on the adjacent matrix[14]. It is suggested that S phase initially dissolves as anode by the selective dissolution of Mg and Al, leaving a Cu-rich layer with a porous structure as shown in Fig. 2.1. The dealloying process leads to increased corrosion potential, which can be higher than the matrix, thus reversing the galvanic relationship with the matrix.

However, the remnants are not stable because of its high local surface area, which leads to dissolution of Cu, although the potential of the sample is much lower than its
The curvature has strong effect on the electrochemical properties, and its effect on the corrosion potential is described by the following equation[24][36]:

\[
E_{Cu}^* = E_{Cu} - \frac{2\gamma_{Cu}\Omega_{Cu}}{nF}\n\]

(Equation 2.3)

where \(\gamma_{Cu}\) is surface energy, \(\Omega_{Cu}\) is the volume of per molar Cu, \(r\) is the radius of curvature.

The dissolution behaviors of copper could cause the remnant detaching from the original sites. The solution movement might also peel off the copper remnants and carry it away. These detached remnants are captured by the surrounding voluminous corrosion products and move with them. On the other hand, the dissolved Cu ions could be reduced and deposited on the surrounding matrix, which is also detected on Al-Cu-Mn-Fe particles[37]. These two kinds of Cu, detached Cu clusters and deposited Cu, trigger secondary pitting in the matrix[36]. This process is shown in Fig. 2.2.

The Cu-rich remnant is good cathodic site for the oxygen reduction, even more efficient than pure Cu, Al and Mg[35], among which no individual or combined elements accounted for this. Buchheit attributes this to the spongy structure with large surface area by selective corrosion of Al and Mg[35]. Scully suggests the enhanced reaction is due to the Cu clusters in the Al oxide film, which improves the conductivity of Al oxide film and transfer of electrons[29]. However, Leblanc finds that Cu remnants do not support high oxygen reduction reaction and not initiate pitting in the neighboring matrix, which is attributed to the protective films that covered the Cu remnant[18].
The heterogeneous structure in AA2024-T3 improves the mechanical properties, but also increases its susceptibility to localized corrosion. The severity of peripheral pitting increases with the area ratio of the particle to the matrix[18]. It becomes more important to learn the electrochemical characteristics of each IMC under different environmental conditions such as Cl⁻ concentration, pH, and temperature in order to find efficient way to inhibit the localized corrosion. The electrochemical microcell method is an important development, which can focus the test on specific particles using a small capillary. Much work has been done to collect such basic data either using the specially synthesized IMCs[4–6,10,25,35] or on the actual particles in the bulk sheet[38–41] using electrochemical microcell method, which will be introduced in the following section. The acquisition of these basic data deepens our understanding about the localized corrosion.

2.3 Electrochemical microcell

2.3.1 Electrochemical microcell set up

Capillaries were introduced to the electrochemistry about one hundred years ago and are still widely used in the current electrochemical research in some aspects. One example is the Haber-Luggin capillary, which is used to eliminate the potential drop caused by the solution resistance[42]. The capillary can also be used to conduct electrochemical tests on a tiny area with a diameter ranging from a few micrometers to a few millimeters, and the schematic set up is shown in Fig. 2.3. The capillary acts as a conduit to connect samples to the reference electrode and counter electrode, comprising a standard three electrode setup.
The capillary cell can be divided into two groups, depending on how the testing area is defined: free droplets held by surface tension or silicon rubber gasketed [43]. The capillary with free droplets was first used to measure the corrosion potential on aluminum surface[44]. This method is further developed to scanning droplet cell, which could make measurements across a surface by moving the electrode[45]. However, the free droplets are sustained by the surface tension, which limits its usage to the hydrophobic materials. Additionally, the test area is not well defined and the current density cannot be calculated. This problem can be solved by using photo resist to mask a small area for testing [46–48]. However, this process is time consuming and may cause contamination and crevice corrosion. The second method involves using a silicon rubber gasket to dress the end of the capillary tip (Fig. 2.4a) [49,50]. The capillary filled with electrolyte contacted the sample and a small force is applied, which causes the deformation of the silicone rubber and prevents leakage as shown in Fig. 2.4b. Hence, the testing area is defined by the region inside the silicone sealant. What is more, the silicone is hydrophobic and the crevice corrosion between the paste and the sample is minimized.

The capillary is mounted on a Teflon chamber, which contains the counter electrode and is connected to the reference electrode through a salt bridge as shown in Fig. 2.5. Such a fixture can be used to conduct traditional corrosion tests such as potentiodynamic polarization, impedance spectroscopy and potentiostatic measurements. The microcell is fixed at the position of the objective lens on the microscope, which is used to adjust the position of the sample and place the capillary in the testing position. The current is extremely small, a few nA or even fA, and the whole set up is placed in a Faraday cage to
block the external electric fields as shown in Fig. 2.6. The quality of the capillary fabrication has a strong effect on the test results. The microcapillary is small enough to carry out electrochemical tests on individual inclusions in steel such as MnS[49–51], single grain[52], grain boundary[53] and intermetallic compounds in Al alloys[4,5,14]. These measurements provide detailed information about electrochemical characteristics of inclusions, which cannot be obtained using the traditional bulk samples.

2.3.2 Localized corrosion study using the microcell method

The microcell is an enabling research tool for the study of localized corrosion. Traditional corrosion tests using the bulk samples in the range of square millimeters to centimeters provide the general electrochemical properties of the sample, but not necessarily much information about localized corrosion. For example, in Al alloy, the pitting potential is determined by active particles in the large area tests[50]. Microcell approaches allow the individual microstructural elements thought to be responsible for corrosion to be studied.

The microcell was initially used to study the localized corrosion of MnS inclusion in high sulfur stainless steels[54]. Capillaries with diameter about 2.5 µm were used to study the corrosion properties at the region of a single MnS inclusion, interface and the matrix without inclusions. The anodic polarization curves show the interface has the lowest pitting potential, indicating that it is the weakest zone and possible pit initiation site. This is supported by corrosion morphology assessments using AFM[50]. It is found that microcrevice forms at the interface after anodic polarization tests, while the center of MnS corrodes slightly. Pit initiation around active MnS particles was also studied using
the potentiostatic measurements[49,53,55]. More current transients representing the oxidizing dissolution of MnS inclusion are observed in the high Mn steel using the microcell method. These studies also indicate that MnS is critical for the pit initiation. The effects of chloride and Mo were also studied. Chloride ions could initiate the metal dissolution and maintain the pit growth. However, Mo shows little effect on the pit initiation but is efficient in promoting repassivation. These studies led to better understanding about the effect of MnS inclusion on the pitting initiation in the stainless steel.

The microcell can be modified to study the effect of other environmental parameters such as temperature, stress, stirring, pH and flowing rate on the localized corrosion as shown in Fig. 2.7[50]. pH measurement is achieved by the insertion of 25 µm tungsten wire into the tip of the capillary. It is shown the pH of solution near the MnS inclusion decreases as MnS dissolution proceeds[56]. The effect of friction is also studied using microcell by a rotating alumina tube, whose load and speed could be adjusted. The effect of solution flow is also studied by inserting a smaller microcapillary to the microcell and injecting the solution with certain velocity. These three kinds of modifications are mainly limited by the small size of the microcell and the difficulty in assembly of the additional components (W wire, alumina tube, and smaller capillary). The insertion of a pH meter or alumina tube may block the solution path, resulting in higher solution resistance and experimental errors. Another problem is that the soft silicone sealant might be broken either by the mechanical damage or the high hydraulic pressure in the capillary. They are seldom used and few studies are reported. Measurements under stress are achieved by
holding the sample on the edge and applying stress in the middle by a screw. This method was used to study pit initiation at MnS inclusions in stainless steel under stress[56]. It was shown that the stress could lower the onset potential of the MnS dissolution and increase the dissolution kinetics. This method was also adopted to study the intergranular stress corrosion[57]. The effect of temperature on localized corrosion could be studied by introducing a temperature controller, which adjusts the temperature of samples. The tiny volume of solution could be quickly heated or cooled to the designed temperature by the contacted samples. It is found that increasing temperature lowers the pitting potential of MnS and accelerates the dissolution rate[50,51].

The microcell has also been widely used to measure the corrosion properties of IMCs commonly found in Al alloys such as Al2CuMg using synthesized compounds[5]. Their corrosion characteristics have been described in the second section in detail. The microcell method is more accurate than a more traditional approach, in which bulk sample is used and the data shows great variation[3]. These electrochemical measurements on IMCs using microcell methods provide accurate corrosion information for corrosion simulation.

2.3.3 Limitations of the microcell

The microcell shows many advantages over the traditional methods to study localized corrosion, but its limitations, resulting from small size and sealing method, cannot be ignored.
2.3.3.1 Effect of ohmic resistance

In electrochemical measurements, ohmic resistance is caused by the electrical resistance of an electrolyte[58]. The capillary of the microcell has a small cross-sectional area (a few micrometers on the pulled tip and 1 millimeter on the bulk part in diameter), resulting in high ohmic resistance. It is found ohmic resistance is inversely proportional to the square of capillary diameter[59]. However, because of the space limitation as shown in Fig. 2.4, the ohmic resistance in the microcell cannot be mitigated by the techniques analogous to Haber-Luggin capillary. This high ohmic resistance is not a problem if the current is small, but it leads to inaccurate results when the current becomes sufficiently large. In microcell work on corrosion, the current is usually a few nA or smaller, and the potential drop can be ignored. For the measurement of active materials, ohmic compensation methods such as current interruption must be adopted to eliminate the potential drop.

2.3.3.2 Effect of the capillary size

The long and thin capillaries affect the diffusion of the reactants and products to and from the sample surface, which needs to be considered during measurement. For anodic polarization measurements, samples are oxidized and cations enrich near the surface. Some cations might hydrolyze and form solid hydroxides on the surface, which block the capillary and prevent further reactions. Larger capillaries or capillaries with injected solution[43] can overcome this drawback, but special care is needed to prevent the leakage of silicone sealant due to hydrodynamic pressure. The size of the tip also affects pitting potential measurements. The pitting potential is closely related to the number of
weak zones in the small test region. Larger tips usually encompass more weak points, leading to a lower pitting potential[50,60]. For cathodic polarization measurements, the cathodic limiting current increases with the diameter of the capillary[59]. The cathodic reactions are generally oxygen reduction, and limitation of oxygen diffusion in the electrolyte becomes more obvious in small capillaries. Hence, the pitting potential obtained using the microcell needs to be treated carefully.

2.3.3.3 Electrochemical Impedance Spectroscopy (EIS) in the microcell

Electrochemical impedance spectroscopy is used to study the response of a steady-state system to low amplitude potential perturbation (10mV) over a range of frequencies (10 mHz~100 KHz)[42]. Much information about the interface such as capacitance and polarization resistance (R_p) can be obtained. However, EIS is a very sensitive technique and certain conditions need to be met in order for the measurement to be valid. The system response must be linear and originate from the applied perturbation and the system should return to its original stationary state after the perturbation is removed[61]. The application of EIS in the microcell provides useful insights about the interface between the electrolyte and IMCs. However, measurements last a long time, about half an hour or longer, depending on the frequency range. For the microcell test, pitting can occur, leading to metastability during the measurements [60]. This is problematic because it does not meet the requirement of a valid EIS.

To solve this problem, many approaches have been explored. One approach is single frequency EIS. This method is initially used to test the degradation of the coating in the solution at high frequency (1 kHz). Capacitance changes as function of time can be
recorded, indicating coating degradation[62,63]. Lohrengel applied this method in the microcell and measured the capacitance on different particles and grains with varied orientations[64,65]. This method is very fast, but the analysis of the response is based on presupposed equivalent circuit, which might not reflect the actual system. For example, the behavior of an electrochemical interface is often represented by the equivalent circuit in Fig. 2. 8. However, the EIS measurements on a heterogeneous sample by microcell showed two different time constants[65], indicating the commonly used equivalent circuit in Fig. 2. 8 are not accurate. Fast Fourier Transformation (FFT) of potential has been proposed to obtain the EIS response[59,66,67]. The system response as function of time is collected after an injection of charge, and then is transformed to frequency domain data through Fourier transformation equation[68]:

\[
E(f) = \int_0^T E(t)e^{-j2\pi ft} dt
\]

(Equation 2.4)

where \( E(t) \) is the potential transient;

The impedance is obtained by the following equation:

\[
Z(j\omega) = K \frac{1}{I_G} F\{E(t)\}
\]

(Equation 2.5)

where \( I_G \) depends on the coulstatic perturbation method; \( K \) is a constant and depends on implementation of the Fourier transformation[69].

The frequency range of obtained impedance spectra is dependent on the sample time \((\Delta t)\) and total time \((t)\): lowest frequency is \( \frac{1}{t} \); highest frequency is \( \frac{1}{2\Delta t} \). This method is very fast and does not require the system to be in steady-state. The effect of solution
resistance can also be eliminated. What is more, it is not necessary to assume an equivalent circuit. This method has been used to acquire the impedance spectra of various materials in aqueous solution[59,70] and concrete[71,72].

The microcell is a powerful tool to study the localized corrosion and is widely used in the corrosion study of many materials. Much work has been done and it provides us with more insights about the mechanisms of localized corrosion. However, EIS study for Al alloys using the microcell is somehow difficult because of electrochemical instability. The FFT is a good method to solve that, and the evaluation of inhibitors on different intermetallic compound using the EIS is possible. What is more, single frequency EIS can monitor the changes of capacitance, which can be a parameter to indicate the pit initiation and growth, if the equivalent circuit is determined first.

Significant amounts of data have been reported about the corrosion characteristics of IMCs in different environments, but the presentation and application of these fundamental data is rarely done. Buchheit adopted “electrochemical microscopy” method to present the data, which overlapped the reaction rate (anode or cathode) from the polarization curves on each IMC in AA7075-T6 and compared theoretical pit with actual corrosion morphology[73]. This method is a good way to relate the basic data to the actual corrosion. But some assumptions are made for simplicity, and opportunities to extend the approach exist.

2.4 Vanadate and rare earth inhibitors

The passive films on the intermetallic compound surface protected the particles from corrosion, but it can be easily damaged by exposure to aggressive environments (such as
Cl-) or mechanical loading conditions, initiating localized corrosion[18,74]. For example, the pitting potential of Al decreases with the chloride concentration[60]. What is more, the second phase particles and the surrounding matrix comprise a localized galvanic cell, accelerating pit initiation and propagation. Hence, much work has been done to find good inhibitors to provide extra protection and to extend the service time of the alloys. It is found that chromate provides modest corrosion protection by anodic inhibition on pit initiation[18,75] and extensively reduces oxygen reduction reaction[28,29,75,76]. Chromate has been widely used in various ways (chromate conversion coating, additive in aqueous solution and pigment in the painting primers) in industry [77–81], but its application is now becoming limited due to its toxic and carcinogenic properties[82]. Vanadate and rare earth metals with less negative effects on the environment are promising replacements for chromate.

2.4.1 Rare earth metals inhibitors

In the pursuit of a replacement of chromate, rare earth metals (REM) salts such as (CeCl₃) have attracted significant attention due to their high efficiency and low toxicity [83]. Hinton et al. conducted the pioneering work in the corrosion inhibition of aluminum alloys by adding rare earth metals salts in the aqueous solution [84,85]. The subsequent efforts have shown that rare earth metals can also inhibit the corrosion of other alloys including zinc[86], steels[87] and bronze[88]. The inhibition efficiency of REMs on localized corrosion and uniform corrosion has been studied by various techniques such as mass loss, anodic and cathodic polarization.
Hinton studied the inhibition of CeCl₃ addition on the corrosion of AA7075 alloy in the NaCl solution by the mass loss and linear polarization measurements[84]. The cathodic current density could be reduced by an order of magnitude after 10 minutes immersion in NaCl plus 0.05 wt.% CeCl₃ compared to that in NaCl without inhibitors. The inhibition efficiency is observed to increase with longer immersion time [89]. The corrosion rate decreased dramatically with addition of 100 ppm of CeCl₃, and then remained constant up to 1000 ppm. Similar inhibition efficiencies and trends are also observed for other lanthanide salts such as YCl₃, LaCl₃, PrCl₃ and NdCl₃[90]. However, Ce is found to be most efficient among all inhibitors examined. The effect on pitting corrosion was evaluated by the pitting generation resistance, which is the potential difference between pitting potential and corrosion potential [90]. In NaCl solution without any inhibitor, there is no obvious pitting potential, which is almost the same as the corrosion potential, and the pitting generation resistance is negligible. However, with addition of CeCl₃, a slight increase in resistance is observed up to 100 ppm, and the resistance steeply increased from 100 to 1000 pmm, and remained steady value, thereafter at about 160mV, as the concentration increased up to 10000 ppm [84]. Yasakau et al. studied the inhibition of REM on AA2024-T3 by scanning Kelvin probe (SKP), atomic force microscopy (AFM) and scanning electron microscopy (SEM) [89]. They found that cerium precipitation only formed on S phase particles and not on AlCuMnFe particles after 1 hour free corrosion in solution containing REM salts. The precipitation growth rate of hydroxides is estimated to be about 0.4 nm/min in the low chloride solution, but increased to 20 nm/min in concentrated chloride solution. The dependence
on the chloride concentration is caused by the high corrosion activity in the aggressive Cl⁻ environments, which could promote the local pH increase and formation of precipitation on these intermetallic compounds. These rare earth precipitations could hinder the oxygen reduction reaction and anodic dissolution of Mg and Al.

**2.4.1.1 Inhibition mechanism**

REM ions such as Ce³⁺ can form hydroxide caps by precipitation of islands on the corroding surfaces with thicknesses ranging from 100 to 500 nm[90]. The composition of the precipitated cap material is very complex, but is mainly composed of CeO₂ (crystalline), Ce(OH)₄, Ce₂O₃ and Ce(OH)₃ in the oxidation state of 3⁺ and 4⁺. The precipitated cap also show good adhesion with the substrate, and can only be removed by chemical dissolution or abrasion[91]. Precipitated caps result from the local pH increase due to the electrochemical reactions associated with microstructure, grain boundaries and inclusions. The oxygen reduction reaction occurring at cathodic sites could produce OH⁻ and lead to local increased pH, which induces precipitation on the cathodic region. Once formed, the further growth of these precipitates requires that the surrounding pH remains high. These precipitations are a barrier to limit the transportation rate of the dissolved oxygen to the metal surface. However, the presence of porosity in the hydroxides infers that corrosion process cannot be completely stopped but occurs at a reduced rate.

**2.4.1.2 Cerium oxide conversion coating**

Cerium is also used in the form of a conversion coating, which is achieved by immersing a chemically pretreated (degreased and deoxidized) surface in the 10g/L CeCl₃ solution plus 3mL/L H₂O₂ for various times (less than 10 minutes) [92]. The
composition of the conversion coating is hydrated cerium oxides on both samples, but the formation rate on polished samples is faster than that on pretreated ones. The coating morphology is strongly affected by the microstructure: fine films form on the matrix, caps form on IMCs particles. A model is proposed to describe the precipitation process of hydrated cerium oxide as shown in Fig. 2.9. Two stages are proposed for the coating formation. The first stage involves cerium precipitation on the large intermetallic particles due to local increased pH, which is mainly caused by the reduction of hydrogen peroxide, and minor contribution from oxygen reduction. The precipitation on the cathodic particles is thicker than that on the matrix, and shows an island morphology [85]. The second stage involves coating formation on the matrix after dissolution of passive layers on the surface. After the removal this passive film, the formation rate of the conversion coating increases steeply.

2.4.2 Vanadate inhibitors

2.4.2.1 Vanadate species in solution

The $\text{V}^{5+}$ speciation in liquid solution is very complex and strongly dependent on concentration and pH[7]. It is reported that the pH is linearly proportional to the concentration of NaVO$_3$ in aqueous solution[93]. The equilibrium speciation diagram as function of concentration and pH is shown in Fig. 2.10. For a given pH and concentration, one specific species prevails, but is almost always mixed with some other oligomers[94]. Such oligomers are expressed as V$_n$ where n varies from 1 to 10. Generally the species are divided into 5 groups as shown in Fig. 2.10[95]: orthovanadate (Region A), pyrovanadate (Region B), metavanadate (Region C), decavanadate (Region
D) and dioxovanadium (Region E). Orthovanadate (VO₄³⁻) prevails in solutions with pH higher than 13, and forms a colorless solution. In alkaline solutions with pH between 9 and 12, pyrovanadate (V₂O₇⁴⁺, VO₃ (OH), 2⁻) dominates. In near neutral solutions (pH between 6 and 9), metavanadate ((VO₃⁻)ₙ) dominate and the solutions are colorless or yellow. Acidification to pH ranging from 2 and 6 leads to formation of decavanadate (V₁₀O₇₂⁵⁻ (OH)₉ (6-z)⁻, where z=0, 1, 2) and changes the solution color to red or orange. In strong acid solution (pH<0.8), dioxovanadium (VO₂⁺) predominates and shows yellow color. The monovanadate (VO₄₋ (OH)ₙ (3-n)⁻, where n=0, 1, 2) usually exists in dilute solution. Such variation in species makes it difficult to accurately identify the specific species that inhibit corrosion.

The transformation kinetics among vanadate species differ significantly. The transformation among the oligomers Vₙ (n=1-5) is very fast, occurring in a millisecond time scales[96]. The formation of decavanadate by acidification of metavanadate or other species is also fast. However, the depolymerization of decavanadate ions to metavanadate upon alkalization is extremely slow. Under certain conditions, no obvious species changes are observed even after ten days[93], even though the transformation is thermodynamically favorable. The sluggishness in this transformation may be due to the difference in the oligomer structure[97]. This sluggish transformation is exploited to fabricate hydrotalcites containing decavanadate[98].

2.4.2.2 Mechanism of vanadate inhibition

Vanadate efficiently suppresses oxygen reduction reactions and provides modest inhibition of anodic reactions. The extent of inhibition depends strongly on the pH of the
solution. The addition of 0.1 M NaVO₃ in 0.124 M NaCl with pH 6 results in an imperfect passivity and slightly reduced the cathodic reaction[11]. Cook tested the inhibition effect on AA2024-T3 in 0.6M NaCl solution with an addition of 3.4 mM NaVO₃ at different pH (3, 7, 10 and natural pH)[99]. It is found that the vanadate inhibitor showed better performance in basic solutions than in acid solutions. And the suppression of pits by NaVO₃ at pH 10 is even better than that by sodium chromate. Similar phenomena are also reported by Ralston[94], who observed the lowest corrosion rate in aerated and deaerated 50mM NaCl solution with 3.2 or 320 mM NaVO₃ at pH 8. However, all of these results focus on the inhibition performance on AA2024 in general and there is not much analysis about what kind of species are acting and how they interact with the IMCs.

The evidence shows the inhibition is closely related to the vanadate species present in the solution. Iannuzzi studied the effect of vanadate on the cathodic reaction of AA2024-T3[93]. It is found that V₁₀, which dominated in acid solution, exhibited essentially no inhibition of oxygen reduction, and on the contrary, it accelerated the cathodic reaction at high concentration. However, in a neutral solution containing 100 mM NaVO₃, significant suppression of the oxygen reduction to an extent comparable to chromate is demonstrated and the efficiency increased with concentration. By comparing the species in the solution, it is concluded that monovanadate is the most effective inhibiting species. The concentration of monovanadate increased with pH, but not much associated improvement of inhibition was observed due to the full cover of cathodic sites. An analogous inhibition phenomenon is also reported by Ralston[94]. He showed that the
vanadate in tetrahedral coordinated forms (metavanadate and pyrovanadate) inhibited anodic reactions. The pitting potential increased with increasing solution pH and is independent of extent of aeration. However, he attributed the inhibiting effects to the tetrahedral vanadate species such as (VO$^3$)$_n$, not just V$_1$ as in Iannuzzi’s work[93]. But both authors concluded that decavanadate species is not an effective inhibitor.

The interaction of vanadate with the IMCs in AA2024-T3 is also studied. Iannuzzi and Frankel used the in situ atomic force microscopy scratching to monitor the initiation and propagation of localized corrosion around the IMCs in NaCl with and without vanadate inhibitors[100]. The addition of 0.1 mM monovanadate inhibited the dissolution of Al$_2$CuMg (S phase) and the circumferential pitting around the AlCuMnFe particles, and the inhibition efficiency increased with the vanadate concentration. Decavanadate is shown not to provide inhibition. Ralston and Buchheit studied the corrosion behaviors of IMCs in AA2024-T3 using the electrochemical microcell methods[9]. In a 0.5 M NaCl solution with 10 mM NaVO$_3$ adjusted to pH around 9.17, the dominant species ions are single tetrahedrally coordinated vanadium (V$_1$). It is found that vanadate increased the pitting potential of IMCs. For the S phase, the corrosion rate is reduced and pitting potential is increased. It is concluded that vanadate worked by lowering the corrosion potential of the bulk alloy below the pitting potential of S phase, suppressing the selective dissolution of Mg and Al. Vanadate also inhibited the oxygen reduction on all IMCs and matrix, but to different extents.

Tetrahedral vanadate species are the primary species leading to inhibition, which occurs by physical adsorption on the surface. Iannuzzi studied the inhibition mechanism
using polarization measurements and chronoamperometry[8]. It is shown that the monovanadate physically absorbed on the surface with adsorption energy -25.1 kJ/mol. The absorbed vanadate formed a protective film in about 35 mins during the exposure at room temperature. This film suppressed oxygen reduction by impeding either electron transfer or oxygen absorption, and displacing the Cl\textsuperscript{−}. However, such protective films did not show residual protection when the sample first contacted with a vanadate solution is tested again in solution without inhibitor. For the decavanadate, the poor inhibition is attributed to incomplete coverage of IMCs by vanadate.

A physical absorbed vanadate layer blocks oxygen reduction on cathode sites and this effect is expected to increase with the concentration of vanadate in the solution. Higher monovanadate concentration could be achieved by increasing pH[93]. However, the inhibition effect on oxygen reduction does not increase as expected. Instead, the polarization resistance decreased [99], and corrosion rate increased at pH 10[94] compared to that in the natural dissolved solution. Although it is partly attributed to full coverage of all cathodic sites[93], this is not persuasive. The increased corrosion rate of aluminum with increasing pH cannot be ignored. What is more, although tetrahedral vanadate is found to be the most effective species, the inhibition effect of specific species such as V\textsubscript{2} among these vanadate species has not been studied in detail.

\textbf{2.4.3.3 Vanadate conversion coating (VCC)}

Conversion coatings are coatings formed by cations produced by metal dissolution and anions from the bath solution[101]. Conversion coatings improve the corrosion resistance and the adhesion between the substrate and subsequently applied paint. There
are many kinds of conversion coatings such as chromate conversion coatings (CCC), phosphate conversion coating and vanadate conversion coatings (VCC) [101]. VCCs are amorphous films comprised mainly of hydrated vanadium oxide and are formed by immersion of a pretreated surface in a chemical bath containing 10-100 mM NaVO₃, 3 mM K₃Fe(CN)₆ and 2 mM NaF for 3 minutes[11]. Fluoride ions assist the dissolution of the oxide film on the surface, but the role of Fe(CN)₆³⁻ is not clear. However, results show that the role of Fe(CN)₆³⁻ is more important than F⁻ in terms of promoting corrosion resistance[102]. Because of the complexity of vanadate species in the solution, the VCC formation and corrosion protection depend on pH of the bath. It is found that the bath with pH 1.7 yielded the best VCC[11]. At this pH, VO₂⁺ is thought to dominate, but the pH around the surface increased to 2~3 as the oxide film dissolved. VCCs are thought to form in three steps: hydrolysis, condensation and polymerization process. The reactions are expressed as

\[ \text{VO}_2^+ + 2\text{H}_2\text{O} \rightarrow \text{VO(OH)}_3 + \text{H}^+ \]  
(Equation 2.6)

\[ 2\text{H}_2\text{O} + \text{VO(OH)}_3 \rightarrow \text{VO(OH)}_3(\text{OH}_2)_2 \]  
(Equation 2.7)

Electrochemical impedance spectroscopy results show that the performance of VCC is comparable to CCC under full immersion conditions. Like CCC, VCC also shows self-healing characteristics in the simulated scratch cell experiments[11]. These characteristics indicated the VCC is a potent alternative to toxic CCCs.

VCCs are also used to protect the Mg alloys. Yang fabricated VCCs by immersion of polished samples in the 10-30 g/l NaVO₃ solution with pH 8 at different temperature (25, 40, 60 and 80 °C) for varied time (5, 10, 30 and 60 minutes)[103]. Corrosion protection is
assessed by polarization measurements in 0.1 wt% NaCl solution. It is found that the coating thickness increased with temperature and time. However, processing at elevated temperature did not result in obvious improvement on the coating performance. Cracks are observed in the SEM image, which is also reported in others’ work[11]. The crack width increased with the bath temperature, and it is attributed to the dehydration after removal from the bath. The optimal parameters for the conversion coating formation are 30 g/l NaVO<sub>3</sub> at 80 °C with an immersion time 10 minutes.

These parameters are quite different from Guan’s work on VCCs on Al alloys[11]. She found that the vanadate concentration should be between 10-100 mM/L (1.22~12.2g/L) and immersion time shorter than 3 minutes. These difference may be caused by the formation rate of the conversion coating on Al and Mg substrates and possible reduction of vanadate, which has been observed on Zn substrates[104].

### 2.4.4.4 Vanadate hydrotalcites

Hydrotalcites are naturally occurring magnesium and aluminum hydroxyl carbonates and a kind of anionic exchange clay. They are comprised of positively charged hydroxide layers and interstitial carbonate anions[105]. The formula of hydrotalcites are usually presented as [Mg<sub>0.75</sub>Al<sub>0.25</sub> (OH) <sub>2</sub> ] (CO<sub>3</sub>)<sub>0.125</sub>·0.5H<sub>2</sub>O. Many synthetic hydrotalcites have been made [106]. The general formula is usually expressed as

\[
[M_{1-x}^{2+}M_{x}^{3+} (OH)]^{b+} \left[ \frac{A_{n-}}{b} \right] mH_2O
\]

Where M represents metal, A represents interlayer anions, b is equal to x for z=2, while b=2x-1 when z=1, 0<x<0.33.
The structure of the hydroxide layer is similar to that of brucite, Mg(OH)$_2$, but the substitution of Mg$^{2+}$ by Al$^{3+}$ makes hydroxide layer positively charged. The hydroxides are separated by anions and water in the interlayer to balance the charge, giving the ability to store anions. Because of the disordered structure of the interlayer, these anions possessed high mobility and an ability to exchange with anions present in a containing solution. Anions of a small diameter and high charge density are favorable for exchange[107]. It is possible to store inhibitor anions such as CrO$_4^{2-}$[108] and V$_{10}$O$_{28}^{6-}$[109] in hydrotalcites and exchange them with aggressive ions in the solution such as Cl$^-$. However, the selectivity of OH$^-$ and CO$_3^{2-}$ is very high because of their small size. Hence, the CO$_2$ contamination from the air and the solution pH should be controlled carefully during the synthesis of hydrotalcites[107].

There are two ways to synthesize hydrotalcites[106]: indirect and direct synthesis. Indirect synthesis is achieved either by anion exchange or by structure reconstruction. Hydrotalcites can also be synthesized by co-precipitation through the pH adjustment (about 8-10). Direct synthesis is easier and simpler, and the crystallite size can be increased through hydrothermal treatment[110]. This method is widely used to fabricate the ion exchanged compound for coating.

Hydrotalcites ion exchange compounds involving vanadate used in organic coating protect the aluminum alloys from corrosion. Mahajanam fabricated Al-Zn-V$_{10}$O$_{28}^{6-}$ compound (HT-V) by a co-precipitation method[98]. Incorporation of V$_{10}$O$_{28}^{6-}$ into hydrotalcites is achieved by adjusting the pH of NaVO$_3$ solution to 4.5, and then back to 6.5[93]. The compounds are dispersed into an organic epoxy resin to make a primer
coating. \( V_{10}O_{28}^{6-} \) is released into solution by exchanging with anions such as \( \text{Cl}^- \) and adsorbed on the surface, lowing oxygen reduction reaction and increasing the pitting resistance. The release rate of \( V_{10} \) is fast, which is comparable to chromate in CCC[111], and reached an equilibrium concentration about 10mM/L. The similar release kinetics from a Sr(VO\(_3\))\(_2\)·2H\(_2\)O pigment is also observed in NaCl solution[104]. EIS measurements indicated that the HT-V primer coating pigment provided both barrier and active protections[98]. For HT-V pigment, it is also found that Zn ions are released. Zn\(^{2+}\) has been shown to be a good cathodic inhibitor and likely a contributor to corrosion protection observed with HT-V primer[109].

2.5 Critical issues

The heterogeneous microstructure of high strength Al alloy increases the strength and toughness, but also makes these alloys prone to localized corrosion. An understanding of the mechanisms of localized corrosion will enable identification of effective methods to prevent corrosion. The electrochemical microcell method is a critical development in measurement of corrosion properties of second phases in Al alloys[50], and much work has been done to characterize the dependency of electrochemical behavior on environmental conditions such as \( \text{Cl}^- \) [5] and pH [6]. However, there are still many unsolved problems:

1. The electrochemical properties of IMCs are affected by many factors including temperature, and it is necessary to fully understand how their electrochemical behavior depends on temperature. It is known that temperature can increase the chemical reaction rate[61], but how the temperature affects electrochemical reaction corrosion rate of IMCs
has not been studied and described in any detail. Rare earth inhibitors (La$^{3+}$, Pr$^{3+}$, Ce$^{3+}$) are reported to suppress the oxygen reduction on Al alloys[91], but how they interact with IMCs and to what extent they can inhibit the cathodic reductions on the different IMCs in Al alloy have not been studied in detail. What is more, the effect of temperature on the inhibition efficiency of rare earth inhibitors, especially on the localized corrosion, is not well characterized.

2. Although much work has been done to collect the corrosion behaviors of IMCs such as corrosion potential and pitting potential, the information about the surface film on IMCs is rarely reported. Electrochemical Impedance Spectroscopy (EIS) is a good method to obtain such information, but the unstable condition makes the data obtained by the traditional EIS method unreliable. Fourier Fast Transformation is a good way to overcome that drawback by transforming the time domain response into frequency domain response. The equivalent circuit reflecting the interfacial behaviors can be determined, and the interfacial data such as polarization resistance and capacitance can be obtained. This method can also be used to evaluate how the inhibitors affect the properties of the double layer.

3. Vanadate conversion coating is a potent alternative to chromate conversion coating. It is found both concentration and pH have great effect on the coating formation and performance. But there is little work reported about the temperature effect. The optimal parameters (concentration, temperature, and pH) of the bath need to be studied in detail in order to get the best coating.
2.6 Figures

Fig. 2.1 Porous structure of S phase after free corrosion in 0.1M NaCl with pH 3 for 90mins[77]

Fig. 2.2 Schematic redistribution of copper from the corrosion of S phase[36].

Fig. 2.3 Capillary microcells with different address area: a, b by free droplet, c by silicon rubber gasket[65].

Copyright (2006), with permission from Elsevier.
Fig. 2.4 Capillary with silicone sealant without deformation (a) and with deformation (b) [50]

Fig. 2.5 Schematic set up of the microcell
Fig. 2.6 a, Schematic set up of microscope with microcell and electrochemical equipment; b, Microcell assembled on the microscope[50].

Fig. 2.7 Modified microcell set up[50].

Fig. 2. Commonly used equivalent circuit and the impedance spectrum (Bode plot)[64].

Fig. 2.9 Two stages proposed for the cerium oxide conversion coating formation[92].

Fig. 2.10 Equilibrium species ions of $\text{V}^{5+}$--OH$^-$ as function of pH and concentration (adapted from reference[94]).

Reference


Chapter 3 Effect of Temperature on the Localized Corrosion of 2024-T3 and the Electrochemistry of Intermetallic Compounds during Exposure to Dilute NaCl Solution

Abstract

In this study, the electrochemical properties of intermetallic compounds (IMCs) commonly in the AA2024-T3 in neutral 0.1M NaCl at 10, 30, 50 and 70 °C developed using the electrochemical microcell method are reported. Anodic and cathodic polarization curves were collected on specially synthesized Al$_2$Cu, Al$_7$Cu$_2$Fe, Al$_2$CuMg, Al$_{20}$Cu$_2$Mn$_3$ bulk intermetallic compounds (IMCs) and an Al-4%Cu solid solution. Results reveal that corrosion rates of all the IMCs increase with temperature according to an Arrhenius relationship. When sufficient cathodic polarization is applied to the oxygen reduction reaction becomes mass transport limited under these experimental conditions. The limiting current density exhibited a temperature dependence that was related to temperature dependencies in oxygen solubility, diffusivity and thickness of diffusion layer. ORR kinetics were greatest at around 50°C; consistent with calculations made using a simplified version of the Cottrell equation. A dominant attribute of S phase (Al$_2$CuMg) dissolution is dealloying. Dealloying kinetics of the S phase (Al$_2$CuMg) were found to increase with increasing temperature. Increased dealloying rates were evident in both open circuit potential (OCP) transients and characterization of post-exposure
corrosion morphology by scanning electron microscopy of focused ion beam cross-sectioned samples. Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$ were studied as proxy phases for a range of AlCuMnFe-type particles found in 2024-T3. The temperature dependence of the corrosion potential of these phases was such that the phases were noble relative to the 2024 matrix phase at temperatures below 50°C, but more active above 50°C. Characterization of 2024-T3 samples subject to free corrosion exposures showed that AlCuFeMn particles induced trenching at their periphery below 50°C, but dealloyed and dissolved above this temperature consistent with a galvanic polarity reversal observed in OCP measurements.

3.1 Introduction

Copper and magnesium are added to aluminum to improve alloy mechanical properties such as strength and toughness through precipitation strengthening and thermochemical processing [1,2]. However, these alloying additions react with other alloying elements (e.g., Mn) and impurity elements (e.g., Fe) to form constituent intermetallic compound particles (IMCs) such as Al$_2$Cu, Al$_2$CuMg and a range of Al-Cu-Mn-Fe-types during solidification processing [1]. Constituent particles are comparatively large, 0.1 µm and larger in diameter. They form as a result of dendritic solidification and are distinct from precipitate particles and dispersoids that form as a result of heat treatment. Constituent IMC particles often possess different corrosion potentials from the surrounding matrix phase, leading to localized galvanic effects and localized corrosion[3–5]. IMC particles whose corrosion potential is higher than that of the matrix are relatively noble. These particles catalyze oxygen reduction in aerated aqueous
environments leading to localized cathodic corrosion and dissolution of the matrix immediately adjacent to the particle generated what is often referred to as “trenching” corrosion. IMC particles whose corrosion potential is lower than the of matrix phases are relatively active. These particles tend to be selectively dissolved in aerated aqueous environments and often leave insoluble remnants at the particle location [6]. As might be expected, pit morphology such as width and depth strongly depends on the environmental conditions and alloy microstructure. The pit initiation rates and pit number density are closely related to alloy microstructure [7], but the propagation rate and the pit morphology are more sensitive to environmental conditions [8]. Cavanaugh et al. observed the morphology of pits formed in 7075-T6 under free corrosion conditions in NaCl solutions using an optical profilometer. It was found for aluminum alloys, that solution pH and exposure time were the primary determinants of damage accumulation, while temperature and rolling direction affected pit morphology to the greatest extent [9]. It was also found that for a wide range of environmental conditions (pH, temperature, chloride ion concentration), a $t^{1/3}$ power law generally characterized pit growth rate [10].

All aspects of localized corrosion in aluminum alloys are strongly dependent on the electrochemical properties of IMC particles. In turn, these properties have notable dependencies on environmental conditions. The corrosion potentials of most IMC particles decrease as $[\text{Cl}^-]$ increases. Because pH affects oxide film stability and because IMC compounds are mixtures of different elements that can contribute to protective oxide film formation, the effect of pH on corrosion and pitting potentials of IMC particles depends on composition in a complex manner [4, 5, 10, 11]. To have a full understanding
of the pit initiation and localized corrosion, it is necessary to have comprehensive characterization of IMC particle electrochemical properties.

The micro capillary electrochemical cell (microcell) allows electrochemical measurements to be made at small length scales using a glass capillary tube drawn to a small opening whose diameter ranges from a few micrometers to a few millimeters [12–14]. The microcell approach has been used to characterize the electrochemical properties of small, specially prepared IMC crystals in aqueous solutions over a range of different pH and NaCl concentrations [4,5]. This information can then be used to develop mechanistic interpretations of localized corrosion damage accumulation.

Solution temperature is also an important environmental factor that affects localized corrosion. For example, in alkaline chloride solutions, anodic and cathodic kinetics of the corrosion cell process on Cu and Fe increase with increasing temperature under mixed reaction control. In acid solutions (0.1 M NaCl + 0.1 M HCl), corrosion rates of pure metals (Cu, Fe, Zn and Ni) increases exponentially with 1/T according to an Arrhenius equation [15]. For corrosion processes that involve oxygen reduction, temperature can exert a secondary influence through its affect on equilibrium oxygen solubility and the dissolved oxygen diffusion coefficient. Furthermore, the solubility of hydrated corrosion products is temperature-dependent, which can affect the corrosion process[16].

The electrochemical characteristics of IMC particles exposed to dilute chloride solutions at temperatures other than ambient room temperature have not been reported widely. In this work, the electrochemical polarization curves of IMCs at temperatures ranging from 10° to 80°C were collected using the microcell method, and the data
gathered were used to interpret corrosion damage accumulation of 2024-T3 samples after exposure in NaCl over the temperature range investigated.

3.2 Experimental

3.2.1 Materials and sample preparation

A 0.1 M NaCl solution was prepared by dissolving reagent grade NaCl (purchased from Fisher Scientific) in 18 MΩ*cm deionized (DI) water. After equilibration with air, this water attained a pH of 5.7 due to CO₂ buffering. The NaCl solution used in microelectrochemical cell measurements and free exposure experiments with 2024-T3 samples was naturally aerated. IMCs of interest in the study included Al₂CuMg and Al₂Cu. The phases Al₇Cu₂Fe and Al₂⁰Cu₂Mn₃ were proxy phases used to represent the range of Al-Cu-Fe-Mn IMC particles observed in 2024. Measurements of Al-4%Cu were included in this study. Al-4%Cu is not an intermetallic compound, but is an analog for the matrix phase of 2024.

Ingots containing the requisite alloying elements were cast using standard laboratory methods to produce samples that contained crystals of the desired IMCs. The ingots were cast according to specific protocols based on the appropriate phase diagram to produce IMC crystals with diameters of several hundred micrometers[5]. This facilitated electrochemical characterization by the microcell method. In certain experiments Cu samples were subject to electrochemical testing. Cu samples were 99.999% pure (purchased from Alfa Aesar).

In preparation for electrochemical testing, all samples were polished from 600 to 1200 grit using SiC sand paper lubricated by ethyl alcohol. Surfaces were then polished using
1µm diamond paste lubricated by a light weight mineral oil. Finally, samples were degreased ultrasonically in ethanol and dried using compressed air.

Electrochemical measurements were carried out immediately after polishing. A specially designed Cu stage was used to control the temperature of the samples (Fig. 3.1). The Cu stage was pre-cooled or pre-heated to the designated temperature with circulating water from a heating bath (Isotemp® 4100 Circulators/Baths, purchased from Fisher Scientific). The samples were cut thin so that they attained the target temperature quickly. The temperature was calibrated using a contact thermometer.

Samples were polished through to 1200 grit with SiC paper lubricated with ethyl alcohol for free corrosion exposure experiments with 2024-T3. Samples were then ultrasonically cleaned in ethanol and dried using compressed air.

### 3.2.2 Potentiodynamic polarization measurements

Anodic and cathodic polarization curves were collected in 0.1M NaCl solution using the microcell at 10°C, 30°C, 50°C and 70°C, respectively. Measurements were made using a standard three-electrode setup, with platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The measurement was controlled and data were recorded using a Gamry Reference 600™ potentiostat. The opening of the capillary was about 100 micrometers, and a layer of silicon rubber was used to dress the capillary tip to make a leak-free seal with the sample surface. Anodic and cathodic polarization curves were initiated after a around 60s OCP measurement using a scan rate of 0.01 V/s. At least 6 replicate polarization curves were collected, and the average values of the corrosion potential, pitting potential, corrosion rate, passive
current density and limiting current density were used to characterize IMC electrochemical response. For 2024-T3, polarization curves were measured using a scan rate of 0.3 mV/s in water-jacketed cell (described later). The sample and a Pt mesh counter electrode were immersed in the temperature-mediated NaCl solution, while the reference electrode was connected to the electrolyte using a Luggin capillary to avoid temperature changes that would alter its potential.

Free exposure corrosion tests were performed in a water-jacketed cell. The NaCl solution was precooled or preheated to the designed temperature, and then the polished samples were placed at the bottom of the cell. After a 1 hour exposure, samples were taken out, rinsed with DI water, dried with compressed dry air and then stored in a desiccator. The corrosion morphology was characterized using an FEI/Philips XL-30 field emission environmental scanning electron microscope (ESEM) and Sirion scanning electron microscope (SEM) coupled with (energy dispersive X-ray spectroscopy) EDS. Certain samples were cross-sectioned for characterization of corrosion damage in the near surface region. These samples were prepared using a FEI Helios Nanolab 600 dual beam focused ion beam (FIB) with 30 kV Ga ion beam.

3.3 Results

3.3.1 Potentiodynamic response of IMCs as a function of temperature.

Fig. 3.2 shows the anodic polarization curves for high purity Cu, Al 4%Cu, Al7Cu, Al7Cu2Fe and Al20Cu2Mn3. The curves show forward and reverse scans with the forward scan marked on the figure. The curves presented here were chosen from the replicate curves based on proximity of their corrosion potential or pitting potential to the average
value. Fig. 3.3 and Fig. 3.4 show the corrosion potential and pitting potential of IMCs studied, respectively. IMC corrosion rates were estimated by extrapolating the linear part of the polarization curves to the intersection of corrosion potential, and these data are summarized in Fig. 3.5. The cathodic current density at –1.00 V_{SCE} are shown in Fig. 3.7. At this potential the dominant cathodic reaction is expected to be oxygen reduction and a comparison of these data shows the ability to support oxygen reduction and to and evaluate the effect of temperature on oxygen reduction kinetics.

3.3.1.1 Al-4%Cu

The anodic polarization curves of Al-4%Cu, the matrix phase analog, are shown in Fig. 3.2a. This binary alloy is spontaneously passive at all temperatures tested. The corrosion potential varies in a range of -0.800 to -0.950V_{SCE} over the temperatures tested. Up to 50°C there is little variation in the pitting potential, which falls in the range of -0.350 to -0.450V_{SCE}. At 70°C, the polarization response indicates several breakdown potentials. This is believed to be an artifact associated with crevicing, with the true breakdown potential associated with pitting of the alloy at about -0.35 V_{SCE} (Fig. 3.4). The tendency of the alloy to repassivate is strong and repassivation potentials are all greater than about -0.70V_{SCE}.

The corrosion rate of Al-4%Cu is not strongly temperature-dependent ranging from a few tenths of a μA/cm² at 10°C to just a few μA/cm² at 70°C. Cathodic kinetics increase with increasing temperature up to 70°C as shown in Fig. 3.6
3.3.1.2 Al$_2$Cu

The Al$_2$Cu phase was found to be spontaneously passive at all temperatures measured but does not show a strong tendency to repassivate under conditions of potentiodynamic polarization. In fact, corrosion potentials (repassivation potentials) on the reverse scans during anodic polarization were all more negative than corrosion potentials measured on forward scans (Fig. 3.2 b). Repassivation potentials did increase with increasing temperature up to 70°C.

The corrosion and pitting potentials show modest temperature dependencies. The corrosion potential decreased from about -0.450 to -0.600V$_{\text{SCE}}$ over the temperature range 10$^\circ$C to 70$^\circ$C as shown in Fig. 3.3. The pitting potential decreased from about -0.300 to -0.550V$_{\text{SCE}}$ over that same range (Fig. 3.4). There was notably wide dispersion in replicate pitting measurements. The smallest passive window as defined by the difference between pitting potential and corrosion potential was about 80 mV at 70°C.

The Al$_2$Cu corrosion rate and the passive current density increased with increasing temperature from about 2 $\mu$A/cm$^2$ at 10°C to nearly 100 $\mu$A/cm$^2$ at 70°C. It is noticeable that the corrosion potential at 10°C of 0.455V$_{\text{SCE}}$ is very close to the pitting potential at other temperature.

Cathodic kinetics increase modestly all along the cathodic polarization curve as temperatures increase from 10$^\circ$C to 50°C. The mass transport limited current density for the oxygen reduction reaction falls in the range of 20 to 40 $\mu$A/cm$^2$. There is a noticeable change in the cathodic polarization curve at 70°C. The cathodic kinetics are greater in the
region were oxygen reduction is expected to dominate the kinetic response, in cathodic reaction rates on going from 50° to 70°C (Fig. 3.6).

3.3.1.3 Al$_7$Cu$_2$Fe

The Al$_7$Cu$_2$Fe phase is spontaneously passive at all temperatures tested (Fig. 3.2). Passivity is robust at all temperatures as judged by the difference in pitting potential and corrosion potential. The phase shows a very strong tendency to repassivate and in many instances repassivates shortly after the scan direction is reversed in the anodic polarization curve. At all temperatures tested, the repassivation potential is well above the corrosion potential and in some experiments was observed to be above the observed pitting potential.

The corrosion potential is not strongly temperature dependent from 10 to 70 °C, varying from -0.79 to -0.70V$_{SCE}$ (Fig. 3.3). The pitting potential drops by about 50 mV as temperature increases from 10 to 70 °C (Fig. 3.4).

Generally, the passive current density increases with temperature, while corrosion rate increases exponentially with temperature. As was observed with Al$_2$Cu, cathodic kinetics increase from 10° to 50°C, and then decrease as temperature in increased to 70°C (Fig. 3.6).

3.3.1.4 Al$_{20}$Cu$_2$Mn$_3$

Like the previous two IMCs, Al$_{20}$Cu$_2$Mn$_3$ is spontaneously passive over the temperature range investigated in this study (Fig. 3.2 d). The phase shows a strong tendency to repassivate, and repassivation may be promoted by increasing temperature. As with Al$_7$Cu$_2$Fe, the repassivation potential was always observed to be more positive.
than the corrosion potential, and at temperatures at and above 50°C, repassivation on the reverse polarization scan occurred near or above the pitting potential.

The corrosion potential was modestly dependent on temperature, increasing with temperature up to 30 °C, but then it decreasing by about 200 mV from 30 to 70 °C through the range of -0.700 to -0.900V_sce. The pitting potential decreased from about -0.350 to -0.450 V_sce with temperature from 10 to 50°C, but increased somewhat at 70°C. Replicate corrosion potential and pitting potential measurements were scattered reducing confidence in the determination of temperature-dependent trends (Fig. 3.3 and Fig. 3.4). Passive current densities increased from about 1 to 10 µA/cm² with increasing temperature below 50 °C, but no obvious changes are observed from 50 to 70 °C, while continued increase of corrosion rate with temperature is observed. Fig. 3.6 d reveals that cathodic kinetics are slowest at 70 °C, followed by that at 10 °C, while those at 30 and 50 °C are similar.

3.3.1.5 Al₂CuMg (S phase)

The S phase is reactive due to the presence of Mg, making the corrosion process of the phase complex. S phase corrodes initially by selective dissolution of Mg and Al acting in a dealloying process. This process enriches the surface of the phase with Cu, which ennobles the phase rendering it a net cathode after some time. Dealloyed S phase can support oxygen reduction at an appreciable rate [17–19]. The dealloying process is electrochemically chaotic and the open circuit potential of the phase oscillates between noble and active values as the process occurs [20]. This chaotic behavior is observed in 0.1 M NaCl even at temperature as low as 10 °C as shown in Fig. 3.8. As exposure time
increases from 13 s to 430 s, the corrosion potential changes from -0.933 to -0.58 V\(_{\text{SCE}}\). Further increasing the exposure time (2000 s) does not change the corrosion potential (around -0.58 V\(_{\text{SCE}}\)), but no pitting potential is observed in subsequent polarization measurements even though the potential is increased to as high as 0.3 V\(_{\text{SCE}}\). This response is attributed to a protective character imparted by the Cu-rich layer that forms on the surface due to dealloying.

These results show that the effect of temperature on the dealloying corrosion kinetics, polarity reversal between S phase and the matrix and dissolution behavior of S phase cannot be fully evaluated from anodic polarization curves alone. To address this, OCP transients were used to characterize the effect of temperature on the corrosion properties of S phase. The OCP at each temperature is shown in Fig. 3.9. Extensive fluctuation upon initial exposure is shown in the insert. At 10 °C, the OCP is fairly stable at about -912 mV\(_{\text{SCE}}\), and there is no obvious variation during the 2000 s measurement. At 30 °C, a stable OCP (around -914 mV\(_{\text{SCE}}\)) is observed in the first 670 s, and then potential increases to -685 mV\(_{\text{SCE}}\) and returns to its original value after 70 s. This stable potential lasts for about 200 s, and then is followed by a period of oscillation. At 50 °C, the OCP demonstrates great fluctuation upon exposure to NaCl, which lasts for the entire duration of the measurement. The most positive potential is about -370 mV\(_{\text{SCE}}\). At 70 °C, the OCP oscillation is observed upon exposure similar to that at 50 °C, but the extent of oscillation is much greater. The oscillation lasts only for about 100 s, and the OCP gradually increases without variation to -240 mV\(_{\text{SCE}}\), which is close to the corrosion potential of pure Cu at 70 °C.
3.3.2 Electrochemical behavior and corrosion morphology of AA2024-T3 at different temperatures

Fig. 3.10 shows OCP of AA2024-T3 versus time during a six-hour exposure at each temperature. The steady-state OCP decreases from about -550 mV$_{\text{SCE}}$ at 10 °C to about -650 mV$_{\text{SCE}}$ at 70°C. A distinguishing attribute of the OCP response is the activation transient at the beginning of the exposure period. The transient is comparatively brief at temperatures up to 50°C, but is extended at 70°C. Activation of the surface is significant causing the potential to drop to nearly -1100 mV$_{\text{SCE}}$.

The localized corrosion morphology of AA2024-T3 after a one-hour exposure in 0.1 M NaCl at each temperature is summarized in Fig. 3.11. Fig. 3.11 a and b show that only dealloying corrosion occurs on the S phase particles at 10 °C, and no trenching corrosion is observed around the AlCuMnFe particles (insert in Fig. 3.11a). For the S phase particles, nano-scale porous structure is observed on the particle due to dealloying. Dealloying is localized to the surface as shown in bottom insert in Fig. 3.11 b. The image also reveals obvious deep trenching with a width of 300 nm around the dealloyed S phase particle. As temperature increases to 30 °C, similar dealloying and trenching morphology related to S phase particles is observed, but the pore size and trenching width become larger (Fig. 3.11 c). For AlCuMnFe particles, a slight trench forms around the particles, and it is covered by loose corrosion products. The trenching becomes larger at 50 °C as shown in Fig. 3.11 e, however, a detailed view of the surface reveals porous and loose corrosion products on the surface. This structure is more obvious in the tilted samples (Fig. 3.11 f), and the smooth surface seems to reveal slight corrosion of S phase. The
cross-section of the particles (insert in Fig. 3.11 f) clearly shows severe dealloying corrosion penetrating half of the particles depth, and the scale of the porosity is much larger than those at 10 and 30 °C. At 70 °C, most of S phase particles is dissolved, and some corroded remnants remain, but EDS shows that the Mg component is almost completely absent. Cross-sections of S phase remnants (Fig. 3.11h) reveal the dealloyed layer penetrates the through the whole particle, and some large holes are formed. Significant amounts of Al and Cu, about 50 wt.%, are detected on these remnants by EDS. For AlCuMnFe particles, some particles fully dissolve as shown in the left insert in Fig. 3.11 g. But most are covered with non-conductive corrosion products as indicated by the charging brightness in the SEM image (Fig. 3.11e). BSD images reveal that these particles are also severely corroded, showing a fragmentary morphology (Fig. 3.11 g), and the Al concentration is dramatically reduced while the Cu concentration is increased.

3.4 Discussion

3.4.1 Effect of temperature on the anodic response

Temperature exerts a strong effect on the electrochemical properties of IMCs. The corrosion potential for Cu decreases linearly with increasing temperature, which has also been reported in neutral and acid 1 M NaCl solutions [21]. For Al20Cu2Mn3 and Al7Cu2Fe, the corrosion potential first increases with temperature up to 30 °C, and then decreases at greater temperatures. To better evaluate the roles of IMCs in the localized corrosion at each temperature, the corrosion potentials of AA2024-T3 matrix without constituent particles visible in the optical microscope were collected by anodic polarization curves at each temperature and the results are shown in Fig. 3.3. The
corrosion potential of Al₂Cu is higher than that of the matrix at all tested temperatures, remaining noble to matrix. The corrosion potentials of Al₂₀Cu₂Mn₃ and Al₇Cu₂Fe are higher than that of the matrix at 10 and 30 °C, but they are lower at 50 °C and 70 °C. As a result, their galvanic relationship with the matrix changes from anode to cathode. This transition from cathode to anode indicates that IMCs would dissolve upon exposure at temperatures higher than 50 °C, and more localized corrosion might be expected. What is more, the increased corrosion rate with temperature (Fig. 3.5) also contributes to localized corrosion. The pitting potential of most IMCs decreases with increasing temperature and the distribution of the characteristic potentials become more scattered at high temperature as shown in Fig. 3.4. Al₂Cu does not exhibit an obvious pitting potential at 10 °C (Fig. 3.4), suggesting that the corrosion potential is equivalent to the pitting potential and spontaneous passivity does not occur at 10 °C. The decreasing trend of pitting potential for all IMCs indicates that the passive film becomes less stable and can break down as the temperature increases.

The electrochemical reaction rate is closely related to the temperature, and can be described using Arrhenius equation [22]:

\[ i_{corr} = A e^{B/T} \]  
(Equation 3.1)

where A is a pre-exponential factor, B is the activation energy and T is temperature.

This expression can be rearranged by taking logarithm of both sides of Equation 3.1, and logarithm of corrosion rate should be linear with the reciprocal of temperature. The corrosion rate as a function of temperature is plotted in this way and shown in Fig. 3.5, including the best linear fit derived using Microsoft Excel™. For most IMCs, the \( R^2 \)
value is very close to 1, indicating a good fit between corrosion rate and temperature using the Arrhenius equation. This suggests that corrosion reactions of most IMCs are activation-controlled, at least during short term exposure. One exception is Al-4%Cu, of which corrosion rate remains constant up to 50 °C, but then dramatically increases at 70 °C.

It is generally believed that the initiation of pits is associated with local galvanic action between the secondary phase and the surrounding matrix. The corrosion of noble second phase particles are also important in localized corrosion. Based on this work, AlCuMnFe particles will act as anodes at 50 °C and above dissolving at relatively rapid rates, leading to more dissolution of the particles. The dissolution of AlCuMnFe particles is observed in exposure experiments (Fig. 3.11), with particles being partially or fully dissolved.

The electrochemistry of S phase is a very complex [17,18,23,24], which makes it difficult to characterize. Simple comparison of corrosion potential or pitting potential obtained from anodic polarization measurements does not reveal the evolution in its electrochemical behaviors at elevated temperature. In this work, the OCP transient was recorded at each temperature and used for analysis. The complex dealloying kinetics was reflected by the duration of a period of potential oscillation as a dealloyed surface layer formed and stabilized. As shown in Fig. 3.9, the OCP is very stable at 10 °C and does not show any fluctuation, indicating the dealloying corrosion is slow under these conditions. Slow dealloying kinetics are corroborated by the actual corrosion morphology as shown in Fig. 3.11 b, which reveals the formation of nano-scale porous structure on the surface.
From OCP data, S phase remains anodic over the course of the 2000s measurement, but corrosion morphology shows trenching around S phase, which is probably due to the galvanic corrosion or localized cathodic corrosion. In exposure tests, S phase will form a galvanic couple, acting as anode, with the surrounding matrix, which could accelerate the dealloying process compared to the OCP test on single S phase using microcell. In addition to the galvanic coupling effect, the longer exposure times (3600 s) might contribute to this severe corrosion. At 30 °C, the extent of potential fluctuation is more severe and dealloying kinetics are accelerated compared to that at 10 °C. At 50 °C and 70 °C, significant fluctuations of OCP are observed, revealing a fast dealloying process. The large porous structure shown in the corrosion section (Fig. 3.11e and h) is also believed to be a consequence this fast dealloying kinetics. At higher temperatures, the OCP rises to -240 mV SCE, which is essentially the open circuit potential of pure Cu, indicating that Mg or Al have dissolved almost completely from the phase. These elemental changes were also confirmed by the EDS analysis on the remnant of S phase particles.

3.4.2 Effect of temperature on the cathodic response

In aerated solutions, the cathodic reaction in the Al alloy corrosion cell is generally oxygen reduction, which is a diffusion-controlled process [25]. The limiting current density is closely related to the oxygen diffusion coefficient and solubility and can be expressed by the following approximation:

\[ i_{lim} = \frac{nFDC}{\delta} \]  

(Equation 3.2)
where $D$ is the oxygen diffusion coefficient, $C$ is the oxygen content in the solution, $\delta$ is the thickness of diffusion layer, $F$ is the Faraday constant, $n$ is the number of reacted per mole of $O_2$.

Oxygen solubility decreases with increasing temperature, while diffusion coefficient increases with increasing temperature[26,27]. The thickness of diffusion layer is mainly affected by temperature-dependent diffusion and viscosity, convection, and stirring [28]. Under hydrodynamic conditions such as rotating electrode, $\delta$ only slightly increases with temperature; about 10% as temperature increases from 20 to 80 °C[28]. However, $\delta$ decreases with increasing temperature in the stationary condition. These inverse trends of ($\delta$, $D$, $C$) with temperature lead to a peak current at an intermediate temperature. Diffusivity and solubility of oxygen as function of temperature have been established[26,27], but the means to calculate thickness of diffusion layer is rarely reported. An experimental relation between the thickness of diffusion layer and temperature on Fe and Cu in NaCl solution ([28]) is used to calculate the limiting current density as a function of temperature based on Equation 3.2, coupled with the $D$ and $C$ from reference [26,27]. The result is shown in Fig. 3.12. The maximum limiting current density is observed at around 55 °C. In these experiments, most IMCs show the highest cathodic current at 50 °C (Fig. 3.7) except $Al_7Cu_2Fe$, which is at 30 °C. The most sluggish kinetics occurs at 10 °C for $Al_7Cu_2Fe$, Cu and Al-4%Cu, while at 70 °C for $Al_{20}Cu_2Mn_3$, $Al_2Cu$, and the matrix. $Al_2Cu$ and Cu show similar cathodic kinetics at low temperature (10 and 30 °C), but $Al_2Cu$ becomes smaller than Cu at 50 and 70 °C. The large difference at 70 °C might be caused by the large amount of Al in $Al_2Cu$, which
forms barrier layer (Al$_2$O$_3$·3H$_2$O). The cathodic kinetics on Al$_2$Cu and Cu are much faster than other IMCs at all temperatures and fast kinetics are attributed to relatively high amount of Cu in the phase.

### 3.4.3 Local corrosion morphology and its relationship to microcell data

The corrosion morphology of AA2024-T3 after 1 hour exposure in 0.1 M NaCl solution at each temperature (Fig. 3.11) reveals that the dealloying corrosion kinetics of S phase increases with increasing temperature as indicated by the size of the porous structure and thickness of dealloyed S phase, which is also reflected by the increased extent of OCP fluctuation at high temperature (Fig. 3.9). Fig. 3.13 shows the corrosion morphology of S phase particles after 1 hour exposure at 70 °C. Obvious trenching around the particles is observed, and the brightness in the SEM image indicates it is covered by the non-conductive corrosion products. Dehydration cracks in the remnants are well demonstrated in the BSE image, and the brightness indicates that Cu gets richer after exposure. The composition changes were examined by EDS, and the results are show in Table 3.1. The remnant of S phase is depleted of Mg, but rich in Cu. The low oxygen concentration indicated that Cu exists in the form of Cu oxides and pure metal, which is also reflected from the similar OCP of S phase to copper at 70 °C in Fig. 3.9. The significant composition change indicates that Mg almost completely dissolves and dealloying penetrates the whole particle as shown in the cross-section of S phase (Fig. 3.11). This severe dealloying corrosion might also lead S phase particles to detach from the matrix to for dissolution pits as observed in Fig. 3.11.
For AlCuMnFe particles, no trenching is observed at 10 °C, and this is attributed to the slow cathodic kinetics (Fig. 3.7). As temperature increases, the width of trenching becomes larger. But some AlCuMnFe particles dissolve completely at 70 °C, while others leave a fragmentary remnant as shown in Fig. 3.11. Furthermore, the polarization measurement indicates that AlCuMnFe particles will reverse their polarity relative to the matrix to become anodes at 70 °C, and shows higher corrosion rate. These changes are attributed to the fast dissolution of Al from the particles. The morphology and element content of AlCuMnFe particles before and after 1 hour exposure in 0.1 M NaCl at 70 °C are examined using SEM coupled with EDS. The brightness in SEM images (Fig. 3.14) might be caused by the charging of nonconductive corrosion products on the particles. But (back scattered electrons) BSE images clearly demonstrate that the remnants of AlCuMnFe particles are fragmentary, and their composition changes are summarized in Table 3.2. The Al weight percent drops by 28 % to 85%, while Cu percent increases by a factor of 1.3 to 4.3. Mn and Fe elements also decrease after exposure, but for some particles, an increased Fe concentration is observed. This composition changes indicate that AlCuMnFe particles also show similar dealloying corrosion as S phase at 70 °C, but through selective dissolution of Al. This selective dissolution of Al might also explain why Al₂Cu₂Fe and Al₂₀Cu₂Mn₃ switch from cathode to anode as temperature exceeds 50 °C. Taking into account the increasing corrosion rate with temperature (Fig. 3.5), the activation-controlled corrosion process might be the main contributor to the formation of these pits or the porous structure (Fig. 3.11 g and h). However, as the Al dissolves into the solution as ions, they hydrolyze and form aluminum oxides or hydroxides on the
surface as revealed in the tilted samples Fig. 3.11 f. The structure of these corrosion products is not identified in this work, but it has been reported that bayerite (Al₂O₃·3H₂O) can form on the surface at temperature lower than 70 °C in aqueous solution [29], and will transform to boehmite (Al₂O₃·H₂O) as temperature rise up to 70 °C [30]. These nonconductive corrosion products can act as a barrier hindering the diffusion of reaction reagents and products, and as an insulator limiting electron transformation. This dissolution and hydroxylation process is also reflected by the OCP changes of bulk alloy in 0.1 M NaCl at each temperature (Fig. 3.10). The sharp drop of OCP of AA2024-T3 at 70 °C is ascribed to the fast dissolution of Mg and Al, which lasts for about 3000s and the following OCP rise is attributed to the formation of corrosion products.

The corrosion processes of AA2024-T3 in aerated 0.1 M NaCl solution at high temperature is complex, and there are three main factors affecting the corrosion kinetics: activation-controlled reaction, oxygen diffusion-limited reduction reaction, and oxide or hydroxides corrosion products. In the one-hour exposure experiments, ORR kinetics show strong effect on the localized corrosion at low temperature. At 10 °C, the absence of trenching around the AlCuMnFe particles indicates that the diffusion of oxygen is the limiting step for the cathodic reduction, although oxygen solubility is very high. As temperature increases to 30 °C, the diffusion coefficient increases and wider trenching corrosion is observed on the cathodic particles. At 50 °C, wider trenching forms but the whole surface of the samples is covered by the hydroxides or oxides, which could not be explained just based on the galvanic corrosion. As shown in the microcell data, the corrosion rates of both matrix and secondary phases increase exponentially with
temperature. These metal ions could combine with the hydroxyl ions produced by oxygen reduction, which shows highest kinetics at around 55 °C. However, as hydroxide deposits form on the surface as observed at 50 and 70 °C, the corrosion rate may be reduced.

3.5 Conclusions

The corrosion rate of most IMCs examined increases with increasing temperature according to an Arrhenius relationship.

Temperature has complex effect on the corrosion potential of IMCs. The corrosion potential of $\text{Al}_2\text{Cu}$ slightly decreases with temperature, but it remains as a cathode relative to the matrix with an ability to support oxygen reduction reaction efficiently. The corrosion potential of $\text{Al}_7\text{Cu}_2\text{Fe}$ and $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ increase from 10 to 30 °C, but decreases with temperature up to 70 °C, which causes a polarity reversal relative the matrix.

Temperature generally decreases the pitting potential of most IMCs and leads to a more scattered pitting potential distribution, indicating the IMCs are more susceptible to pitting at high temperature.

Most IMCs show highest limiting current density for ORR at 50 °C due to the effect of temperature on oxygen solubility and diffusivity, and thickness of diffusion layer, which is consistent with the calculated theoretical limiting current density.

The OCP changes of S phase with temperature are used to assess the effect of temperature on dealloying process and role switch of S phase. Temperature accelerates the dealloying process of S phase, and Mg is depleted in the S phase remnant.
At high temperature (70 °C), AlCuMnFe particles leave fragmentary remnants or completely dissolve. The low Al concentration in the remnants indicates that AlCuMnFe particles corrode by selective dissolution of Al.

At lower temperature (10 and 30 °C), the localized galvanic corrosion kinetics is strongly affected by the ORR, especially the oxygen diffusion, but activation-controlled reactions become dominant factor at high temperature (>70 °C). As the corrosion occurs, corrosion products form on the surface and will become a barrier for further corrosion.
3.6 Figures and Tables

Fig. 3.1 Sectional view of the copper stage and the water flow path
Fig. 3.2 Anodic polarization curves of Al4%Cu (a), Al2Cu (b), Al7Cu2Fe (c) and Al20Cu2Mn3 (d) in 0.1 M NaCl at 10, 30, 50 and 70 °C (continued)
Fig. 3.2 (continued)

![Graph showing E (V SCE) vs. Current Density (A/cm²) for different temperatures. The graphs are labeled as follows: c, Al₇Cu₂Fe and d, Al₁₂Cu₂Mn₃. The graphs display multiple curves for each temperature: 10 °C, 30 °C, 50 °C, and 70 °C.]
Fig. 3.3 Corrosion potential of IMCs in 0.1 M NaCl at 10, 30, 50 and 70 °C (The corrosion potential of S phase was obtained from the open circuit potential curves at 80 seconds)
Fig. 3.4 Pitting potential of IMCs in 0.1 M NaCl at 10, 30, 50 and 70 °C
Fig. 3.5 Corrosion rate (\( \log i_{\text{corr}} \)) of IMCs in 0.1 M NaCl as function of 1/T.
Fig. 3.6 Cathodic polarization curves of Al4%Cu (a), Al2Cu (b), Al7Cu2Fe (c) and Al20Cu2Mn3 (d) in 0.1 M NaCl at 10, 30, 50 and 70 °C (continued)
Fig. 3.6 continued

E (V \text{SCE})

Current Density (A/cm\(^2\))

10 °C
30 °C
50 °C
70 °C

c, Al\(_7\)Cu\(_2\)Fe

d, Al\(_{20}\)Cu\(_2\)Mn\(_3\)
Fig. 3.7 Cathodic current density of each sample at -1 V\textsubscript{SCE} as a function of temperature in aerated 0.1 M NaCl
Fig. 3.8 The anodic polarization curves of Al$_2$CuMg after different delay time in 0.1 M NaCl at 10 °C
Fig. 3.9 OCP changes of Al₂CuMg as a function of time in 0.1 M NaCl at different temperatures
Fig. 3.10 OCP transient of AA2024-T3 bulk sheet at different temperature in 0.1 M NaCl
Fig. 3.11 The localized corrosion morphology of AA2024-T3 bulk sheet after 1 hour exposure in the 0.1M NaCl at each temperature (continued)
Fig. 3.11 continued
Fig. 3.12 Theoretical limiting current density of diffusion-limited oxygen reduction reactions in DI water based on the data (D from [26], C from [27], δ from [28])
Fig. 3.13 Corrosion morphology of a region rich in S phase particles before (a) and after (b) 1 hour exposure in 0.1 M NaCl at 70 °C, and its BSE image (c)
Fig. 3.14 Corrosion morphology of a region rich in AlCuMnFe particles before and after 1 hour exposure in 0.1 M NaCl at 70 °C
Table 3.1 Composition changes of S phase particles in Fig. 3.13a after 1 hour exposure in 0.1 M NaCl at 70 °C

<table>
<thead>
<tr>
<th>Position</th>
<th>wt.%</th>
<th>Al</th>
<th>Cu</th>
<th>Mg</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>47.77</td>
<td>36.96</td>
<td>15.26</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>After</td>
<td>31.74</td>
<td>62.13</td>
<td>0.58</td>
<td>5.57</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>48.08</td>
<td>36.43</td>
<td>15.49</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>After</td>
<td>39.71</td>
<td>49.03</td>
<td>0.86</td>
<td>10.41</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before</td>
<td>52.14</td>
<td>34.49</td>
<td>13.38</td>
<td>/</td>
<td></td>
</tr>
<tr>
<td>After</td>
<td>40.11</td>
<td>43.24</td>
<td>1.41</td>
<td>15.24</td>
<td></td>
</tr>
</tbody>
</table>
Table 3.2 Composition changes of AlCuMnFe particles in Fig. 3.14 a after 1 hour exposure in 0.1 M NaCl at 70 °C

<table>
<thead>
<tr>
<th>Position</th>
<th>wt.%</th>
<th>Al</th>
<th>Cu</th>
<th>Mn</th>
<th>Fe</th>
<th>Si</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>56.41</td>
<td>28.38</td>
<td>7.26</td>
<td>7.96</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>18.28</td>
<td>38.66</td>
<td>2.77</td>
<td>10.99</td>
<td>/</td>
<td>28.03</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>61.34</td>
<td>8.8</td>
<td>12.11</td>
<td>13.25</td>
<td>4.5</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>44.47</td>
<td>38.48</td>
<td>/</td>
<td>3.46</td>
<td>/</td>
<td>13.59</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>58.33</td>
<td>25.09</td>
<td>7.65</td>
<td>8.92</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>24.17</td>
<td>46.35</td>
<td>/</td>
<td>7.25</td>
<td>/</td>
<td>22.23</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>59.82</td>
<td>21.15</td>
<td>7.37</td>
<td>9.53</td>
<td>2.13</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>9.09</td>
<td>48.47</td>
<td>3.24</td>
<td>19.69</td>
<td>/</td>
<td>19.51</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Before</td>
<td>59.31</td>
<td>16.85</td>
<td>9.62</td>
<td>11.11</td>
<td>3.13</td>
<td>/</td>
</tr>
<tr>
<td></td>
<td>After</td>
<td>32.86</td>
<td>51.93</td>
<td>/</td>
<td>4.09</td>
<td>/</td>
<td>11.13</td>
</tr>
</tbody>
</table>
References


97


Chapter 4 Microelectrochemical Characterization of the Effect of Rare Earth Inhibitors on the Localized Corrosion of AA2024-T3

Abstract

The anodic and cathodic polarization characteristics of the phases commonly found in AA2024-T3 were studied in an aerated 0.1 M NaCl solution with 4 mM additions of the rare earth metals (REM) inhibitors (Ce\(^{3+}\), La\(^{3+}\) and Pr\(^{3+}\)), using an electrochemical microcell method. The phases examined were Al\(_2\)Cu, Al\(_2\)CuMg (S phase), Al\(_7\)Cu\(_2\)Fe and Al\(_{20}\)Cu\(_2\)Mn\(_3\). Comparative measurements were made in a 0.1 M NaCl solution containing 1 mM K\(_2\)CrO\(_4\). It was found that the REM inhibitor additions have little effect on the corrosion potential, pitting potential and corrosion rate, which was likely due to the short duration of these measurements. This is in contrast to effects observed with chromate inhibitor additions where the pitting potential increased by several hundred millivolts depending on the phase. Measured corrosion rates were dramatically decreased in the chromate-containing solution. All of the REM inhibitor additions decreased the oxygen reduction reaction kinetics on each phase examined by a factor ranging from 1.2 to 58, but none reduced the rate as much as chromate did. The results in this study were consistent with the idea that inhibition by REM inhibitors results from hydroxide precipitation at intermetallic sites due to a local pH increase associated with oxygen reduction occurring at those sites. Because hydroxide precipitation is a comparatively
slow process, REM inhibitors cannot inhibit the initial dealloying of the S phase, which is also proofed by presence of dealloyed S phase under hydroxide precipitation on S phase. However, once the hydroxide precipitate forms on the surface, the corrosion of S phase is strongly inhibited. Because inhibition action depends on the formation of a hydroxide deposit, REM inhibitors are “slow” inhibitors, and this characteristic must be considered in their application.

4.1 Introduction

Alloying elements such as Cu and Mg are intentionally added to AA2024-T3 to improve the mechanical properties such as strength and toughness [1]. However, transition metal alloying element solubility in Al is low and those elements precipitate to form many second phase intermetallic compound (IMC) particles during solidification processing and heat treatment. These IMCs usually possess different electrochemical properties from the surrounding matrix, and can cause localized galvanic corrosion [2–4]. The passive film on an IMC particle surface can protect the particle from corrosion, but it can be easily ruptured or broken down under aggressive environmental condition or mechanical stress to initiate pits [5–7]. Inhibitors have been used to stifle the localized corrosion and improve corrosion resistance to extend the service time of the aluminum alloys. Chromate is a noteworthy inhibitor with an ability to self-heal if chemical or mechanical damage occurs [8–14]. Unfortunately, chromate is toxic and carcinogenic in nature and there have been intensive efforts to develop environmental friendly alternative inhibitors. Rare earth metals (REM) such as Ce, Pr and La, are potential replacements and have attracted much attention [15–20].
REM inhibitors were first used to inhibit the corrosion of AA7075 alloy in a NaCl solution, and their inhibition was evaluated by the mass loss and linear polarization measurements[15]. The corrosion rate was observed to decrease dramatically with addition of 100 ppm of CeCl₃, with the level of inhibition remaining constant up to 1000 ppm. Similar inhibition efficiencies and trends were observed for other lanthanide salts including YCl₃, LaCl₃, PrCl₃ and NdCl₃[21]. Results showed that the cathodic current density was reduced by an order of magnitude after a 10-minute immersion in NaCl plus 0.05 wt.% CeCl₃ compared to that in NaCl without inhibitors. The inhibition efficiency was observed to increase with longer immersion time [22]. The inhibition of rare earth metals results from precipitation of a REM-bearing hydroxide on local cathodic sites thus blocking the oxygen reduction reaction (ORR) [17,23,24]. Yasakau et al. found that cerium hydroxide precipitation formed on second phase particles after a 1 hour free corrosion exposure in solution containing a Ce salt. The growth rate of hydroxide was estimated to be about 0.4 nm/min in the low chloride solution, but increased to 20 nm/min in a concentrated chloride solution. The dependence on the chloride concentration is caused by the high corrosion activity in aggressive Cl⁻ environments, which promoted the local pH increase near the intermetallic particles. REM hydroxide precipitation hindered oxygen reduction reaction and anodic dissolution of the particle.

Aside from soluble salts [18,22,25], other forms of rare earth metal inhibitors have been investigated. These include hydrotalcite-based conversion coatings [26] and REM conversion coatings [27–30]. Most research conducted on bulk aluminum alloys has been done by immersing samples in a solution with rare earth metal salt, and then observing
the corrosion morphology and precipitation on the surface. However, the electrochemical interactions between individual IMCs and rare earth metals ions and the extent to which they can inhibit the oxygen reduction has not been characterized comprehensively. In this paper, data is reported regarding the electrochemical characteristics of IMCs commonly found in AA2024-T3 during exposure to a 0.1 NaCl with presence of rare earth metals (Ce$^{3+}$, Pr$^{3+}$, La$^{3+}$) using the electrochemical microcell method. REM inhibition efficiencies are compared with that of a chromate inhibitor.

4.2 Experimental

4.2.1 Sample and solution preparation

The IMCs studied in this work were Al$_2$Cu$_2$Fe, Al$_{20}$Cu$_2$Mn$_3$, Al$_2$CuMg (S phase), and Al$_2$Cu. These samples were specially synthesized and heat treated as discussed in [4]. A binary alloy, Al 4wt.%Cu, was also examined. This alloy was used as a proxy for the matrix phase in an Al-Cu-X alloy. All samples were ground to 1200 grit using SiC papers and ethyl alcohol as lubricant. They were then polished using 1 µm diamond paste lubricated with light-weight oil. Finally they were ultrasonically cleaned in ethanol to remove any organic residue. Samples were air-dried and used for experiments immediately. A 0.1 M NaCl solution was prepared by dissolving reagent grade NaCl in deionized water with 18.2 MΩ*cm resistivity. Rare earth metal solutions of Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$ were prepared at a concentration of 4 mM by adding CeCl$_3$, LaCl$_3$ and PrCl$_3$ (99.9% pure) in 0.1 M NaCl solution with a pH of around 5.2. A chromate solution was also prepared by adding 1 mM K$_2$CrO$_4$ into 0.1 M NaCl. “REM” solutions in this paper refer
to solutions containing 0.1 M NaCl plus 4 mM rare earth metal salt, while the “chromate” solution refers 0.1 M NaCl with 1 mM K$_2$CrO$_4$.

### 4.2.2 Electrochemical measurements

Anodic and cathodic polarization curves were collected on each IMC in all solutions using the electrochemical microcell method. The diameter of capillary tips was about 100 µm. All experiments with IMCs samples were conducted in a standard three-electrode setup with a saturated calomel electrode (SCE) as reference electrode and platinum wire as the counter electrode. The data were recorded using a Gamry™ Reference 600 potentiostat. The anodic polarization measurements were initiated at -0.02 V vs. OCP and were collected at a rate of 2 mV/s. The cathodic polarization curves were initiated at 0.01 V vs. OCP and were collected at the same scan rate. Each measurement was repeated at least three times. For experiments with the S phase, the cathodic polarization was initiated after a 1000 second exposure under free corrosion conditions so as to measure cathodic kinetics on a surface that was partially or fully dealloyed.

### 4.2.3 Corrosion morphology and cerium precipitation on the S phase and AlCuMnFe particles

The corrosion morphology of AA2024-T3 after various exposure times in each solution was examined using scanning electron microscopy (FEI Quanta and XL-30 Field Emission SEM) coupled with energy dispersive X-ray spectroscopy (EDS). Cross sections of dealloyed S phase particles with Ce precipitation were prepared using focused ion beam (FEI Helios Nanolab 600 FIB).
EDS mapping was performed on two kinds of particles, AlCuMnFe and S phase, after a 52.5 hour exposure in CeCl₃ solution at room temperature. The working distance in ESEM was 10 mm, and the voltage was 20 kV with a spot size of 6. In this measurement, only the Ce EDS signal was analyzed, and an element overlay file in a .bmp format was generated showing the cerium distribution across the surface. A 3D matrix was extracted from the element overlay file using Matlab on files that contained location and intensity data for each pixel. The signal intensity on AlCuMnFe and Al₂CuMg particles was then integrated. The average cerium intensity on each particle was then obtained by dividing the integrated intensity by the area of the particle [31]. The average cerium density on each particle was then compared to the cathodic kinetics on the corresponding particles in NaCl solution.

4.3 Results

4.3.1 Electrochemical response of IMC in 0.1 M NaCl solution with and without inhibitors

Fig. 4.1 shows anodic polarization curves for Al 4%Cu solid solution, Al₂Cu, Al₇Cu₂Fe, Al₂₀Cu₂Mn₃ and S phase in each test solution. These representative polarization curves were selected from replicate measurements based on their proximity to the average value of corrosion potential (Ecorr) and pitting potential (Epit). Fig. 4.2 shows cathodic polarization curves of IMCs, and curves for S phase were collected after a 1000 second free corrosion exposure that allowed dealloying occur. The data distribution of Ecorr and Epit and their average values (horizontal line) is summarized in Fig. 4.3.
4.3.1.1 Al-4%Cu

With addition of 4 mM REM salts in 0.1M NaCl, both $E_{\text{corr}}$ and $E_{\text{pit}}$ were increased by about 0.1 V and 0.06 V respectively, and the corrosion rate was slightly reduced (Fig. 4.1). Among the three REM inhibitors, Pr was the most effective in raising the pitting potential, but La was the most superior in reducing corrosion rate. A slightly decreased passive current density was also observed in the presence of the REM inhibitors. Both $E_{\text{corr}}$ and $E_{\text{pit}}$ are reproducible and fall in a small band ($\sim 10$ mV) as shown in Fig. 4.3. Overall the inhibition observed in these experiments was modest.

On the contrary, chromate strongly inhibits the corrosion: both $E_{\text{corr}}$ and $E_{\text{pit}}$ are increased by about 0.2 and 0.3 V respectively, while $i_{\text{corr}}$ is reduced by a factor of around 3. As shown in Fig. 4.2, cathodic reaction kinetics is strongly inhibited by the addition of REMs and chromate, but to different extents. Both Ce and Pr reduce ORR by a factor of 6.5, while La by a factor of 3. Chromate is most effective, reduces the ORR rate by an order of magnitude.

4.3.1.2 Al2Cu

There was no obvious anodic inhibition of Al2Cu by addition of REM inhibitors as shown in Fig. 4.1 b. In both NaCl and REM inhibitor solutions, $E_{\text{corr}}$ was about 0.55 V$_{\text{SCE}}$, while $E_{\text{pit}}$ was about 0.51 V$_{\text{SCE}}$. A slightly higher corrosion rate was observed in the REM solution compared to that in NaCl-only solution. The response in chromate solution is distinct from those in NaCl and REM solution. Chromate increased $E_{\text{pit}}$ by 0.18V and reduced the corrosion rate by a factor of 40 compared to NaCl. The corrosion potential and pitting potential in all REM solutions was reproducible in a 45 mV widow. Chromate
was different. In this case, $E_{pit}$ varied over a range of 110 mV in replicate measurements. Strong inhibition of the cathodic kinetics was observed with addition of REM inhibitors (Fig. 4.2 b). Ce and La show similar inhibition efficiency, reducing the cathodic current by a factor of about 3. Pr is the most effective among REMs, reducing ORR by a factor of 7. Cathodic kinetics in the chromate solution were strongly inhibited.

### 4.3.1.3 $\text{Al}_7\text{Cu}_2\text{Fe}$

$E_{corr}$ in Ce and La solutions did not change much compared to that in 0.1 M NaCl, but it was decreased by 0.1 V in the Pr solution (Fig. 4.1 c). The Pr addition did not have much of an effect on $E_{pit}$ while Ce and La increased $E_{pit}$ by about 60mV. All REMs reduced corrosion rates slightly with Pr being the most effective with reduction in rate by a factor of about 3. There was no obvious effect on the passive current density by addition of REMs. Fig. 4.3 reveals a large distribution in $E_{corr}$ in REM inhibitor solutions (hundreds of mV), while a smaller distributions were observed for $E_{pit}$ (60 mV). Compared to a 0.1 M NaCl, chromate increased $E_{pit}$ by 0.27 V, reduced $E_{corr}$ by 0.15 V and reduced corrosion rate by a factor of 4. All REMs showed strong inhibition of the ORR in the order: Pr > La > Ce (Fig. 4.2 c), but all were less efficient than chromate, which reduced ORR kinetics by a factor of 500.

### 4.3.1.4 $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$

Fig. 4.1d shows the anodic polarization curves of $\text{Al}_{20}\text{Cu}_2\text{Mn}_3$ in each test solution. REMs increased $E_{pit}$ by 45~95mV, while $E_{corr}$ increased by 144~77mV in Pr and La solutions, but decreased in Ce solution. Decreased corrosion rates and passive current densities in REM inhibitor solutions are also observed. Pr was the most effective and Ce
was the least. $E_{\text{corr}}$ measurements in REM solutions was reproducible, while large distributions in $E_{\text{pit}}$ (33-140mV) were observed. Again, chromate showed the strongest inhibition. The corrosion rate was decreased by an order of magnitude, $E_{\text{pit}}$ was increased by 130 mV and $E_{\text{corr}}$ was decreased by 200 mV. Fig. 4.2 d shows the cathodic polarization response of $\text{Al}_2\text{Cu}_2\text{Mn}_3$. The ORR is reduced by REMs by a factor of 2.5 to 58 with Pr being the most effective. The inhibition efficiencies of REMs become more obvious as the potential moves lower than -0.8 $V_{\text{SCE}}$, and Pr showed inhibition efficiency comparable to chromate. Chromate was the most effective among all inhibitors, and reduced the ORR kinetics by more than an order of magnitude.

4.3.1.5 Al$_2$CuMg(S phase)

The corrosion behavior of S phase is complex. It initially corrodes by dealloying and has an active corrosion potential. Dealloying results in the formation of porous Cu-rich layer that ennobles the phase and support oxygen reduction at increased rates [32–35]. Cu-rich surface layer formation induces significant dispersion in polarization measurements [4,36–38], which is reflected in Fig. 4.3. To suppress initial dealloying of the S phase prompt inhibiting action is needed. No obvious effects were observed on $E_{\text{corr}}$, $E_{\text{pit}}$ and $i_{\text{corr}}$ by addition of REM inhibitors to solution (Fig. 4.1 e), suggesting that REM inhibitors do not act fast enough to inhibit dealloying corrosion and the associated formation of a Cu-rich layer. To determine inhibition efficiency of REMs on ORR that is supported on the Cu-rich layer formed on S phase due to dealloying, cathodic polarization curves in REM inhibitor solutions (Fig. 4.2e) were collected after 1000 seconds of pre-exposure under free corrosion conditions (Fig. 4.4). Cathodic polarization
curves were also collected in chromate solution after 1000s OCP measurement in Fig. 4.2 e. The OCP of S phase in REM inhibitor solutions was about -915 mV$_{SCE}$, which is slightly more positive than that in NaCl. There is some fluctuation in OCP, while in the chromate solution, the OCP was very stable at about -875 mV$_{SCE}$. As shown in Fig. 4.2 e, the cathodic current density of dealloyed S phase was two or three orders of magnitude larger than other IMCs in NaCl, and only slight inhibition of ORR kinetics in REM inhibitor solutions was observed. In a chromate solution, the pitting potential was increased by 200 mV (Fig. 4.3) and the corrosion rate was reduced by two orders of magnitude. The chromate addition inhibited the ORR by more than 2 orders of magnitude compared to that in 0.1 M NaCl.

### 4.3.2 Localized corrosion morphology of AA2024-T3 after 50 hours immersion in NaCl and inhibitor solutions

To relate the polarization responses of IMC to corrosion that occurs on AA2024-T3, the corrosion morphology of AA2024-T3 was examined by SEM after free corrosion exposures (Fig. 4.5 a). The microstructure of polished AA2024-T3 is shown in Fig. 4.5 a. Round particles are S phase, and the irregularly shaped ones are AlCuMnFe (Si). The insert in Fig. 4.5a is an enlarged S phase particle with a radius of about 2.5µm. The corrosion morphology after 6 hours immersion in NaCl at room temperature is shown in Fig. 4.5 b. Severe localized corrosion associated with IMC particles is observed. Trenching occurs around AlCuMnFe (Si) particles and dealloying occurs with Al$_2$CuMg, which is shown in detail in the BSE images (Fig. 4.5 b). Most of the smallest Al$_2$CuMg particles were completely dissolved. Obvious trenching corrosion occurred around the
corroded S phase particles. With the addition of REMs, localized corrosion was strongly inhibited as shown in Fig. 4.5 c, d and e, even when the exposure time was extended to 50 hours. Although some corrosion was still observed on the S phase particles, trenching around AlCuMnFe particles was not observed. EDS spectra were collected on two different particles (point 1 and 2) in Fig. 4.5 c, and the results are shown in Fig. 4.6 a and b. Ce was detected on the S phase particle but not on the AlCuMnFe particle. EDS line scans across the S phase particle (Fig. 4.6 c) indicated that Ce concentrated at the particle center, and decreased moving away from the particles. The high concentration of Ce on the particle demonstrates the presence of cerium precipitation on the surface. Dehydration cracking of the Ce deposit allowed observation of the dealloyed S phase beneath the precipitation as shown in Fig. 4.6 d. The dealloyed S phase was comprised of fine nano-scale granules, which were Cu-rich and mixed with a gel-like substance, which is most likely to be Ce hydroxide precipitation. No localized attack was observed on samples after exposure chromate solution as shown in Fig. 4.5 f.

4.3.3 Cross-section observation of precipitation and S phase after different exposure time in NaCl plus 4mM CeCl₃

The cerium hydroxide precipitation on S phase is due to its ability to support the ORR efficiently. Localization of the ORR to the particle resulted in a localized pH increase that triggered localized hydroxide precipitation. However, the observation of the S phase under the hydroxide layer revealed that dealloying corrosion had occurred (Fig. 4.6 d). Dealloying is clearly demonstrated in the cross section of the S phase particle in Fig. 4.7. The typical structure found at an S phase particle site after exposure to a Ce inhibited
solution from top to bottom is: hydroxide cap, dealloyed S phase, un-corroded S phase and matrix. The thickness of the dealloyed layer on an S phase particle increases from 100 nm to 130 nm as the immersion time increases from 1 to 52.5 hours. This suggests the dealloying occurs rapidly during initial exposure, but is soon strongly inhibited. Ce hydroxide layer thickness was observed to be about 230 nm after 1 hour immersion and 240 nm after 52.5 hours. This suggests that hydroxide layer formation occurs early during exposure and then stops. In some instances, the hydroxide layer detached from the dealloyed S phase, as shown in Fig. 4.7 a and b. Examination showed that the layer is not compact, and many black voids are dispersed throughout it (Fig. 4.7 c). This porosity might allow the dissolved oxygen to reach the interface to maintain the corrosion process at some slow rate.

4.4 Discussion

4.4.1 Effect of REMs on $E_{corr}$, $E_{pit}$ and $i_{corr}$

Fig. 4.8 shows the plot of $E_{pit}$ vs. $E_{corr}$, in which each circle represents one IMC. The figure includes both $E_{pit}$ and $E_{corr}$ data in 0.1 M NaCl and three REM solutions (4 mM Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$), while the data in chromate solution is represented by a purple dot and connected to each circle by a dash line with the same color. All the data are in the portion of the plot where $E_{pit} > E_{corr}$, indicating that samples show passive behavior to some extent in all solutions. The closer a data point is to the dashed line, the smaller the passive range for the associated material. For example, Al$_2$Cu has a passive range of less than 60 mV in 0.1 NaCl, and is located close to the line. Compared to the data in 0.1 M NaCl, $E_{pit}$ and $E_{corr}$ of all IMCs in REM inhibited solutions do not change much, 2 to 119mV and 5
to 160mV, respectively. The data in both NaCl and REM inhibitor solutions can be restricted to very small regions as indicated by the size of circumscribed region. Although a wider $E_{\text{corr}}$ distribution is observed for Al$_{20}$Cu$_2$Mn$_3$ and Al4%Cu, $E_{\text{pit}}$ does not change much. This indicates that REM inhibitors do not significantly affect $E_{\text{pit}}$ and $E_{\text{corr}}$ in short-term experiments like these. On the other hand, the data in chromate solution is far from the REM data and $E_{\text{pit}}$ values are dramatically increased, indicating that chromate increases the passive range and is a strong anodic inhibitor for IMCs.

Fig. 4.9 shows the corrosion rates of IMCs obtained by Tafel extrapolation of the linear region of cathodic polarization curve. The data for REM inhibitor solutions are circumscribed with a green line. The corrosion rate in 0.1M NaCl is plotted as a black horizontal line, which is used as a reference corrosion rate, while REM and chromate solutions are represented by discreet closed data points. As indicated by the displacement of the data points below the reference line, REM inhibitors slightly decrease the corrosion rate of all IMCs. One exception is Al$_2$Cu, which shows slightly higher corrosion rate in REM solutions than in 0.1 M NaCl. The reason why $i_{\text{corr}}$ for Al$_2$Cu increases is not clear, but its proximity to the reference line suggests it is within the uncertainty of the measurement. All corrosion rates of IMCs in REM inhibitor solutions are close to the corrosion rate in NaCl, indicating that REMs do not have a significant effect on corrosion rate in these type of corrosion measurements. As indicated by the great distance between the data and the reference line, chromate strongly reduces the corrosion rate, indicating strong inhibition.
4.4.2 Effect of REM inhibition on cathodic kinetics of IMCs

Fig. 4.10 shows the limiting current densities determined from cathodic polarization curves of Al$_7$Cu$_2$Fe, Al$_{20}$Cu$_2$Mn$_3$, Al$_2$CuMg (S phase), Al$_2$Cu and Al 4wt.%Cu to assess the inhibition efficiency of REMs on the ORR. The symbols have the same meaning as those in Fig. 4.9, with horizontal lines presenting the data in NaCl. It is obvious that REMs strongly inhibit ORR on all IMCs by a factor of 3-60 except for the dealloyed S phase. However, among the three REMs, different inhibition efficiencies are observed: Pr is most effective, followed by La and Ce. One exception is Al$_4$%Cu, for which Ce is better than La. The inhibition efficiency of Pr on Al$_{20}$Cu$_2$Mn$_3$ and Al 4wt.%Cu is even comparable to chromate. For the solution with same concentration of REM ions, the minimum pH, at which the hydroxides start to precipitate, depends on the solubility products of the hydroxides. For example, Ce(OH)$_3$ starts to precipitate at pH 8.2, while Pr(OH)$_3$ at pH 6.98 [39]. It is also reported that there is a pH range where REM ions transform to hydroxide [22], during which the fraction of hydroxide increases with pH. This means that more Pr precipitation is expected than Ce at neutral and slightly alkaline environments under steady-state conditions. The amount of precipitation is expected to correlate with the extent of inhibition, but the morphology of precipitation is also important. Cerium hydroxide deposits contain many small pores, consistent with reports in literature[40]. This might also explain why La is more efficient than Ce as an inhibitor.

For the dealloyed S phase, only slight inhibition is observed. Since S phase is exposed to solution for about 1000 s, dealloying corrosion and the subsequent formation of porous
nano-scale Cu-rich layer are expected. The incomplete coverage of the dealloyed S phase might lead to poor inhibition.

4.4.3 A model to simulate the pH distribution around dealloyed S phase based on the cathodic current density.

S phase is one of the main IMCs in AA2024-T3, making up of about 60% of the particles larger than 0.5-0.7 \textmu m[32]. Due to its electrochemical activity, it initially corrodes by dealloying, which may result in complete particle dealloying within 5 minutes at room temperature [2]. The subsequent formation of the Cu-rich remnant catalyzes the ORR. The high rate of ORR increases the pH in the solution near the S phase particle, which in turn triggers polymerization, gelation and precipitation of REM hydroxides, which slow the local corrosion process. Therefore, the pH distribution around the dealloyed S phase is important to understand the precipitation of REM hydroxides. Based on the cathodic current density in 0.1 M NaCl solution (Fig. 4.2 e), a simple model was constructed to simulate the pH distribution in the steady state (Fig. 4.11).

A few assumptions are made in this model. The hydroxyl ions produced by oxygen reduction on the surface (4 electrons reduction), which is described equation 4.1, diffuse uniformly in a hemispherical region. A cathodic current density obtained from the cathodic polarization curves in Fig. 4.2e (2.27mA/cm\textsuperscript{2}) was used to calculate OH\textsuperscript{-} generation rate based on Faraday’s law following Equation 4. 2:

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \leftrightarrow 4\text{OH}^- \quad \text{(Equation 4.1)}
\]

\[
m_{\text{OH}^-} = \frac{i_{\text{cath}}}{4F} \times \pi r^2 \quad \text{(Equation 4.2)}
\]
where $i_{\text{cath}}$ is cathodic current density, 2.27mA/cm$^2$, $r$ is equivalent radius of the round S phase, $F$ is Faraday’s constant.

Diffusion mass at each hemispherical surface was obtained based on Fick’s first law:

$$m_{Dx} = 2\pi R_x^2 (-D \frac{dC_{OH^-}}{dR} |_{R=R_x})$$

(Equation 4.3)

where $R_x$ is the radius of semi hemisphere, $D$ is the diffusion coefficient of OH$^-$, $5.27 \times 10^{-5}$ cm$^2$/s [41,42], $\frac{dC_{OH^-}}{dR}$ is the OH$^-$ concentration gradient at the surface.

In steady state, the OH$^-$ generation rate ($m_{OH^-}$) should be equal to the mass diffused ($m_{Dx}$). The concentration of hydroxyl ion ($C_{OH^-}$) as a function of distance from the center of particle ($R_x$) was expressed by the following equation:

$$C_{OH^-} = 2.2279 \times r^2 \left(\frac{1}{R_x} - \frac{1}{R_o}\right) \text{mol/L}$$

(Equation 4.4)

where $r$ is assumed to be 2.5 µm (Fig. 4.5 a) ; $R_o$, radius of diffusion hemisphere, is taken as 10 µm.

Fig. 4.12 shows the calculated pH distribution around the dealloyed S phase based on Equation 4.4. A pH of around 10 appears at the center of S phase, which is consistent with experimental data [34], and it decreases slowly as it moves away from the center. There is a dramatic drop at about 9 µm where the pH is about 8, which is the critical pH for Ce(OH)$_3$ precipitation in 4 mM Ce$^{3+}$ solution. This distance is much larger than the radius of the S phase, indicating that under steady-state conditions, the pH around the S phase is high enough to induce Ce hydroxide precipitation.
4.4.4 Quantification of the cerium precipitation on S phase and AlCuMnFe particles, and comparison with their ORR kinetics

The pH distribution is closely related to the ability of IMCs to support oxygen reduction reactions, which affects the propagation and amount of REM precipitation. As shown in Fig. 4.2 e, dealloyed S phase possesses the largest cathodic current density in NaCl solution, which is about two or three orders of magnitude larger than that of AlCuMnFe IMCs. Different amounts of precipitation are expected on those two kinds of IMCs. Fig. 4.6 a and b show that Ce concentration on S phase particles varies from 1.64 to 9.62 wt. %, while there is no obvious Ce on AlCuMnFeSi particles.

To study the relationship between the ORR of IMCs and precipitation amount, EDS mapping on AlCuMnFe and Al_{2}CuMg particles after 52.5 hours exposure in 0.1 M NaCl plus 4 mM CeCl\(_3\) were collected and the cerium concentration over each particle was integrated. Fig. 4.13 shows the corrosion morphology of S phase and AlCuMnFe particles after exposure and the associated cerium distribution. Cerium hydroxide precipitation is observed on the S phase particle, while no obvious precipitation on AlCuMnFe. EDS mapping of Ce reveals a higher cerium concentration on S phase (Fig. 4.13c) than that on AlCuMnFe particles (Fig. 4.13d). This difference is more obvious on the Matlab extracted data (Fig. 4.13 e and f). The integrated intensity of the Ce signal on S phase particle (total particle area is 236.4 µm\(^2\)) is 2.0 \times 10^6, and the average signal intensity is 8400 /µm\(^2\), while that on AlCuMnFe particle (183.7 µm\(^3\)) is 7.2 \times 10^5 and the associate average signal density is 3800/µm\(^2\). From the cathodic polarization curves in NaCl (Fig. 4.10), cathodic limiting current density on Al_{7}Cu_{2}Fe and Al_{20}Cu_{2}Mn_{3} is 29
and 54 µA/µm², while that on dealloyed S phase is 3750 µA/µm², which is more than 100 times higher than that on Al₇Cu₂Fe and 70 times higher than Al₂₀Cu₂Mn₉. But the Ce density on S phase particles is only 2.2 times larger than that on AlCuMnFe. The large amount of cerium on the S phase does not necessarily mean that the phase is well protected upon contact with the aqueous solution containing cerium ions. The inhibition of dealloying corrosion is negligible initially, but strong hydroxide precipitation likely occurs after initial dealloying resulting in suppression of corrosion thereafter.

4.4.5 Slowness of inhibition by rare earth metal inhibitors on AA2024-T3

Inhibition by REM inhibitors arises from local hydroxide formation. However, hydroxide formation requires a pH increase. The pH increase at the cathodic sites is caused by the oxygen reduction, which must be accompanied by anodic dissolution. As a result REM inhibition is slow.

In the case of S phase, which is electrochemically active, polarization measurements indicate that REM inhibitors do not provide significant inhibition of anodic kinetics (Fig. 4.1 e). In free corrosion exposure tests of AA2024-T3 in a NaCl solution, the S phase initially corrodes by rapid dealloying. Inhibition on this dealloying process is not expected since the hydroxide precipitation is slow. SEM images of the cross section of S phase particles shows that they are always dealloyed (Fig. 4.7). However, as Al and Mg corrode and Cu-rich layer forms, ORR occurs at a high rate (Fig. 4.2 e). The ORR increases the local pH near the surface of S phase and induces hydroxide formation. Once the hydroxide layer is formed, the subsequent corrosion is inhibited.
Therefore, the effective inhibition of REM inhibitors strongly depends on how fast the corrosion process is before hydroxide formation occurs. This dependence is closely related to ORR on cathodic sites, corrosion resistance of second phase particles, and solubility products of hydroxide phases that form.

4.4.6 Relation of microcell data with the free corrosion morphology of AA2024-T3

Fig. 4.5 a and b reveal that AA2024-T3 is susceptible to localized corrosion in NaCl solution. With addition of REM inhibitors in NaCl solution, (Fig. 4.5 c, d and e), trenching corrosion around noble AlCuMnFe particles is strongly inhibited, which is comparable to inhibition by dilute chromate solutions. Although dealloying still occurs as indicated in the cross section of S phase in Fig. 4.7, corrosion is inhibited though not as completely as by chromate.

The polarization response of IMCs obtained using the microcell method (in Fig. 4.8 and Fig. 4.9) indicate REMs do not provide good inhibition on the anodic corrosion of IMCs, but examination of the corrosion morphology (in Fig. 4.5) shows obvious inhibition of localized corrosion. Since all polarization tests are performed on a single IMC, there is no galvanic corrosion and the local pH and associated precipitation is limited. However, in the free corrosion test of the alloy, these second phase particles couple with surrounding matrix, acting as a local cathode. This is an essential trigger for REM inhibition that is absent in polarization experiments. As shown in Fig. 4.10, REMs strongly inhibit ORR on IMCs. Under free corrosion conditions, when the ORR is inhibited on IMCs, and the associated dissolution kinetics of surrounding matrix will
become sluggish. This explains the discrepancy between anodic polarization measurements with the actual corrosion morphology.

4.5 Conclusions

1. REMs (Ce$^{3+}$, Pr$^{3+}$, and La$^{3+}$) do not show obvious effects in short-term polarization experiments suggesting they are not effective anodic inhibitors for IMCs at short times.

2. All REMs inhibit the oxygen reduction reaction kinetics, but to different extents. Pr is found to be the most effective REM inhibitor, and its effect on Al$_{20}$Cu$_2$Mn$_3$ and Al4%Cu is comparable to chromate. It has a higher efficiency than other two REMs is attributed to its low solubility product.

3. REMs do not inhibit the initial dealloying of S phase, but once Cu-rich layer forms, REMs precipitate on the surface and inhibit further dealloying and trenching corrosion. Ce hydroxide precipitation layers were observed to have a thickness of 120 nm in 1 hour exposure, and 240 nm in a 52.5 hour exposure. These hydroxides dehydrate and crack in the vacuum conditions in an electron microscope, which enables observation of the dealloyed S phase surfaces underneath. The layer also contains many voids, and this porous precipitate may only be partially protective.

4. The pH distribution around the dealloyed S phase in 0.1 M NaCl was evaluated based on a simple diffusion model, and the highest pH estimated was around 10. In solution containing 4mM Ce$^{3+}$, Ce(OH)$_3$ a hemispherical cap of solution can form with a radius of 9 µm, originating from the center of an S phase particle.
5. REMs are ‘slow’ inhibitors compared to chromate, and their inhibition requires local pH increases.
Fig. 4.1 Anodic polarization curves of IMCs in AA2024-T3 in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) + NaCl solutions and chromate solution (continued)
Fig. 4.1 continued

![Graph showing electrochemical behavior for different solutions.](image)

- **c, Al$_2$Cu$_2$Fe**
  - 0.1M NaCl
  - 0.1M NaCl + 4mM CeCl$_3$
  - 0.1M NaCl + 4mM PrCl$_3$
  - 0.1M NaCl + 4mM LaCl$_3$
  - 0.1M NaCl + 1mM K$_2$CrO$_4$

- **d, Al$_{20}$Cu$_2$Mn$_3$**
  - 0.1M NaCl
  - 0.1M NaCl + 4mM CeCl$_3$
  - 0.1M NaCl + 4mM PrCl$_3$
  - 0.1M NaCl + 4mM LaCl$_3$
  - 0.1M NaCl + 1mM K$_2$CrO$_4$
Fig. 4.1 continued

-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0

1x10^-9 1x10^-8 1x10^-7 1x10^-6 1x10^-5 1x10^-4 1x10^-3 1x10^-2

Current Density (A/cm^2)

E(\text{VSCE})

0.1M NaCl
0.1M NaCl+ 4mM CeCl,
0.1M NaCl+ 4mM PrCl
0.1M NaCl+ 4mM LaCl
0.1M NaCl+ 1mM K_2CrO

\text{e, Al}_2\text{CuMg}

123
Fig. 4.2 Cathodic polarization curves of IMCs in AA2024-T3 in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) + NaCl solutions and chromate solution (for Al$_2$CuMg, it is initiated after 1000s OCP) (continued)
Fig. 4.2 continued

Current Density (A/cm
2
)
E( V
SCE
)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M NaCl</td>
<td>-0.6 to -1.3</td>
</tr>
<tr>
<td>0.1M NaCl + 4mM CeCl₃</td>
<td>-0.6 to -1.3</td>
</tr>
<tr>
<td>0.1M NaCl + 4mM PrCl₃</td>
<td>-0.6 to -1.3</td>
</tr>
<tr>
<td>0.1M NaCl + 4mM LaCl₃</td>
<td>-0.6 to -1.3</td>
</tr>
<tr>
<td>0.1M NaCl + 1mM K₂CrO₄</td>
<td>-0.6 to -1.3</td>
</tr>
</tbody>
</table>

Current Density (A/cm
2
)
E( V
SCE
)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Current Density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1M NaCl</td>
<td>-0.5 to -0.9</td>
</tr>
<tr>
<td>0.1M NaCl + 4mM CeCl₃</td>
<td>-0.5 to -0.9</td>
</tr>
<tr>
<td>0.1M NaCl + 4mM PrCl₃</td>
<td>-0.5 to -0.9</td>
</tr>
<tr>
<td>0.1M NaCl + 4mM LaCl₃</td>
<td>-0.5 to -0.9</td>
</tr>
<tr>
<td>0.1M NaCl + 1mM K₂CrO₄</td>
<td>-0.5 to -0.9</td>
</tr>
</tbody>
</table>
Fig. 4.2 continued

![Graph showing current density versus electrode potential for different solutions.](image-url)
Fig. 4.3 Corrosion potential distribution (a) and pitting potential distribution (b) of IMCs in 0.1 M NaCl, REM (Ce\(^{3+}\), La\(^{3+}\), Pr\(^{3+}\))+NaCl solutions and chromate solution
Fig. 4.4 OCP of S phase in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) +NaCl solution and chromate solution
Fig. 4.5 corrosion morphology of AA2024-T3: a. after polishing (The insert is magnified S phase); b, after 6 hours exposure in 0.1 M NaCl; c, 50 hours in 0.1M NaCl+ 4mM CeCl₃; d, 50 hours in 0.1M NaCl+ 4mM LaCl₃; e, 50 hours in 0.1M NaCl+ 4mM PrCl₃; f, 50 hours in 0.1M NaCl+ 1mM K₂CrO₄.
Fig. 4.6 EDS spectra of point 1 on S phase Fig. 4.5 (a), of point 2 on AlCuMnFe(Si) in Fig. 4.5 (b); c, EDS line scanning across an S phase particle; d, magnified SEM image of the crack in c
Fig. 4.7 Cross-section SEM of S phase after different exposure time to 0.1 M NaCl solution plus 4mM Ce$^{3+}$
Fig. 4.8 Relationship between the pitting potential and corrosion potential of IMC in each test solution
Fig. 4.9 Comparison of corrosion rate in 0.1 M NaCl with and without inhibitors (The black horizontal line represented the corrosion rate in 0.1 M NaCl)
Fig. 4.10 Cathodic current density comparison in 0.1 M NaCl, REM (Ce$^{3+}$, La$^{3+}$, Pr$^{3+}$) +NaCl solution and chromate solution
Fig. 4.11 Modeling used to calculate the pH distribution around the dealloyed S phase
Fig. 4.12 pH distribution around the dealloyed S phase in 0.1M NaCl basing on the model in Fig.4.11
Fig. 4.13 EDS of Ce element after 52.5 hour exposure in CeCl$_3$ on S phase and AlCuMnFe particles: a and b: corrosion morphology (a is BSE image); c and d: Ce mapping data obtained by EDS on the corresponding particles in a and b; e and f: replotted Ce distribution only on particle based on the extracted data by Matlab.
References


Chapter 5 The Effect of Temperature on the Inhibition Performance of Cerium on AA2024-T3

Abstract

In this chapter, inhibition by cerium of AA2024-T3 is evaluated based on electrochemical characterization using a microcell method and assessment of corrosion morphology in the vicinity of second phase particles. In a CeCl$_3$ solution, corrosion rates of intermetallic compounds (IMCs) were found to increase with increasing temperature to such as extent that they were similar in magnitude to the corrosion rate in an uninhibited NaCl solution. The pitting potential in CeCl$_3$ solution becomes lower as temperature increases, and cerium additions do not affect the pitting potential at temperatures above 50 °C. The inhibition of cathodic kinetics on IMCs is similar at 30 and 50 °C, but weakens at 70 °C. The inhibition of Ce inhibitor depends on local pH increases and how fast cerium hydroxide forms on the surface. This dependence makes Ce a slow inhibitor, and this sluggishness is amplified at high temperature (>50 °C). The initial dealloying corrosion of S phase cannot be inhibited at ambient temperatures, and this effect becomes more severe at high temperature (> 50 °C). Trenching corrosion around AlCuMnFe particles can be well suppressed with addition of Ce at temperatures up to 50 °C, but less protection is afforded at 70 °C. The decreased inhibition efficiency of Ce at high temperature (>50 °C) is due to increased corrosion kinetics (or dealloying kinetics of S
phase) and decreased ORR kinetics that limits the local pH change that induces Ce hydroxide formation.

5.1 Introduction

Aluminum alloy AA2024-T3 (Al-4.4Cu-2.5Mg-0.6Mn) is a high strength alloy that derives its excellent mechanical properties from a heterogeneous microstructure[1,2]. This heterogeneous microstructure has positive effects on the mechanical properties but leads to localized corrosion susceptibility. Rare earth metal (REM) inhibitors have been studied extensively to characterize their effects on localized corrosion of aluminum alloys[3–5]. With addition of 1000 ppm of CeCl$_3$ in NaCl solution, the corrosion rate of AA7075 was found to be reduced by an order of magnitude [6][7]. The cathodic kinetics of AA7075 were reduced by an order of magnitude after 10 minutes immersion in NaCl plus 0.05 wt.% CeCl$_3$. Other rare earth metal inhibitors such as YCl$_3$, LaCl$_3$, PrCl$_3$ show similar inhibition of anodic and cathodic kinetics [8]. Inhibition is attributed to the formation of hydroxide precipitate layer at and around intermetallic particles. Hydroxide formation is triggered by an increase in local pH due to oxygen reduction reaction occurring on the particles. Chapter 4 focused on the effect of REM inhibitors on the electrochemical chemical properties of second phase particles. It was found that REMs could strongly inhibit the oxygen reduction reaction (ORR) kinetics on the cathodic sites, but provided little inhibition of anodic reactions. REM inhibitors form hydroxide caps on dealloyed Al$_2$CuMg (S phase) particles, and these impede oxygen reduction reaction, controlling the rate of the subsequent corrosion processes.
REM inhibitors cannot effectively suppress the initial dealloying corrosion of S phase, since S phase acts as an anode initially, any pH increase is limited, which, in turn limits the formation of a hydroxide layer. Since REM inhibition depends on the formation of a hydroxide layer that forms in response to the establishment of localized corrosion cell action. As a result REM inhibition is slow. The inhibition efficiencies of REM inhibitors are strongly dependent on many factors including oxygen reduction (to increase local pH), the extent of corrosion before REM hydroxide formation, and solubility the products of hydroxide precipitates. All of these factors depend on temperature. Oxygen reduction reaction kinetics are dependent on temperature in aerated solutions, and are highest value at around 55 °C (Fig. 3.12 in Chapter 3). The time to build up the minimum pH to trigger hydroxide formation is expected to change with temperature. Furthermore, the corrosion rates of second phase particles increase with increasing temperature. For the S phase, dealloying kinetics dramatically increase with temperature as discussed in Chapter 3. The solubility products of rare earth metal hydroxides also decrease with increasing temperature, and the minimum pH for the precipitation is expected to decrease at high temperature for a REM solution of a given concentration. All of these temperature-dependent factors suggest that the inhibition efficiency of REM inhibitors at high temperature will change. However, the effects of temperature on the inhibition performance and localized corrosion morphology by cerium have not been studied in detail.

In this work, the inhibition of electrochemical activity on second phase particles in AA2024-T3 by Ce as a function of temperature has been studied using a microcell
approach. The corrosion morphology of AA2024-T3 after exposure in NaCl solution containing a Ce inhibitor has also been examined in an attempt to relate the microcell data to localized corrosion morphology.

5.2 Experimental

5.2.1 Materials and sample preparation

The IMCs of interest in the study were Al$_7$Cu$_2$Fe, Al$_{20}$Cu$_2$Mn$_3$, Al$_2$CuMg and Al$_2$Cu. A solid solution of Al 4%Cu was also studied. These samples were specially synthesized and heat treated based on the Al-Cu, Al-Cu-Mg, Al-Cu-Fe and Al-Cu-Mn phase diagrams, to achieve a grain size of hundreds of micrometers, which facilitated microcell measurements [9]. All samples were ground from 600 to 1200 grit using SiC paper (Buehler) and ethyl alcohol, then polished using 1μm diamond paste (Buehler) and lubricated by 1 micrometer diamond compound extender (Leco). Samples were then degreased ultrasonically in ethanol and dried using compressed air. The experiments were carried out immediately after polishing. To adjust temperature, the samples were placed on a specially designed Cu stage, which was precooled or preheated to the designed temperature with circulating water from a temperature bath (Isotemp® 4100 Circulators/Baths, Fisher Scientific). The temperature was calibrated using a thermometer and the samples were also cut thin to make sure the temperature of samples was uniform. The bulk AA2024-T3 was ground to 1200 grit with SiC paper (Buehler) and lubricated using ethanol alcohol, and then ultrasonically cleaned in ethanol. A 0.1 M NaCl solution was prepared by dissolving NaCl (Chemical reagent, purchased from Fisher Scientific) in DI water with a resistivity of 18 MΩ*cm and it has a pH of 5.7. A 4 mM CeCl$_3$ solution
was prepared by dissolving reagent grade CeCl₃·7H₂O salt in 0.1 M NaCl. In this work, the “CeCl₃ solution” refers to a 0.1 M NaCl plus 4 mM CeCl₃ solution. Both solutions used in microcell measurements and free exposure experiments were naturally aerated, and no efforts were made to remove dissolved oxygen.

5.2.2 Potentiodynamic measurements

Anodic and cathodic polarization curves were collected at 30 °C, 50 °C and 70 °C in NaCl and CeCl₃ solutions using an electrochemical microcell approach[10]. The experiments were controlled by Gamry Reference 600™ potentiostat. The microcell was a standard three-electrode setup, with platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The opening of the capillary was about 100 micrometers. The end of the capillary was dressed using a layer of silicone rubber to avoid leakage. Both anodic and cathodic polarization curves were collected using a scan rate of 0.01 V/s after a short initial hold time, which allowed the solution contacting the samples to equilibrate stage and sample temperature. The anodic polarization measurements were repeated at least 3 times, and the average values of the characteristic potentials were used for analysis. The corrosion rate was obtained by extrapolating the linear part (about 100mV below the corrosion potential) of the anodic curves to the corrosion potential using Gamry Echem Analyst™ software.

5.2.3 Corrosion morphology

Free corrosion exposure experiments on bulk alloy samples were performed in a water-jacketed cell. NaCl and CeCl₃ solutions were precooled or preheated to the designed temperature, and then the polished samples were placed at the bottom of the cell
horizontally for 1 hour. After 1 hour exposure, samples were taken out, rinsed with DI water, dried with compressed dry air and then stored in the desiccator. The corrosion morphologies were characterized using FEI/Philips XL-30 field emission environmental scanning electron microscopy (ESEM) coupled with energy dispersive X-ray spectroscopy (EDS), and cross-sections of samples were prepared by FEI Helios Nanolab 600 dual beam focused ion beam (FIB) with 30 kV Ga ion beam.

5.3 Results

5.3.1 Electrochemical response of IMCs at high temperature in CeCl₃ solutions.

Fig. 5.1 shows the anodic polarization curves of Al₂Cu, Al₄wt.%Al₂₀Cu₂Mn₃ and Al₇Cu₂Fe at 30, 50 and 70 °C in CeCl₃ solution. The variation in corrosion potential, pitting potential and corrosion rate as a function of temperature for each IMC examined is summarized in Fig. 5.2, Fig. 5.3 and Fig. 5.4 respectively. The electrochemical response of each IMC examined in 0.1 M NaCl without inhibitors were reported in Chapter 3 and these data were also included in Fig. 5.2- Fig. 5.4 for comparison.

5.3.1.1Al₂Cu

The corrosion potential of Al₂Cu in CeCl₃ solution decreased by about 25 mV as the solution temperature increased from 30 to 70 °C. The dispersion in measured corrosion potential was less than 120 mV (Fig. 5.2). The pitting potential is not strongly dependent on temperature but did exhibit significant dispersion in 3 replicate measurements. The pitting potential at 70 °C is more negative than at lower temperature. The corrosion rate decreases slightly with temperature, but becomes constant at 50 and 70 °C as shown in Fig. 5.4. The addition of 4 mM CeCl₃ to NaCl reduced the corrosion rate by an order of
magnitude at 50 and 70 °C, but only slight inhibition was observed at 30 °C. Fig. 5.5 a shows the cathodic polarization curves of Al<sub>2</sub>Cu at each temperature. The cathodic kinetics observed at 30 and 50 °C were similar in magnitude, and increased at 70 °C. However, cathodic current densities at each temperature in CeCl<sub>3</sub> solution (Fig. 5.5 a) are strongly inhibited decreasing by an order of magnitude compared to those in NaCl (Fig. 3.6 b).

5.3.1.2 Al 4wt.%Cu

The corrosion potential of Al 4wt.% Cu in CeCl<sub>3</sub> is independent of temperature at about -1.045 V<sub>SCE</sub> (Fig. 5.2). This corrosion potential was about 200 mV lower than that in NaCl. The pitting potential at 30 and 50 °C was similar, and decreases at 70 °C (Fig. 5.3). The addition of CeCl<sub>3</sub> to NaCl increased the pitting potential by tens of millivolts at 30 and 50 °C. The corrosion rate increased with temperature in CeCl<sub>3</sub> solution but was lower than that in NaCl at each temperature (Fig. 5.4). The cathodic kinetics in CeCl<sub>3</sub> at 30 and 50 °C were similar, but were greater at 70 °C as shown in Fig. 5.5. With addition of cerium the cathodic kinetics was inhibited, especially at 30 and 50 °C.

Fig. 5.5.3.1.3 Al<sub>20</sub>Cu<sub>2</sub>Mn<sub>3</sub>

The corrosion potential in CeCl<sub>3</sub> decreased by 200 mV as temperature increased from 30 to 70 °C (Fig. 5.2). This decreasing trend was similar to that in NaCl. However, the corrosion potential in CeCl<sub>3</sub> was about 100 mV lower than in NaCl at each temperature. The pitting potential also decreased with temperature in CeCl<sub>3</sub> as shown in Fig. 5.3. The Ce addition to NaCl solution shifted the pitting potential to more noble values at 30 °C, but this effect became negligible at 50 °C, and negative at 70 °C as shown in Fig. 5.3. Fig.
5.4 reveals that corrosion rate increased with temperature up to 50 °C and became independent at 70 °C. The corrosion rate in the presence of CeCl₃ was reduced compared to that in NaCl. The highest cathodic kinetics were observed at 70 °C, which was followed by that at 50 °C and 30 °C as shown in Fig. 5.5. However, cathodic kinetics at each temperature was all on the order of 10 µA/cm². The comparison of cathodic kinetics in CeCl₃ and NaCl solutions revealed that oxygen reduction reactions were retarded with addition of Ce.

5.3.1.4 Al₇Cu₂Fe

Both corrosion potential and pitting potential decreased with temperature (Fig. 5.2 and Fig. 5.3), but pitting potential became independent of temperature at 50 °C and above. The corrosion potential in CeCl₃ was higher than that in NaCl at 30 °C, but was smaller at 50 °C. This difference was larger at 70 °C; about 230 mV. Fig. 5.3 reveals that Ce additions to NaCl increased the pitting potential, but this effect disappeared at 50 and 70 °C. The corrosion rate increased with increasing temperature in CeCl₃. The corrosion rate in CeCl₃ is slightly smaller than those in NaCl except at 50 °C as shown in Fig. 5.4. The cathodic kinetics in CeCl₃ solution was independent of temperature (Fig. 5.5d) and were strongly inhibited by the CeCl₃ addition.

5.3.1.5 Al₂CuMg (S phase)

The work in Chapter 3 (Fig. 3.9) showed that the corrosion characteristics of S phase were dependent on exposure time. As exposure time increased, the corrosion potential increased and the pitting potential disappeared. This dependence on the exposure time is attributed to dealloying corrosion and formation of Cu-rich layer. In chapter 3, the open
circuit potential response was used to judge the dealloying kinetics by comparing the extent of potential oscillation and the duration of the initial negative transient. The potential oscillation is caused by the formation and breakdown of the Cu-rich layer. Stabilization of the open circuit potential is an indication that a stable layer of Cu has formed by the dealloying process. The effect of Ce additions to solution is shown in Fig. 5.6. The open circuit potential in CeCl$_3$ at 30 °C was very stable at about -900 mV$_{SCE}$. By contrast, two obvious potential fluctuations in NaCl were observed, indicating that dealloying corrosion completed at a certain time. This comparison demonstrates that the dealloying corrosion kinetics were reduced with addition of Ce. At 50 °C, significant fluctuation was observed in the CeCl$_3$ solution upon initial exposure and this indicated fast dealloying kinetics. However, the increase in potential to 0 V$_{SCE}$ within 500s indicated strong ennoblement caused by dealloying and stabilization of the layer by corrosion products or cerium hydroxide precipitation. By contrast, the oscillation of open circuit potential in NaCl at 50 °C was observed for the entire duration, and the highest potential was about -370 mV$_{SCE}$. This indicates that the dealloying corrosion of S phase in NaCl is faster than that at 30 °C and does not stop. At 70 °C in a CeCl$_3$ solution, strong ennoblement of the open circuit potential was also observed, but the kinetics were much more rapid with the OCP reaching 0 V$_{SCE}$ in just 165 seconds. By comparison, the potential of S phase in NaCl also showed significant oscillation in the initial 120 seconds and then gradually increased to as high as -0.24 V$_{SCE}$. 

150
5.3.2 Free corrosion morphology after 1 hour exposure in CeCl$_3$ at 10, 30, 50 and 70 °C

Fig. 5.7 shows the localized corrosion morphology after a one-hour exposure in 4 mM CeCl$_3$ at 10, 30, 50 and 70 °C. At 10 °C, there is no obvious corrosion around AlCuMnFe particles. For the S phase particles, nano-scale pores form on the surface and small isolated granular particles were observed (Fig. 5.7 a and b). As the temperature increased to 30 °C, some S phase particles were covered by hydroxide caps, while others remained intact (Fig. 5.7 c). The detailed structure and formation of the hydroxide cap, and porous dealloyed S phase underneath was discussed in Chapter 4 (Fig. 4.7). The trenching corrosion around the AlCuMnFe particles was strongly inhibited. Fig. 5.7 e reveals that Ce can provide strong inhibition of the trenching corrosion around AlCuMnFe(Si) particles at 50 °C. However, the dark contrast immediately around the particle indicates the corrosion probably initiates but does not propagate. Fig. 5.7 f shows the corrosion morphology of single S phase particles. Trenching corrosion formed around S phase and matrix, and may have been caused by the dissolution of the surrounding matrix. S phase still retained a round shape and sharp edge, which is in contrast to the smooth edge in NaCl at 50 °C (Fig. 3.11). The remnant of S phase demonstrated some pits, but they were very shallow as shown in the SEM image of cross section of S phase in Fig. 5.8 a and b. As temperature increased to 70 °C, loose products formed and cover the whole matrix (Fig. 5.7 g and h). This morphology was similar to that in NaCl solution (Fig. 3.11). S phase particles showed a bright color in the SEM image (Fig. 5.7 h), which was in contrast to the surrounding black regions. SEM images of the cross section of S phase in
Fig. 5. 8 c and d indicate that a layer with a thickness of 30 nm formed on the dealloyed S phase. Combined with cerium concentration (5.6 wt.%) on S phase determined by EDS, this layer is attributed to cerium hydroxide precipitation. However, severe dealloying corrosion was revealed in the cross-section (Fig. 5. 8 c), which penetrated half of the particles. No obvious corrosion surrounding and on AlCuMnFe particles was observed (Fig. 5.7 g), and the concentration of cerium on these particles was about 3.54 wt.%. However, the similar black region around AlCuMnFe particles to S phase indicated that corrosion might initiate but did not propagate.

5.4. Discussion

5.4.1 Effect of temperature on the electrochemical properties of IMCs in CeCl₃ solution

The effect of temperature on the corrosion behavior of IMCs is complex. The corrosion potential of Al₇Cu₂Fe and Al₂₀Cu₂Mn₃ decreases with increasing temperature, but that of Al 4wt.% Cu and Al₂Cu are independent of temperature (Fig. 5.2). The pitting potential of most IMCs decreases with temperature with the exception of Al₂Cu, which does not show an obvious dependence on temperature (Fig. 5.3). The corrosion rates of most IMCs generally increase with increasing temperature (Fig. 5.4). The cathodic kinetics of IMCs in CeCl₃ does not show an obvious dependence on temperature, and the limiting current densities are on the order of $1 \times 10^{-5}$ A/cm² (Fig. 5.5). The highest cathodic kinetics of most IMCs occurs at around 70 °C. CeCl₃ additions do not lead to obvious inhibition of the anodic response, but can reduce the cathodic kinetics at large polarizations at elevated temperatures. The addition of CeCl₃ to NaCl solutions slightly
decreases the corrosion potential of Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$, and does not show any effect on Al$_2$Cu (Fig. 5.2). One exception is Al4%Cu, the corrosion potential of which is reduced by about 200 mV. For most IMCs, no obvious improvement on pitting potential is observed by addition of CeCl$_3$ at 50 and 70 °C (Fig. 5.3). The exception to this is Al 4wt.% Cu at 50 °C. The addition of CeCl$_3$ to NaCl solution has no obvious effects on corrosion rates of most IMCs except Al$_2$Cu, which shows decreased corrosion rate at 50° and 70 °C. The cathodic kinetics are reduced with addition of CeCl$_3$ at all temperatures examined, but inhibition is weak at 70 °C as shown in Fig. 5.5 and Fig. 3.6. The corrosion potential depends on several kinetic factors including the exchange current density and reduction reaction kinetics. The presence of rare earth metals inhibitors makes corrosion responses more complex. In aerated solutions, the local pH will increase due to ORR during the cathodic polarization, which induces cerium hydroxide precipitation on the surface. The precipitation will slow down cathodic reactions, and this is observed in cathodic polarization response (Fig. 5.5). The similar cathodic kinetics in CeCl$_3$ solution at 50 and 30 °C indicate that kinetics become independent of the temperature in aerated CeCl$_3$. However, at 70 °C inhibition by CeCl$_3$ becomes weak. This might be caused in part by the dependence of the ORR limiting current density on temperature. Fig. 3.12 shows the estimated ORR limiting current density as a function of temperature in NaCl. The peak cathodic current appears at around 50 °C, and then drops at 70 °C. The drop in the oxygen reduction reaction rate may limit any pH increase and associated Ce hydroxide precipitation on the surface. Decreased ORR kinetics might also lead to decreased corrosion potential of IMCs (Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$).
For pitting potential, the absence of inhibiting effect by CeCl$_3$ might be caused by the limited cerium hydroxide precipitation on the surface. Anodic polarization measurements in CeCl$_3$ are performed on isolated IMCs using microcell, and ORR and the associated cerium precipitation are reduced due to a smaller cathodic overpotential during these measurements. Corrosion rates of IMCs in NaCl increase with temperature according to an Arrhenius relation (Chapter 3). The addition of cerium does not show significant inhibition on the corrosion rate, indicating that cerium has limited effects on the activation-controlled corrosion process of IMCs—at least in short term measurements such as these. All these data indicate that cerium is not an effective anodic inhibitor at elevated temperatures in short duration testing. Its inhibition of the ORR is similar from 30 to 50 °C, but becomes weak at 70 °C due to decreased ORR kinetics.

5.4.2 Inhibition performance of cerium on S phase particles at elevated temperature

The inhibition of the localized corrosion by CeCl$_3$ is achieved by formation of hydroxide precipitation on local cathode sites. This is due to a local pH increases, which is generally triggered by oxygen reduction reactions in aerated solutions. Therefore, the inhibition performance is closely related to oxygen reduction kinetics, which is itself dependent on temperature. The electrochemical behavior of the S phase is dominated initially by a strong anodic response. However, as Mg and Al preferentially dissolve, a Cu-rich layer forms and S phase reverts to net cathode supporting oxygen reduction. As oxygen reduction produces an excess of hydroxyl, the pH increases and hydroxide precipitation is expected. However, the initial anodic response of the S phase is stimulated by increasing temperature, and the dealloying corrosion rates are expected to
increase. This hastens the transition of S phase from net anode to net cathode potentially leading to more rapid onset of Ce hydroxide precipitation and passivation of the cathodic site.

Fig. 5.7 a-d shows that corrosion of S phase and the associated trenching corrosion of the matrix phase are strongly inhibited compared to that in NaCl (Fig. 3.11) at 10 and 30 °C. However, the formation of coarse dealloyed morphology at 30 °C (Fig. 5.7 d) suggests that dealloying kinetics are increased as compared 10 °C where a finer dealloyed morphology is observed (Fig. 5.7 b).

The small isolated precipitated islands at 10 °C, and precipitation caps at 30 °C are attributed to formation of high surface area dealloyed structures and an increase in cathodic kinetics due to a strongly increased reactive surface area (Fig. 3.12). At 50 °C, the S phase is well protected and the scattered pits on the surface are very shallow (Fig. 5.8 b). The dealloying corrosion kinetics are also expected to increase compared to that at lower temperature (< 50 °C). However, the fastest ORR kinetics at 50 °C could trigger fast production and accumulation of hydroxyl near the S phase. Additionally, the diffusion coefficient of cerium ions in solution is also increased. Therefore, once a Cu-rich surface forms and shows an ability to support oxygen reduction reaction, cerium hydroxides can form on the surface rapidly. The requirement on the formation of Cu-rich layer might explain the observed pits on the S phase. However, once precipitation begins, the following dealloying corrosion is expected to be inhibited. This hydroxide deposit is expected to thin and compact because fast cathodic kinetics and enhanced diffusion of cerium facilitate cerium precipitation. The precipitated layer stifles the corrosion cell
process and the attendant corrosion damage accumulation and Ce hydroxide precipitation. The deposit on S phase particles (Fig. 5.7 f) and the rising potential of S phase (to as high as 0 \( V_{\text{SCE}} \)) in the microcell test (Fig. 5.6) support this idea.

**5.4.3 Inhibition performance of cerium on AlCuMnFe particles and matrix at elevated temperatures**

AlCuMnFe particles are cathodic relative to the matrix up to 50 °C in CeCl\(_3\) solution, but their corrosion potential becomes similar to that of Al 4wt.%Cu at 70 °C (Fig. 5.2). At cathodic sites at a temperature less than 50 °C, oxygen reduction reactions occur on the particle surface, inducing local pH increases and cerium hydroxide precipitation. As is the case with other IMC particles, hydroxide precipitation reduces ORR kinetics as observed in the cathodic polarization response (Fig. 5.7). The trenching corrosion around AlCuMnFe particles is expected to be inhibited as suggested by the corrosion morphology at these particle sites (Fig. 5.7 e). The corrosion rate increases with temperature (Fig. 5.4), which can induce more dissolution of IMCs before cerium hydroxide forms and starts to limit further corrosion. As temperature increases to 70 °C, the ORR kinetics drop and the corrosion potential approaches to that of Al 4%Cu limiting any galvanic interaction surrounding matrix. A decreased inhibition efficiency of the ORR on IMCs by cerium precipitation is observed in the cathodic polarization curves (Fig. 5.5). What is more, increased corrosion rates of IMCs with temperature lead to more dissolution of particles, which is shown in Fig. 5.7 g.

The corrosion rate of matrix during a 1-hour exposure in NaCl is relatively low at 10 and 30 °C compared to the localized corrosion associated with second phase particles.
There is still no obvious corrosion of matrix with addition of cerium into NaCl at 10 and 30 °C. However, its corrosion in NaCl can be severe at 50° and 70 °C, as loose hydroxide products are observed on the matrix (Fig. 3.11 f). Cerium additions do not provide significant inhibition on the matrix as these loose corrosion products are still observed at 50 °C and above (Fig. 5.7h). The absence of inhibition is attributed to limited precipitation on the matrix, which has been confirmed by EDS.

5.5 Conclusions

1. The inhibiting effects of Ce are not readily apparent in short-term polarization testing.

2. A cerium inhibitor suppresses cathodic kinetics of the ORR to about the same extent on all IMCs studied at temperatures up to 50 °C. Its inhibition efficiency decreases when temperature is higher than 50 °C. This decreased inhibition efficiency is attributed to a decrease in ORR kinetics, which leads to decreased precipitation of a protective hydroxide deposit.

3. Inhibition of the S phase by cerium strongly depends on temperature. Ce does not inhibit the initial dealloying of S phase and this effect is magnified at elevated temperatures (> 50 °C). Additionally, the ORR rate also dramatically decreases with increasing temperature (> 50 °C), and the cerium precipitation is decreased.

4. Cerium provides effective inhibition of AlCuMnFe particles at temperatures up to 50 °C. When the temperature is higher than 50 °C, protection of AlCuMnFe particles by cerium is weaker due to increased IMC dissolution rates and slower ORR kinetics at elevated temperatures.
5. The corrosion of AA2024-T3 matrix was not inhibited by cerium at temperatures higher than 50 °C.

6. Cerium provides good protection against localized corrosion at temperatures up to 50 °C. However, when the temperature is higher than 50 °C inhibition is limited. The increased corrosion rate of IMCs and decrease of ORR kinetics with temperature magnify the sluggish nature of cerium inhibition. It is recommended that cerium be used with care in aqueous solutions with a temperature greater than 50 °C.
5.6 Figures

Fig. 5.1 Anodic polarization curves of IMCs in 0.1 M NaCl with 4 mM CeCl$_3$ at 30, 50 and 70 °C (continued)
Fig. 5.1 continued

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.1 continued}
\caption{Electrochemical behavior of different Al-based alloys at various temperatures.}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Temperature & $E$ (V vs SCE) & $E$ (V vs SHE) & Current density (A/cm$^2$) \\
\hline
30°C & -0.2 & -0.6 & $1 \times 10^{-8}$ \\
50°C & -0.4 & -0.8 & $1 \times 10^{-7}$ \\
70°C & -0.6 & -1.0 & $1 \times 10^{-6}$ \\
\hline
\end{tabular}
\caption{Electrochemical data for different alloys at varying conditions.}
\end{table}
Fig. 5.2 Corrosion potential of IMCs as a function temperature in 0.1 M NaCl with 4 mM CeCl₃
Fig. 5.3 Pitting potential of IMCs as a function temperature in 0.1 M NaCl with 4 mM CeCl$_3$
Fig. 5.4 Corrosion rate of IMCs as a function temperature in 0.1 M NaCl with 4 mM CeCl₃
Fig. 5.5 Cathodic polarization curves of IMCs in 0.1 M NaCl with 4 mM CeCl₃ at 30, 50 and 70 °C (continued)
Fig. 5.5 continued

![Graph showing current density vs. voltage for different temperatures and alloys.](image)

- **Al_{20}Cu_{2}Mn_{3}**: 30°C, 50°C, 70°C
- **Al_{7}Cu_{2}Fe**: 30°C, 50°C, 70°C

Current density (A/cm²) vs. E (V SCE) for different temperatures and alloys.
Fig. 5.6 Open circuit potential of S phase in 0.1 M NaCl with 4 mM CeCl₃ at 30, 50 and 70 °C
Fig. 5.7 Corrosion morphology of second phase particles after 1 hour exposure in 0.1 M NaCl+4 mM CeCl₃
Fig. 5. 8 SEM images of cross-section of S phase after 1 hour exposure in 0.1M NaCl+4 mM CeCl₃ at 50 and 70 °C
References


Chapter 6 Inhibition Performance Study of Vanadate on AA2024-T3 at High Temperature by SEM, FIB, Raman and XPS

Abstract

The inhibition of AA2024-T3 by vanadate in 4mM NaVO$_3$ at temperatures ranging from 10° to 80° C was studied using various characterization techniques including FIB, Raman, XPS and SEM. SEM showed that in the presence of vanadate, no corrosion was observed on any intermetallic particles, including the reactive Al$_2$CuMg (S phase) at temperatures up to 50°C. Although trenching occurred around the S phase particles when solution temperature increased to 70°C and above, S phase was protected by vanadate-bearing film and the residual S phase was not obviously dealloyed as evident by analysis of the Mg content of the particles. No obvious trenching was observed around AlCuFeMn (Si) particles. Vanadium was determined to be present in an amount equivalent to 1.5wt. % by EDS on S phase after 1 hour exposure in 80°C solution. An amount of vanadium just above detection thresholds was present after exposure at 70°C, but no vanadium was detected at temperatures of 50°C and below. Raman spectroscopy showed a peak indicating polymeric vanadate, which increased in intensity with increasing temperature with the highest intensity at 80°C. This intensity was about 10 times larger than that observed at 30°C. The high vanadium concentration at 80 °C was attributed to fast reduction reaction kinetics of vanadate by Al or Mg. This reduction reaction is confirmed by XPS, which showed that vanadium with lower valence (4+) was present after
immersion test at 80 °C. The reduced forms of vanadium appeared to promote vanadate (V$^{5+}$) polymerization leading to the formation of vanadate films. Additionally, elevated temperatures appeared to increase vanadate polymerization kinetics. This reductive adsorbed vanadate film also enabled the samples treated in vanadate at higher temperature to have residual inhibition in NaCl without inhibitors. The reduced forms of vanadium were found to be easily oxidized under ambient aerated solution conditions. Exposure of treated samples in air further increased the corrosion resistance.

Key words: vanadium, vanadate, temperature, FIB, XPS, SEM, Raman, corrosion

6.1 Introduction

AA2024-T3 (Al-4.4Cu-2.5Mg-0.6Mn) is a high strength Al alloy that is susceptible to many forms of localized corrosion due to its heterogeneous microstructure[1,2]. Localized corrosion is focused at second phase intermetallic compounds (IMCs) [3,4]. Two common IMCs of interest in AA2024 are S-phase (Al$_2$CuMg) and AlCuFeMn(Si) particles. These two IMC types account for the majority particles found in AA2024, both in number and surface area[4,5]. AlCuFeMn(Si) particles generally act as cathodes to the matrix, and corrosion occurs as trenching around the particles under corrosive conditions[3,6–10]. S-phase particles are initially active and dissolve by dealloying. However, upon the dissolution of Mg and Al from these particles, they become Cu-rich and thereafter act as local cathode[4,6,11–13].

In view of recent advances in understanding the chemistry of vanadate, it has become an intriguing inhibitor to the research community[14–20]. Vanadate has proven to be a
promising candidate to replace toxic chromate as a corrosion inhibitor. In particular, vanadate has shown good inhibition on aluminum alloys in the form of soluble vanadate[17–26], vanadate-based coatings [27–29], and ion exchange compounds pigment for primers [30]. Iannuzzi et al. used polarization and split cell experiments to show that vanadate acted as a cathodic inhibitor on AA2024 by suppressing the oxygen reduction reaction (“ORR”) by a physically adsorbed vanadate monolayer[23,24]. The inhibition of vanadate on AA2024-T3 was also reported by Ralston et al. while studying corrosion inhibition imparted by vanadate on IMCs found in AA2024 and AA7075-T6[25,31].

The effect of temperature on protection provided by corrosion inhibitors has been the subject of many studies. For example, the rate of film formation of chromate conversion coatings on metal surfaces is accelerated when the solution bath is heated[32]. Slight improvement in corrosion resistance can be obtained when a chromate conversion coating is applied to Ni-P alloys at elevated temperatures[33]. Lin et al. noted a temperature-dependent reduced incubation time for the formation of a stannate conversion coating on AZ61 Mg alloys[15]. Previous work examining vanadate as a corrosion inhibitor on aluminum alloys was undertaken under ambient temperatures[17,18,20–22,24,25,27,28,31]. The Arrhenius Law dictates the acceleration of corrosion at higher temperatures[34] and this acceleration would be expected to affect galvanic couples, specifically coupling between active S-phase sites and alloy matrix. This work examines the temperature-dependence of vanadate corrosion inhibition of AA2024-T3. Characterization of vanadate films formed at various temperatures is
compared and contrasted with current understanding of vanadate inhibition and knowledge of previously successful corrosion inhibition systems such as chromate to develop insight into the value of vanadate as an inhibitor at elevated temperatures.

6.2 Experimental

6.2.1 Materials and Sample Preparation.

NaVO₃ (96%) was purchased from Acros Organics. AA2024-T3 sheet, 0.0635 inch (1.6 mm) thick, was obtained from Alcoa. All solutions were prepared with deionized water with a minimum of 18.2 MΩ*cm resistivity. All aqueous NaVO₃ solutions were 4.0 mM; the natural pH of 7.7 was adjusted to 9.2 with the drop-wise addition of concentrated NaOH (99.9%, Fisher). All samples were (1) cut to ~15 mm x 15 mm, (2) abraded with successive grades of SiC paper (Buehler) to 1200 grit using ethanol as a lubricant, (3) polished in 1 μm diamond paste (Buehler) on polishing cloth with DP-Lubricant Blue (Struers) and (4) ultrasonically cleaned with ethanol to remove organic residue. Immersion at the desired temperature (described below) was carried out immediately after polishing.

Exposure tests at a various temperatures were accomplished with the use of a 400 mL jacketed beaker equipped with two hose connections to permit circulation of temperature-controlled water between jackets. The immersion procedure consisted of the following steps: (1) ~100 mL of room temperature, pH (9.2) adjusted, aqueous 4.0 mM NaVO₃ was placed in the jacketed beaker and was pre-heated or pre-cooled to 10, 30, 50, 70, or 80 °C with circulating water from the temperature bath for ~40 minutes; (2) a polished sample was placed horizontally on the bottom of the jacketed beaker in the heated/cooled
electrolyte; (3) temperature-controlled water continued to flow through the jacketed walls for an additional 60 minutes; (4) after 60 minutes at the desired temperature, each sample was immediately rinsed in DI water and ethanol and air dried. Exposure of control samples followed the same steps, except that DI water was substituted in place of 4.0 mM NaVO₃.

6.2.2 Instrumental.

Energy dispersive spectroscopy (EDS) analysis was performed on either an FEI/Philips XL-30 Field Emission ESEM or a Sirion scanning electron microscope (SEM) with a working distance of 10 mm. Focused Ion Beam (FIB) analysis was performed on an FEI Helios Nanolab 600 with a 30 keV Ga ion beam. Raman spectra were acquired with 514 nm excitation on a Renishaw inVia Raman microprobe system with a Leica 50X objective (NA=0.75), power of ~12 mW at sample, and an integration time of 10 s. Raman spectra of the matrix were acquired once for each temperature exposure condition, except 50⁰C. Raman spectra of samples exposed at 50 °C were acquired a minimum of 3 times from different samples which had each been exposed at 50⁰C on different days. Raman spectra of unidentified IMCs exposed at various temperatures were acquired a minimum of 2 times.

XPS spectra were acquired on a Kratos Axis Ultra equipped with a monochromatic 120 W Al source. Survey scans (range of 5 eV to 1400 eV) were performed with a pass energy of 80 eV; O 1s and V 2p spectra were acquired simultaneously (range of 510 eV to 540 eV) with a pass energy of 20 eV. Samples were transferred from controlled environments to the XPS chamber under ambient conditions as quickly as possible. All
spectra were calibrated with the 284.6 eV C 1s signal. The data were analyzed using CasaXPS software. Mixed Lorentzian-Gaussian (30% Lorentzian) fitting was performed on the O 1s and the V 2p peaks. The constraints used for the fitting of the V 2p peaks (Table 6.1) were established based on literature values for V$_2$O$_5$ and VO$_2$[35], while the constraints used for fitting the O 1s peaks (Table 6.1) were based on literature values for vanadium oxides[35] and aluminum oxide[36]. For V 2p signal fitting, the area ratio of V 2p$_{3/2}$ to V 2p$_{1/2}$ was set as 2:1. For each sample, the XPS spectra were collected at two different positions.

NMR spectra ($^{51}$V) of 4.0 mM vanadate with a pH of 9.2 at 30, 50, and 70 °C were collected using a Bruker DRX 500MHz superconducting magnet to identify temperature dependent vanadate species changes. A 5 mm detection probe with a 90° pulse duration of 55 µs was used. Spectra were collected with an accumulation of 1024 transients. The spectra window was 66006 Hz with an acquisition time of 0.03 s and relaxation delay of 0.02 s. The $^{51}$V chemical shift was referenced to external pure liquid VOCl$_3$ ($\delta^{51}$V=0ppm).

Electrochemical Impedance Spectroscopy (EIS) was carried out in a 0.1M NaCl solution at room temperature using a Gamry Reference 600 employed with a standard 3-electrode setup. A saturated calomel electrode (SCE) served as the reference electrode and Pt mesh as the counter electrode. EIS spectra were collected from 10 kHz to 10 mHz using a 10 mV amplitude sinusoidal voltage perturbation superimposed on a direct current potential set as the open circuit potential. Spectra were collected at a rate of 7 points per decade, and each experiment was replicated 2 times.
6.3 Results

6.3.1 NMR Analysis

To determine vanadate species present in the 4.0 mM vanadate solution at various temperatures, *in situ* temperature-controlled NMR spectra were acquired of the pH-adjusted solution at 30, 50, and 70 °C and shown in Fig. 6.1. At 30 °C, two chemical shifts were observed at -539.6 and -565.49 ppm and were determined to be HVO$_4^{2-}$ ($V_1$) and HV$_2$O$_7^{3-}$ ($V_2$), respectively[37]. The fraction of $V_2$ was very small at 30° C (~9%) and appeared to decrease with increasing temperature, with no visible peak in the spectrum acquired at 70 °C. However, when the sample was re-cooled to 30 °C from 70 °C, the peak attributable to $V_2$ reappeared and its fraction was the same as that determined in the original spectrum acquired at 30 °C. The chemical shift attributed to $V_1$ moved about 2.3 ppm lower as the temperature increased to 70 °C, but it also returned to its original position when the sample was returned to 30° C.

6.3.2 Raman Analysis

Raman surface analysis was performed on the matrix and on unidentified IMCs of samples exposed for 60 min in 4.0 mM NaVO$_3$ at 10, 30, 50, 70 and 80° C. Fig. 6.2 shows spectra of the matrix after exposure at the various temperatures. The wide band between 700 and 980 cm$^{-1}$ dominating the spectra of samples exposed at 70 and 80 °C can be attributed to polymerized vanadate[19]. In general, the results show an increase in polymerized vanadate on the matrix surface with increasing temperature, with little if any evidence of the presence of polymerized vanadate on samples immersed at 10, 30 and 50° C. It should be noted that control spectra of untreated AA2024 revealed that the
untreated matrix also produces a very weak band in the range from 725 to 1000 cm$^{-1}$. Fortunately, in addition to being exceptionally weak, the band produced by the untreated matrix (most likely due to Al$_2$O$_3$) has a different shape than that produced by polymerized vanadate, making it possible to distinguish between the two overlapping bands. Analysis of samples exposed at 50 °C repeatedly produced spectra weaker than those from samples exposed at 10 and 30° C. In addition to the spectra of the exposed matrix shown in Fig. 6.2, spectra were also acquired of IMCs on the same samples. The specific identity of the IMCs analyzed could not be obtained with the Raman microprobe, but it is noteworthy that a similar trend was present on IMCs. The quantity of polymerized vanadate increased with increasing temperature. Perhaps significantly, the 700-980 cm$^{-1}$ band arising from spectra of exposed IMCs indicated the presence of polymerized vanadate at all temperatures; it was weak but definite for IMCs exposed at 10, 30 and 50 °C and exceptionally strong for IMCs exposed at 70 and 80° C.

6.3.3 XPS Analysis

XPS analysis was undertaken on two types of samples exposed to 4.0 mM NaVO$_3$ at 80 °C for 60 min. After exposure, rinsing and air drying, samples were placed in either an argon gas environment or a desiccator. These two samples produced distinctly different spectra as can be seen in Fig. 6.3 A. The sample kept in dry air (desiccated) produced a sharp O 1s peak with maximum intensity at 530.4 eV and a shoulder observed at a slightly higher binding energy, a somewhat broad V 2p$_{1/2}$ peak with maximum intensity at 525.1 and a sharp V 2p$_{3/2}$ at 517.4 eV. The sample kept in argon produced a more complex spectrum, with broader peaks and more shoulders. In general the sample
in argon produced an O 1s peak with its maximum value at 532.0 eV and a shoulder at lower binding energy, a broad V 2p\textsubscript{1/2} peak with maximum intensity at 524.0 eV, and a somewhat broad V 2p\textsubscript{3/2} with a maximum at 516.8 eV. Using the constraints noted in the Experimental section, a mixed Gaussian-Lorentzian fit provided the fitted peaks noted in Table 6.2 and shown in Fig. 6.3 B and Fig. 6.3 C.

6.3.4 SEM/EDS Analysis

Fig. 6.4 shows SEM images of samples immersed in DI water at 50 and 70 °C for 60 min. Fig. 6.4 A and B present full surfaces view of the matrix and surrounding IMCs, while Fig. 6.4 C and D present magnified views of IMCs. As can be readily seen in Fig. 6.4 B, considerable localized corrosion and trenching around IMCs was present after 60 min at 70°C. The magnified image in Fig. 6.4D displays the trenching morphology observed after exposure at 70 °C at an AlCuFeMn(Si) particle. The color contrast displayed in the SEM images of the AlCuFeMn(Si) particle shown in Fig. 6.4D combined with the cracked nature of the trenched area suggest the presence of hydroxide between the particle and matrix. The cracks are most likely due to dehydration caused by the low pressure of the SEM chamber. What remains of the IMC shown in Fig. 6.4D appears to have undergone dealloying, as indicated by the porous texture on its surface. EDS analysis of this AlCuFeMn(Si) particle indicated a decreased Al content of ~18 wt.%, whereas the typical weight percent of Al in an AlCuFeMn(Si) particle was found to range from 50 to 80 wt.%. Similar trenching is not as obvious on the full surface exposed at 50 °C (Fig. 6.4A), however, a magnified view of an IMC (Fig. 6.4C) reveals trenching at 50°C, also.
Fig. 6.5 shows SEM images of samples immersed in 4.0 mM NaVO₃ at 10, 30, 50, and 70°C. For samples exposed at 50 °C and below, no obvious localized corrosion such as trenching was observed on either the noble AlCuFeMn(Si) IMCs or the active S-phase, which displayed dealloying or dissolution after 60 minutes at all temperatures in the absence of NaVO₃. Slight discoloration surrounding S-phase, however, suggests the possible initiation of trenching at 50 °C (Fig. 6.5E). Likewise, no obvious localized corrosion is observed on the sample exposed at 70 °C (Fig. 6.5D), however, a magnified view of an S-phase particle (Fig. 6.5F) reveals some corrosion at the edge of the particle. EDS analysis detected no vanadium on S-phase particles exposed at temperatures of 50 °C and lower. EDS analysis of S-phase particles exposed at 70 °C revealed a very small peak for vanadium, while analysis of S-phase exposed at 80 °C (Fig. 6.6) resulted in a strong, measureable peak for vanadium, which is about 1.5 wt.% Similar to the samples exposed at 70°C, corrosion was present at the edge of S-phase particles, and, not surprisingly, it appeared to be more pronounced on samples exposed at 80°C. Even at this high temperature, however, no corrosion was observed at the AlCuFeMn(Si) particles. EDS mapping over an area containing an S-phase particle exposed at 80 °C (Fig. 6.6) indicates that vanadium was not uniformly distributed over the entire surface; vanadium was more concentrated on the S-phase. Also of note is the color of samples exposed in aqueous vanadium at both higher temperatures. Visual inspection of samples exposed at 70 °C showed a light yellow surface after 60 minutes of exposure which became darker after exposure to room air. A similar shade of yellow was visually
observed on the samples treated at 80\(^0\) C, however, it was more intense than that noted on the samples exposed at 70\(^0\) C.

6.3.5 FIB Analysis

FIB was employed to study the oxide film on S-phase and AlCuFeMn(Si) particles exposed at 80 °C in 4.0 mM NaVO\(_3\). Cross sections of these samples are shown in Fig. 6.7. (The Pt present in Fig. 6.7A was sputtered onto the sample after immersion but before FIB analysis to prevent damage from the ion beam.) Trenching with a width of ~800 nm was observed along the edges of the rounded S-phase particles (Fig. 6.7A). EDS analysis of the remaining S-phase in the cross-section indicated a Mg concentration of 7.3 wt.% which is approximately the same as was found in uncorroded S-phase. FIB also revealed a thin dark region with a thickness of ~70 nm surrounding the S-phase particle, most likely due to dealloying and vanadate film formation. Fig. 6.7B shows the FIB cross-section analysis of an AlCuFeMn (Si)/matrix interface. No attack is observed at the interface or on the particle.

6.3.6 EIS analysis

EIS was conducted on samples treated in 4.0 mM vanadate at 80\(^0\)C and samples treated in DI water at 80 °C to study corrosion inhibition and determine whether vanadate provides any residual protection. As shown in Fig. 6.8, samples treated in vanadate displayed higher total impedance than those treated in DI water only. The polarization resistance (R\(_p\)) increased by a factor of 4 after vanadate treatment, compared to that in DI water. Aging in dry air of vanadate-treated samples further increased R\(_p\), which was about 7.5 times larger than the R\(_p\) value of samples treated in DI water.
6.4 Discussion

Past work with vanadate as corrosion inhibitors on aluminum alloys has emphasized the importance of the speciation in solution[17–19,23,24]. Although speciation is somewhat concentration dependent, pH is the primary determining factor with tetrahedrally coordinated species found at higher pH values and octahedrally coordinated species found at lower pH values at room temperature. In short, at ambient temperatures, exposure of aluminum alloys to aqueous solutions of tetrahedrally coordinated vanadate provides corrosion inhibition, while exposure to aqueous solutions of octahedrally coordinated vanadate does not. As this work adds the additional parameter of temperature control, it was first necessary to establish the speciation in the 4.0 mM NaVO₃ solution at various temperatures. As noted in the results section, NMR analysis determined that at all temperatures used for this work the speciation of vanadate in the pH adjusted solutions was either HVO₄²⁻ or HV₂O₇³⁻ (V₁ or V₂, respectively), both tetrahedrally coordinated compounds. V₁ predominated at all temperatures and was, most likely, the only species present at temperatures ≥70⁰ C. In addition to the noted diminution and disappearance of the peak attributed to V₂ as temperature increased, thermodynamic calculations also support the greater stability of V₁ versus V₂ at higher temperatures[38]. The reactions between these two vanadate species can be described by the following equation:

\[ \text{H}^+ + 2\text{HVO}_4^{2-} \leftrightarrow \text{HV}_2\text{O}_7^{3-} + \text{H}_2\text{O} \]  

(Equation 6.1)

The equilibrium constant can be described by the following equation
\[
\log K = \log \left( \frac{HV_2O_7^{3-}}{H^+ \times (HVO_4^{2-})^2} \right) = \log \left( \frac{HV_2O_7^{3-}}{(HVO_4^{2-})^2} \right) + \text{pH} \quad \text{(Equation 6.2)}
\]

The NMR data has shown that the dominant species is HVO_4^{2-}, which makes up about 91\% at 30 °C, and it is assumed to be 4mM in this work for simplification. The equation 6.2 can be written as

\[
\log K = \log \left( \frac{HV_2O_7^{3-}}{HVO_4^{2-}} \right) + \text{pH} + 2.40 \quad \text{(Equation 6.3)}
\]

The log K value are obtained from reference [38], and the pH of the solution is 9.2. The calculated logarithm ratios of HV_2O_7^{3-} to HVO_4^{2-} are -0.5, -1.4 and -1.9 at 0, 25 and 50 °C respectively. The thermodynamic analysis indicates that the ratio of HV_2O_7^{3-} to HVO_4^{2-} HVO_4^{2-} decreases with temperature and HV_2O_7^{3-} is more stable at high temperature.

The origin of the 2.3 ppm shift in the V_1 peak at higher temperatures is not known but is mostly like due to a decrease in intermolecular interactions at higher temperatures leading to additional shielding[39]. The reappearance of the peak attributed to V_2 and the reversal of the 2.3 ppm shift when the solution was returned to the original 30 °C temperature indicate that the processes that caused the changes observed when the temperature was increased to 70 °C were reversible. It can, therefore, be reasonably assumed that the desired tetrahedral coordination was present at each of the exposure temperatures.

Raman data established the presence of polymerized vanadate on the surfaces exposed at each temperature, albeit with little evidence of vanadate on the matrix at lower temperatures, but clear evidence of the presence of vanadate on IMCs exposed at all
temperatures, including lower temperatures. Furthermore, the intensity of the band attributed to the transparent polymerized vanadate film increased with increasing exposure temperature on both the matrix (Fig. 6.2) and IMCs. In addition to the likelihood that higher temperatures increased the kinetics of the polymerization process, a further discussion of how temperature might have played a role in film formation is provided below in the discussion of the XPS data. Because the intensity of the scattering is theoretically linear with the amount of polymerized vanadate in the sampled volume, it can be concluded that the film thickness or density increased with increasing exposure temperature on both the matrix and the IMCs. The Raman spectra displayed significant background (which was not removed) making quantitative measurements of the polymerized vanadate difficult. However, by integrating peak areas with imposed baselines between 600 and 1100 cm\(^{-1}\), it can be said with certainty that the film on the matrix exposed at 80 °C contained over 10 times as much polymerized vanadate as the matrix exposed at 10 °C. Similar calculations from the spectra of the film formed on IMCs (not shown) at different temperatures are not directly comparable since the identity of the IMCs were unknown, but it can be fairly said that the temperature effect on the intensity of the spectra of IMCs was similar to that observed on the matrix; on all analyzed IMCs the intensity of the band attributable to polymerized vanadate increased with temperature. Additionally, this band was stronger when originating from an IMC than from the matrix for each temperature, although the difference in intensity for IMC versus matrix decreased in magnitude as temperature increased. This implies that the
vanadate film is more likely to form on IMCs than on the matrix at all temperatures, especially at lower temperatures.

As noted above, the EDS data also support an increased presence of vanadium with increasing temperature (no vanadium was detected on samples exposed at 50 °C or lower, a very small amount at 70 °C and easily measureable amounts at 80 °C). It is difficult to determine if the lack of evidence of vanadium from the EDS analysis of surfaces exposed at 10, 30 and 50 °C was due to a true absence of vanadium or if it resulted from limited sensitivity. It is possible that vanadate was present (and inhibiting corrosion) while the samples were immersed in the 4.0 mM NaVO₃ at all temperatures, but that the majority of it was rinsed away before the EDS analysis was performed. Iannuzzi et al. found that vanadate provided corrosion inhibition on AA2024 while the samples were immersed in aqueous NaVO₃, but that the inhibition effect disappeared when the same samples were removed, rinsed and placed in a corrosive environment without vanadate [18].

The above Raman and EDS data clearly establish that, under the temperature-controlled exposure conditions herein, vanadate coverage on AA2024 increases as exposure temperature increases and that coverage on IMCs is greater than coverage on the matrix at each temperature. Enhanced coverage on IMCs and accompanying inhibition is in agreement with previous work which indicated that vanadate inhibition is more closely tied to its interactions with IMCs, notably cathodic inhibition at IMCs, than with the interactions on the matrix[19,23,25]. Additionally, simple visual observation of the yellow film formed on samples exposed at 70 and 80 °C clearly indicated the presence of a thicker film with increasing exposure temperature. It should be noted that, with
aging, visual inspection also showed an increase in the intensity of the yellow color on films treated at the higher temperatures.

XPS data performed on samples exposed at 80⁰ and then immediately stored under two different conditions provide strong evidence that vanadium is reduced during the film formation (Fig. 6.3). Samples stored in the desiccator (dry air) were exposed to oxidizing conditions whereas samples stored under argon would not be exposed to oxidizing conditions and, therefore, the original oxidation states of vanadium established on the sample surface might be expected to be maintained under argon. Fig. 6.3A displays a shift to higher binding energy values for O 1s (530.4 to 532.0 eV) and a shift to lower binding energy values for V 2p₃/₂ (517.4 to 516.8 eV) for samples kept in argon versus samples kept in air. Both the O 1s and the V 2p₃/₂ peaks resulting from the sample kept in argon clearly display broad, unsymmetrical peaks indicating the presence of more than one species. The binding energy values at maximum intensity of the O 1s (530.4 eV) and the V 2p₃/₂ (517.4 eV) peaks for the sample kept in air are in agreement with binding energy values for vanadium oxides with vanadium in a 5+ state[35]. The shoulder on the O 1s peak (with a fit value of 532eV) for the sample kept in air (Fig. 6.3C) can be attributed to oxygen in Al₂O₃[36]. Fitting of the O 1s peak for the sample kept in argon resulted in two peaks with binding energies similar to the two fitted O 1s peaks for the sample kept in air (530.4 and 532.2 eV). These peaks are attributed to O 1s in VₓOᵧ and Al₂O₃, respectively[35,36]. Silversmit et al. noted that the range of O 1s binding energy values for vanadium oxides ranging from V⁵⁺ to V³⁺ is only 0.3 eV[35]. Therefore, differences in the oxidation state of vanadium cannot easily be determined using O 1s
values. However, Silversmit et al. also showed that the range of V 2p3/2 binding energy values for vanadium oxides ranging from V^{5+} to V^{3+} is more revealing with a difference of over one eV. As is expected, vanadium oxides with vanadium in a higher oxidation state display higher binding energy. Fitting of the V 2p3/2 peak originating from the sample stored in argon resulted in two distinct peaks at 517.2 and 515.8 eV, attributed to V^{5+} and V^{4+}, respectively[35,40]. Fitting of the V 2p3/2 peak for the sample stored in air also revealed two peaks at similar binding energy values, however, the peak attributable to V^{5+} is clearly dominant and only a small peak is attributable to V^{4+}. These data combined with the other analyses discussed above indicate that the sample stored in argon-contained vanadate with vanadium in both a 5+ and a 4+ state. Likewise, it suggests that the sample stored in air-contained vanadate with vanadium predominantly in a 5+ state. Based on the fitting data in Fig. 6.3, the ratio of V^{5+} to V^{4+} was 3:2 for the sample stored in argon and 22:1 for the sample stored in air. The lack of V^{4+} present in the sample stored in air can be attributed to oxidation of V^{4+} by molecular oxygen in air. Since the sample stored in argon is more likely to contain a film representative of the original exposure process, it is reasonable to assume that the adsorption/polymerization process involves and is possibly enhanced by the reduction of vanadium. Furthermore, if reduction does indeed enhance the polymerization of vanadate on a metal surface, the presence of active metals such as Mg in IMCs could provide an explanation for the enhanced presence of vanadate on IMCs. Additionally (or alternatively), the cathodic nature of dealloyed S-phase would also be expected to lead to enhanced reduction of vanadate. The literature appears to be absent of a discussion of the polymerization of
vanadate on a metal surface, however, the presence of vanadium in both the 4+ and 5+
state clearly provides for electrical conductivity in the film[41], which presumably would
be advantageous during the polymerization process. Furthermore, the presence of
vanadium in two oxidation states during the polymerization process can perhaps be
related to the redox mediation and enhanced growth rates afforded by Fe(CN₆)³⁻ in the
formation of the mixed chromium oxide (Cr³⁺/Cr⁶⁺) contained in chromate conversion
coatings[42].

Of note in the XPS data are the O 1s signals originating from the two samples stored
under different conditions. The ratio of oxygen from Al₂O₃ to that of oxygen in VₓOᵧ is
much larger for the sample stored in argon. A clear explanation for this occurrence does
not appear obvious, however, one possibility is that as the mixed valence oxide is
oxidized to a single valence state (sample stored in air), the structure of the film changes
resulting in a thicker film, thereby hindering analytical access to the underlying Al₂O₃
film. Alternatively, perhaps the vanadate on the surface of the sample stored in argon was
not yet fully polymerized but rather contained some polymerized vanadate and some
monovanadate units (in both the 4+ and 5+ states) that did not fully cover the surface,
thereby exposing more Al₂O₃ for analysis.

The latter scenario suggests that at least some (possibly most) of the actual
polymerization process proceeds not in solution, but after exposure to air, during the
subsequent oxidation of monovanadate in the 4+ state. This scenario is not unlike the
regeneration of a single valence V⁵⁺ oxide upon oxidation of a mixed valence (V⁵⁺/V⁴⁺)
oxide by gaseous O₂ during the employment of vanadium oxides as catalysts for
oxidative dehydrogenation reactions, which is dependent on the presence of monovanadate species. Cheng et al. described this catalytic process as involving the insertion of an O\textsubscript{2} molecule at a V\textsuperscript{4+} site to form a cyclic VO\textsubscript{2} peroxide, which in turn leads to oxidative dehydrogenation of a hydrocarbon such as propane. A similar scenario could take place between two monovanadate units (rather than a monovanadate unit and propane), leading to the polymerization of vanadate[43].

Although this scenario is speculative at this point, in addition to similar reactions in vanadate catalysts, there is experimental and theoretical evidence to support the occurrence of a similar process at the surface of a metal electrode exposed to aqueous vanadate. In considering this scenario, it is important to distinguish between two types of O\textsubscript{2} reduction. First, there is the typical ORR occurring at the metal electrode surface at open circuit potential (OCP) in an aerated solution, originating from the oxidation of the metal surface (and possibly some V\textsuperscript{5+} contained in adsorbed vanadate). Second, there is the reduction of O\textsubscript{2} occurring on a dry metal electrode previously exposed to vanadate, in which case the source of electrons would be the oxidation of V\textsuperscript{4+}. The second scenario clearly cannot occur without the presence of V\textsuperscript{4+}, which requires the reduction of V\textsuperscript{5+} at the electrode during exposure in the aqueous solution. As supported by the above XPS data and previously established by other researchers, vanadate is a moderately strong oxidizing agent that is reduced on metal surfaces under conditions similar to these experimental conditions[18,44]. The reduction of vanadate on a metal electrode in aerated aqueous solution, however, will be in competition with the reduction of dissolved O\textsubscript{2} (the ORR). Fig. 6.9 is a plot of the limiting current that can be expected from the ORR
in DI water calculated as a function of the diffusivity of dissolved $O_2$ (increases with temperature)[45], the concentration of dissolved $O_2$ (decreases with temperature)[46], and diffusion thickness[47]. As can be seen, this value reaches a maximum at around 55 oC and then drops sharply with increasing temperature. In other words, the ORR reaction at a sample of AA2024 in aqueous NaVO$_3$ at 80 oC is far less likely to compete with the reduction of vanadate, whereas at 50 oC the ORR is likely to be in strong competition with the reduction of vanadate. This, in turn, could lead to enhanced coverage of V$^{4+}$ on surfaces exposed at higher temperatures. The subsequent oxidation of these V$^{4+}$ units (by either dissolved $O_2$ during the exposure process or by gaseous $O_2$ upon exposure to air) could then lead to enhanced polymerization via the path described above. This speculative scenario would explain the higher ratio of Al$_2$O$_3$ to V$_x$O$_y$ determined by XPS analysis found on the sample stored in argon after exposure at 80 oC as the monovanadate units would be less likely to cover the underlying Al$_2$O$_3$ on the matrix. Since the limiting current for the ORR reaches its maximum at 55 oC, it would be expected to compete with the reduction of vanadate and thereby impede the formation of V$^{4+}$ oxides and the subsequent polymerization of vanadate. Iannuzzi found support for competition between the ORR and the reduction of vanadate on both AA2024 and Cu surfaces in aqueous vanadate solutions[18]. All of this is in agreement with the reproducible anomalous low coverage of polymerized vanadate seen on samples exposed at 50 oC, as determined with Raman analysis. Lastly, this scenario would explain the increase in visual yellow intensity observed with aging on the samples treated at 70 and 80 oC and the enhanced polymerization found in IMCs.
The EDS/SEM data provide strong evidence that not only does vanadate provide corrosion inhibition but that an increase in exposure temperature in the presence of NaVO₃ leads to increased corrosion inhibition. This is evidenced by the corrosion protection it provided at the high temperatures, which lead to significantly increased corrosion activity in the absence of NaVO₃. Not surprisingly, the EDS results of samples exposed in DI water (without the presence of vanadate) demonstrate that localized corrosion is enhanced as temperature increases (Fig. 6.4). SEM images of samples exposed in DI water at 10 and 30 °C (not shown) also presented evidence of significant attack at IMCs, albeit less than that on samples exposed at 50 and 70 °C. With the addition of NaVO₃ during exposure, less attack was observed at the IMCs at each temperature. This is demonstrated by a comparison of Fig. 6.4 B and Fig. 6.5D (without and with NaVO₃, respectively) which shows that localized corrosion was inhibited by the addition of vanadate at 70 °C. At 70 °C, trenching was observed, but it was not as severe and was present only at the very edge of an S-phase particle when vanadate was present in the exposure solution. (Fig. 6.5F) The results observed on the sample exposed at 80 °C (Fig. 6.6) provide further evidence of vanadate’s ability to inhibit corrosion at high temperatures; compare the severe trenching at a AlCuFeMn(Si) particle exposed in DI water at 70 °C (Fig. 6.4D) to the virtually pristine AlCuFeMn(Si) particles shown in Fig. 6.6 (exposure in NaVO₃ at 80⁰ C). The enhanced vanadium present on S-phase particles (Fig. 6.6) suggests that the inhibition exhibited at high temperatures originates from a mechanism similar to that discussed in previous work at ambient temperatures, notably an inhibition of the ORR at copper-rich IMCs[18,25]. Specifically, the oxide on Cu-rich
IMCs has been found to support the formation of polymerized vanadate at a level greater than that of the matrix[19]. Similarly, enhanced amounts of vanadium present on S-phase particles might be attributed to the reduction of vanadate by the active Mg or Al in S-phase resulting in reductive adsorption, producing a mixed valence vanadate oxide ($V^{4+}/V^{5+}$). A similar process was observed by Nazarov et al., wherein reduction of vanadate by zinc resulted in a vanadate-based film[16].

The FIB data provide additional insight into vanadate interactions with IMCs. Although the FIB image in Fig. 6.7A (80 °C exposure) shows clear trenching surround the S-phase particle, it is not clear whether this arose from dissolution of the IMC or from dissolution of the matrix surrounding the IMC (or a combination of both). Because EDS elemental analysis on the cross-section of S phase, however, indicated that the percentage of Mg in the corroded S phase was approximately the same as that in uncorroded particle, dissolution of the matrix is the most likely origin of the trenched volume. This suggests that the exposure in NaVO$_3$ prevented or inhibited the dissolution of Mg from the IMC in addition to the likelihood that it inhibits the ORR on the S-phase surface. The lack of attack in the area surrounding the AlCuFeMn(Si) particle after exposure at 80 °C is further evidence of the inhibiting effect.

The EIS data of samples treated at 80 °C (Fig. 6.8) provide evidence that treatment at high temperatures provides considerable corrosion inhibition. This is particularly noteworthy when one considers that the only source of vanadate was the vanadate film present on the treated sample which had been thoroughly rinsed before placement in the NaCl solution for EIS analysis. Previous work indicated that although vanadate provided
corrosion inhibition on AA2024 surfaces when the surfaces were analyzed in aqueous vanadate solutions at room temperature, the residual vanadate films on these surfaces (present after rinsing or rinsing combined with aging) did not provide corrosion inhibition in subsequent polarization experiments performed in aqueous NaCl without the presence of dissolved NaVO$_3$ [18,19]. If the reductive adsorption of vanadate is instrumental in providing enhanced corrosion inhibition, as discussed above, the residual inhibition displayed by the samples treated at 80 °C can be viewed as evidence that the higher temperatures lead to more reductive adsorption. Furthermore, the increased impedance observed on the aged samples is in agreement with increased polymerization arising from the insertion of oxygen via the oxidation of V$^{4+}$ vanadate units.

The corrosion morphology and EIS measurements clearly demonstrate that the vanadate could provide good inhibition of the localized corrosion. Its inhibition mechanism at high temperature is closely related to the polymeric vanadate film, which is promoted by the chemical reduction of vanadate by Al or Mg and could provide residual protection. This mechanism is similar to that of chromate, which could be reduced by Al or Mg and form a protective compact layer on the surface. However, the inhibition efficiency of vanadate at high temperature is not as good as that provided by chromate, especially for the active S phase particles. Fig. 6.10 Corrosion morphology of IMCs (A, AlCuMnFe particles; B, S phase particle) after 1 hour exposure in 0.1M NaCl+1mM CrO$_4^{2-}$ at 70 °C shows the corrosion morphology of AlCuMnFe and S phase particles after 1 hour exposure in 0.1 M NaCl with 1 mM K$_2$CrO$_4$. No localized corrosion is observed, but the blurred surface indicates that chromate conversion coating might form
on the surface. Compared to corrosion morphology associated with S phase and AlCuMnFe particles in vanadate solution at same condition, inhibition of vanadate on S phase particles is not as good as chromate, while it is comparable for AlCuMnFe particles. All these results demonstrate that vanadate is a strong inhibitor at high temperature, but not as strong as chromate.

6.5 Conclusions

1. Exposure of AA2024 to aqueous tetrahedrally coordinated NaVO₃ results in the formation of a vanadate film on the surface of the alloy. The quantity and location of film formation is dependent on the temperature of the exposure solution. At low temperatures (10⁰, 30⁰ and 50⁰ C), the film is found primarily on IMCs with little or no presence on the matrix. At high temperatures (70⁰ and 80⁰ C) the film is found on both the matrix and IMCs. An increase in the temperature of the exposure solution leads to an increase in the amount of film formed on both IMCs and the matrix. At all exposure temperatures, vanadate film formation was enhanced at IMCs versus the matrix. This effect was more pronounced at low temperatures.

2. Analysis of the film formed on both the IMCs and the matrix (when solution exposure was followed by exposure to air) showed that it consists primarily of polymerized vanadate with the majority of vanadium in the 5⁺ state. Analysis of the film formed after solution exposure but with minimal subsequent exposure to air suggested the presence of a non-continuous film wherein the ratio of $V^{5⁺}:V^{4⁺}$ was 3:2.
3. It is proposed that polymerization of vanadate oxide can proceed through the insertion and reduction of O\(_2\) at V\(^{4+}\) centers (both in solution and in air during aging). Therefore, the reduction of V\(^{5+}\) on the metal surface during exposure enhances subsequent polymerization. Assuming that the ORR and reduction of V\(^{5+}\) occur competitively at the metal surface during exposure, the theoretical temperature-dependent limiting current for the ORR suggests that reduction of V\(^{5+}\) to V\(^{4+}\) will be maximized at higher temperatures. This temperature effect is proposed as a reason for enhanced film coverage at higher temperatures (low ORR current) and exceptionally low coverage at 50\(^0\) C, the temperature at which the ORR is maximized.

4. In addition to enhanced reductive adsorption of vanadium due to high temperatures, it is expected that high temperatures enhance the kinetics of film formation and/or surface adsorption.

5. In addition to providing corrosion inhibition at IMCs exposed at low temperatures, vanadate provides corrosion inhibition at IMCs exposed at high temperatures, where attack at IMCs is especially extensive without the presence of an inhibitor. At all exposure temperatures, in the presence of aqueous NaVO\(_3\), attack at AlCuFeMn(Si) particles was essentially non-existent and the dealloying of S-phase was greatly reduced.
Fig. 6.1 NMR spectra of 4mM NaVO$_3$ with a pH of 9.2 as a function of temperature.
Fig. 6.2 Overlaid Raman spectra of matrix of AA2024 after exposure in 4.0 mM NaVO$_3$ at: (a) 80 °C, (b) 70 °C, (c) 30 °C, (d) 10 °C, (e) 50 °C.
Fig. 6.3 XPS spectra and fitting data of two samples after exposure in 4.0 mM NaVO$_3$ at 80$^\circ$ C: (A) original XPS data; (B) fitting data for sample stored in argon environment; (C) fitting data for sample stored in dried air. Raw data, black; Baseline, gold; Fitting, red.
Fig. 6.4 Corrosion morphology after exposure in DI water. (A) AA2024 at 50°C; (B) AA2024 at 70°C; (C) unidentified IMC on AA2024 at 50°C; (D) AlCuFeMn(Si) particle at 70°C.
Fig. 6.5 Corrosion morphology of AA2024-T3 after exposure in 4.0 mM NaVO₃. (A) at 10°C; (B) at 30°C; (C) at 50°C; (D) at 70°C; (E) S-phase on AA2024 at 50°C; (F) S-phase on AA2024 at 70 °C.
Fig. 6.6 Corrosion morphology and EDS elemental mapping of S phase particle in AA2024 after 60 min exposure in aqueous 4.0 mM NaVO₃ at 80 °C.
Fig. 6.7 Secondary electron microscopy of FIB cross-sections from AA2024 samples after exposure in 4.0 mM NaVO$_3$ at 80 °C. (A) S phase particle; (B) AlCuFeMn(Si) particle;
Fig. 6.8 EIS in 0.1 M NaCl without any inhibitor at room temperature after 1 h treatment in 4mM NaVO$_3$ and DI water at 80 °C.
Fig. 6.9 Limiting current density of the ORR in DI water as a function of temperature.
Fig. 6.10 Corrosion morphology of IMCs (A, AlCuMnFe particles; B, S phase particle) after 1 hour exposure in 0.1M NaCl+1mM CrO$_4^{2-}$ at 70 °C.
Table 6.1  Binding energy constraints used for Gaussian-Lorentzian fitting of XPS peaks.

<table>
<thead>
<tr>
<th>Species</th>
<th>V 2p$_{3/2}$ (V$^{2+}$)</th>
<th>V 2p$_{3/2}$ (V$^{4+}$)</th>
<th>V 2p$_{1/2}$ (V$^{2+}$)</th>
<th>V 2p$_{1/2}$ (V$^{4+}$)</th>
<th>O 1s (V$_x$O$_y$)</th>
<th>O 1s (Al$_2$O$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fit Constraint (eV)</td>
<td>517.2±0.1</td>
<td>515.8±0.2</td>
<td>524.5±0.1</td>
<td>523.2±0.2</td>
<td>530.0±0.5</td>
<td>532.0±0.5</td>
</tr>
</tbody>
</table>
Table 6.2 Values of Gaussian-Lorentzian fit (binding energy) for samples exposed at 80 °C and subsequently stored in either an argon environment or a dry air environment. Fit is shown in Fig. 6.3 B and C. *V_2O_5 and VO_2 literature values were used to establish the presence of V^{5+} and V^{4+}, respectively.[35].

<table>
<thead>
<tr>
<th></th>
<th>Argon Environment</th>
<th>Air Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>Al_2O_3 fit</td>
<td>V_xO_y fit</td>
</tr>
<tr>
<td></td>
<td>531.9 eV</td>
<td>530.5 eV</td>
</tr>
<tr>
<td>V_2O_5 fit*</td>
<td>532.1 eV</td>
<td>530.6 eV</td>
</tr>
<tr>
<td>V 2p 1/2</td>
<td>524.5 eV</td>
<td>523.6 eV</td>
</tr>
<tr>
<td>V 2p 3/2</td>
<td>517.2 eV</td>
<td>516.1 eV</td>
</tr>
<tr>
<td>V_2O_5 fit*</td>
<td>524.9 eV</td>
<td>523.5 eV</td>
</tr>
<tr>
<td>VO_2 fit*</td>
<td>517.5 eV</td>
<td>516.2 eV</td>
</tr>
</tbody>
</table>
References


Chapter 7 Fast Fourier Transform of Potential Transients to Interfacial Characteristics of Intermetallic Phases Present in AA2024-T3

7.1 Introduction

AA2024-T3 has a heterogeneous microstructure, and its localized corrosion is closely related to the second phase particles present in the alloy [1–7]. The localized corrosion rates not only depend on the corrosion potential difference, but also on the electrochemical kinetics of the reactions occurring on intermetallic compound (IMC) particles [3]. For example, although Al\textsubscript{3}Zr is much more noble than the matrix, cathodic reaction kinetics are very slow and its effect on the localized corrosion is negligible [3]. Reaction kinetics on IMCs are closely associated with the electrochemical characteristics of surface films [5,8,9]. Surface films also affect the pit initiation behavior of (IMCs) [9–12]. For example, Al\textsubscript{2}CuMg (S phase) shows a higher Volta potential than the matrix in the air, but the potential of the phase becomes lower upon exposure to an aqueous 0.5 M NaCl solution as the surface film breaks down in this environment [12–14]. The consequence of the film damage is dealloying corrosion by selective dissolution of Mg and Al, and subsequent trenching around the particle [15–19]. However, corrosion at Al\textsubscript{2}CuMg particle sites is suppressed by the addition of chromate, which leads to the formation of a compact Cr\textsuperscript{III}-Cr\textsuperscript{VI} mixed hydroxide film [20–22]. Thus, characteristics of
Surface films strongly affect the corrosion initiation and propagation on IMC particles or in the matrix near particles.

Surface film structure and chemistry affect ion and electron transport and determines phase electrochemical behaviour. Surface film properties such as thickness, resistivity and dielectric constant are reflected in measurable electrochemical characteristics such as polarization resistance and capacitance [8,23–26]. Whilst EIS is a powerful tool for attaining interfacial information, the measurement can be lengthy and specific conditions must be met in order to obtain a valid data set [27]. When studying single intermetallic compounds, the system can be relatively unstable and is very sensitive to the surface condition [28]. These issues are particularly acute on active particles such as the S phase, whose surface condition is very dynamic and changes greatly during a typical electrochemical measurement time (Fig. 7.1), which is a violation of the stability criteria for a valid EIS measurement. For this reason, certain measurements like EIS can be erroneous or noisy. Macdonald discussed the acquisition of impedance data through a time-to-frequency transformation method, in which the response signal was recorded after an electrochemical pulse perturbation [29]. This time-domain excitation can be transformed to frequency domain data by a Laplace or Fast Fourier transformation (FFT), to reconstruct an impedance spectrum[30]. The quality of impedance data obtained by the time-to-frequency transformation method depends on sampling period and rate. Advantages of this methods include: short measurement time; elimination of potential drop from solution resistance and no requirement for the system stability [28]. This last point is especially helpful in making measurements of the S phase, whose behaviour is
the most dynamic of all the phases in heterogeneous Al-Cu-Mg alloys exposed to dilute chloride solutions. This method has been successfully used to acquire the impedance spectra of various materials in aqueous solution [28,31] and concrete [32,33].

In this paper, the microcell method, combined with time-to-frequency transformation method, was used to study the interfacial characteristics of IMC particles in 0.1M NaCl and to study the effect of a chromate inhibitor.

7.2 Experimental

7.2.1 Sample and solution preparation

The fabrication and identification of IMCs (Al$_7$Cu$_2$Fe, Al$_{20}$Cu$_2$Mn$_3$, Al$_2$CuMg, Al$_2$Cu) and a matrix phase analog (Al 4wt.%Cu) in AA2024-T3 have been described elsewhere [3]. All of the intermetallic compounds and bulk alloys, were ground to 1200 grit with successively finer SiC papers lubricated with ethanol. Samples were then polished with 1µm diamond paste and non-aqueous lubricant. After polishing, samples were ultrasonically cleaned in ethanol to remove the organic residual and were dried in air. All experiments were carried out immediately after polishing.

A 0.1M NaCl solution was used as an aggressive electrolyte in corrosion experiments. It was prepared using analytical reagent NaCl from Fisher Scientific and DI water (18.2 MΩ·cm resistivity). In same experiments, a chromate solution was used. These chromate solutions were prepared by dissolving 1mM K$_2$CrO$_4$ (chemical reagent grade, purchased from Fisher Scientific) into 0.1M NaCl. In this paper, the term “chromate solution” refers to solutions containing 0.1 M NaCl plus 1 mM K$_2$CrO$_4$. 

213
7.2.2 Fast Fourier transformation of potential transient, and data analysis procedure

In these experiments, a positive current source was used to cause a coulostatic perturbation, according to the current-time graph shown in Fig. 7.2. Open circuit potential (OCP) was measured, and then specific currents were applied to the sample for a few seconds, followed by potential measurement for about 100 seconds. The potential shift caused by the coulostatic perturbation was tens of millivolts above the corrosion potential, and the potential was sampled at intervals of 0.1 or 0.01 second. An example of the potential transient data (for Al 4wt.%Cu) is shown in Fig. 7.3. The sharp potential drop occurred as the current was removed. This was caused by the iR-drop associated with solution resistance between the working electrode and reference electrode. The potential then decreased slowly until the potential of the sample reached the corrosion potential. The potential transition from the continuous slow decrease was closely related to the nature of the surface passive film and electrochemical interface, and only this part of potential transition data was used for data analysis. The electrochemical impedance data was obtained from the following equation[28]:

\[ Z(j\omega) = \frac{K}{I_1} F\{E(t)\} \]  
(Equation 7.1).

In this expression, \(F\) is the time-to-frequency transformation function. The transformation of the potential transient data (2^n points) is performed using Origin® 7.0. \(E(t)\) is the potential transient after charge injection. \(I_1\) is the applied current, and \(K\) is a constant that depends on implementation of Fourier transform [34]. In this work, the relationship between the value of \(K\) and the modulus of impedance \((Z)\) is determined by a
dummy cell with known values of capacitors and resistors following the above experimental an analytical procedures. It is found that $K$ is related to the modulus of impedance ($Z$), and is described by:

$$K = 1.9Z - 5.9$$

(Equation 7.2).

Fig. 7.4 shows the Bode plots of a dummy cell ($R_1 + R_{//}C$) obtained separately by the FFT of a potential transient and a single sine EIS. A comparison shows that they are consistent with one another.

Potential transients of secondary phases commonly in 0.1 M NaCl and chromate solution were collected, and transformed to electrochemical impedance through FFT method. However, due to long fitting time on the large number of points in the original transformed impedance data, 7 representative data points at certain interval were selected for each decade of frequency. EIS data were fitted to an equivalent circuit model using a complex least-squares fitting routine. The Nyquist plots of the data showed a semicircle, which is the characteristic of a simplified Randles circuit. In this work, an equivalent circuit consisting of an electrolyte resistance ($R_s$) in series with a parallel combination of a constant phase element (CPE) and a polarization resistance ($R_p$) (Fig. 7.5 f), was used for fitting. The CPE was used as many samples showed behaviour consistent with a ‘leaky capacitor’ where the phase angle deviated from -90°. The true capacitance ($C$) was obtained from CPE parameters based on the following equation [35]:

$$C = Y_0(\omega_m^\alpha)^{-1}$$

(Equation 7.3)

where $Y_0$ is CPE constant, $\alpha$ is the exponent, and $\omega_m''$ is the frequency at which the imaginary part of the impedance has a maximum value.
7.2.3 Electrochemical polarization measurements

Anodic polarization of IMCs in 0.1 M NaCl and chromate solution were collected using the microcell method, in which the opening of capillary was about 100 µm. All electrochemical experiments were performed using a Gamry Reference 600 with a standard three-electrode setup (saturated calomel reference electrode and platinum wire counter electrode). Anodic polarization measurements were initiated at -0.02V vs. OCP at a scan rate of 2 mV/s after a 60s OCP measurement in 0.1 M NaCl or a 120s OCP measurement in the chromate solution. Each measurement was repeated at least three times. The corrosion rates were obtained by Tafel extrapolation the linear region of cathodic polarization curves to corrosion potential using Echem Analyst™ software.

7.3 Results

Fig. 7.5 a-e shows Nyquist plots of the IMCs and Al 4wt.%Cu in 0.1 M NaCl solution without (red dots) and with 1mM chromate (black triangles) derived from the potential transient by the time-to-frequency transformation. All impedance spectra were plotted at the same scale in Nyquist plots. The total impedance in NaCl is smaller than that in chromate solution, and the data are magnified (inserted figures) in the corresponding figure. For the majority of the samples, the transformed data plotted as a semicircle on the complex plane, indicating a simplified Randles circuit was appropriate for modelling the impedance response. The impedance spectra in each solution were fit based on the equivalent circuit shown in Fig. 7.5 f, and the fitting results are summarized in Table 7.1. For most intermetallic compounds in NaCl solution, the observed behaviour was that of a pure capacitor as indicated by α values close to 1. Exceptions are Al
4wt.%Cu and Al$_{20}$Cu$_2$Mn$_3$, which had $\alpha$ values of around 0.87. The interfacial reactance of all intermetallic compounds in chromate solution were described by a pure capacitor. $C_{eq}$ and $R_p$ are summarized and compared separately in Fig. 7.6 and Fig. 7.7.

Fig. 7.6 shows $C_{eq}$ in 0.1M NaCl (red solid line) and chromate solution (solid black dots). In a NaCl solution, the S phase has the highest $C_{eq}$ at about 350 $\mu$F/cm$^2$. This was followed by Al 4wt.% Cu, Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$. The large capacitance of the S phase is consistent with the large true surface area resulting from the dealloying process. By comparison, in the presence of chromate, capacitances of all samples were strongly reduced by factors ranging from 15 to 25 though Al$_2$CuMg still demonstrated the highest capacitance. It is noteworthy that capacitance of all samples was distributed around a value of about 10 $\mu$F/cm$^2$.

Fig. 7.7 shows the polarization resistance ($R_p$) of each sample in NaCl solution and chromate solution. The red horizontal line represents the resistance in NaCl, while black dots represent the resistance in the chromate solution. Al$_{20}$Cu$_2$Mn$_3$ demonstrated the largest $R_p$ in NaCl solution followed by Al$_2$Cu, Al$_7$Cu$_2$Fe, Al 4wt.% Cu and Al$_2$CuMg in decreasing order. Al$_{20}$Cu$_2$Mn$_3$, Al$_2$Cu and Al$_7$Cu$_2$Fe had similar $R_p$ values, which were several times larger than that of Al$_2$CuMg. The addition of chromate in NaCl solution dramatically increased the polarization resistance of all samples, but to different extents. The S phase had the lowest $R_p$ in the chromate solution, but it was increased by a factor of 6. The polarization resistance of S phase was comparable to other noble particles in NaCl.
The anodic polarization responses of IMC in the presence of chromate was reported in Chapter 4, and the effect of a chromate inhibitor on the anodic reaction kinetics was discussed in detail. In this chapter, the corrosion rate and pitting potential of IMCs obtained from the anodic polarization curves (Fig. 4.1 in Chapter 4) was summarized in Fig. 7.8 and Fig. 7.9. They were briefly described and are used here for comparison with the impedance obtained from FFT of potential transients.

Fig. 7.8 shows pitting potential distributions and average values (horizontal lines). The pitting potential of Al$_2$CuMg was increased to about -0.4 V$_{SCE}$ with addition of 1 mM chromate, which is similar to that of noble IMCs (Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$) in NaCl solution. The pitting potential of other IMCs are also increased by several hundred millivolts. The corrosion rates in each solution are summarized in Fig. 7.9. In the NaCl solution, the S phase had the highest corrosion rate among all samples, and was followed by Al$_2$Cu, while Al 4wt.% Cu, Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$ had similar corrosion rates. By addition of 1mM chromate in 0.1 M NaCl, corrosion rates of all samples were reduced by a factor of 2 to 70, among which Al$_2$CuMg was reduced by the greatest extent. The corrosion rate of S phase in chromate solution was reduced to a value close to that of Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$ (in NaCl solution).

7.4 Discussion

7.4.1 Comparison of electrochemical characteristics (polarization resistance and capacitance) of passive film on IMCs in NaCl and chromate solution

The measured capacitance of IMCs is dependent on dielectric constant and thickness of passive film on the sample surface. Most IMCs have a capacitance that is larger than
that expected of a compact oxide film or an electrochemical double layer. One possibility is that experiments were performed immediately after the polishing, leading to a very thin passive film on the surface. This thin film can lead to high capacitance according to the inverse relationship between capacitance and film thickness. Furthermore, this passive thin might not completely cover the surface, exposing certain part of samples to solution leading to localized corrosion, which can also cause higher capacitance. Even though the potential transient collection time was short and the potential perturbation was controlled to be small, pits may have developed on the freshly prepared surface, increasing the measured capacitance.

Measured capacitances were especially large for the S phase. As shown in Table 7.1, the S phase had largest capacitance among the IMCs exmined. The S phase is electrochemically active in NaCl solution and corrodes by dealloying [19,36,37]. Dealloying corrosion leads to the formation of a porous microstructure at the nano- and microscale producing a large surface area. This large surface area leads to a high capacitance. Nonetheless, the measured capacitance can be used for comparisons among different IMCs and for evaluation of inhibitor action on the surface film properties. With addition of chromate to NaCl solution, all IMCs shows capacitive behavior as indicated by $\alpha$ values near 1 (Table 7.1), and capacitance magnitudes near 10 $\mu$F/cm$^2$. This characteristic value is attributed to a compact Cr$^{\text{III}}$-Cr$^{\text{VI}}$ mixed oxide film that forms in the chromate solution[20–22]. This protective film dominates the measured capacitance. This capacitance value is also close to that of a passive oxide film[38]. If composition of the film is assumed to be Cr$_2$O$_3$ with a dielectric constant of 12[39], the thickness of film
is estimated to be 1 nm based on Equation 7.4. Such a film would be expected to inhibit oxygen reduction and anodic dissolution. 

\[ t = \frac{\varepsilon_0 \varepsilon}{C} \]  

(Equation 7.4)

where \( t \) is thickness of passive film, \( C \) is the capacitance, taken to be 10 \( \mu \)F/cm\(^2\), \( \varepsilon_0 \) is the permittivity of free space.

\( \text{Al}_{20}\text{Cu}_2\text{Mn}_3 \), \( \text{Al}_7\text{Cu}_2\text{Fe} \), \( \text{Al}_2\text{Cu} \) demonstrated large polarization resistances, indicating that they were resistant to pitting corrosion. Their high intrinsic corrosion resistances were also revealed by large pitting potentials and slow corrosion rates as shown in Fig. 7.8 and Fig. 7.9. I contrast, S phase had a low polarization resistance, consistent with [40], and is prone to corrosion. Therefore, S phase particles are the weak microstructural link with respect to corrosion, and suppression of dissolution at S phase particles is critical for the effective inhibition of localized corrosion of Al-Cu-Mg alloys. With a 1 mM chromate addition to a NaCl solution, polarization resistances of all samples was increased as shown in Fig. 7.7. This was especially so for the S phase. Its polarization resistance increases to that of much more passive particles such as \( \text{Al}_7\text{Cu}_2\text{Fe} \). In the presence of chromate, the S phase also possesses passive behaviors and becomes more resistance to corrosion. This improvement on the corrosion resistance is also indicated by a decreased corrosion rate (Fig. 7.9), increased pitting potential (Fig. 7.8) as well as the suppression of localized corrosion (Fig. 4.5 f in Chapter 4). For other IMCs, their passivation behavior is improved by chromate addition as indicated by the increased \( R_p \). This improvement is attributed to rapid formation of a monolayer of chromate on the surface, which also suppresses oxygen reduction reaction kinetics (Fig.
4.2 in Chapter 4) and trenching corrosion around these particles (Fig. 4.5 f in Chapter 4). Similar changes in the capacitance and resistance in the presence of chromate was also observed on iron [41].

7.4.2 Relationship between polarization resistance and corrosion rate of IMCs in NaCl and chromate solution

When the reactions in a corrosion cell process are activation-controlled, corrosion rate is related to polarization resistance by Stern-Geary equation[42]:

$$i_{corr} = \frac{B}{R_p}, \text{where } B = \frac{b_a b_c}{2.3(b_a + |b_c|)}$$

(Equation 7.5)

where $b_a$ is anodic Tafel slope, and $b_c$ is cathodic Tafel slope and $B$ is a constant dependent on anodic and cathodic Tafel slopes.

To the extent that this is the case in these measurements, $R_p$, which has been obtained by FFT of potential transient, is plotted as function of $i_{corr}$, which was extrapolated from the anodic polarization curves. The result in NaCl solution and chromate solution is shown in Fig. 7.10. Three reference lines with B value of 4 mV, 22 mV and 250 mV were plotted based on Equation 7.5 in the Fig. 7.10, and the experimental data fall between these lines. Two additional reference lines (red dashed) are also plotted based on the recommended extreme values of anodic and cathodic slopes by Stern and Weisert[43]. Most IMCs can be described based on Equation 7.5 with B value ranging from 4 to 52 mV, but the lowest B value reported by Stern and Weisert is 13 mV[43]. The reason for this divergence is not clear. The corrosion rate and polarization resistance are determined with two different distinctive methods in this work and this might lead to this difference. For S phase particles, a B value of around 250mV is found, which is much larger than the
extreme value of 52mV. This great difference suggests that the dissolution of S phase is not activation-controlled, and its corrosion rate cannot be evaluated by Equation 7.5. The B value determined in this work can be used as reference to calculate corrosion rate based on Equation 7.5. But it should be used carefully, as B value is strongly affected by the materials properties and surrounding environments such as pH and inhibitor addition [44–47].

Fig. 7.10 was used to evaluate the interfacial characteristics of passive film in NaCl solution and chromate solution. All samples except S phase in 0.1 M NaCl had a low corrosion rate and high polarization resistance (light orange region in Fig. 7.10). These second phase particles have high corrosion resistance. As is well documented, the S phase, has a large corrosion rate and is located in the right-bottom corner of the plot.

Chromate additions increase the $R_p$ and decrease $i_{corr}$ as the data region is shifted toward left-top corner (light grey region in Fig. 7.10), improving passivity. This change shows that chromate passivates S phase, giving it a corrosion resistance close to those of Al$_7$Cu$_2$Fe and Al$_{20}$Cu$_2$Mn$_3$ particles (in NaCl). Therefore, all second phase particles in alloy possess high corrosion resistance, and their corrosion is strongly inhibited. Furthermore, oxygen reductions on these particles are largely suppressed, and trenching corrosion around particles is also retarded. This inhibition is attributed to the chromate protective film [22].
7.4.3 Evaluation of dealloying corrosion of S phase and alloy using single frequency EIS

Impedance can provide information on the interfacial characteristics of the surface film, such as that formed during chromate addition [13]. FFT of an imposed potential transient combined the microcell technique enables fast impedance characterization on single IMC crystals and a pure Al-Cu matrix analog. Using the microcell approach, it is possible to scan the capacitance across grains [48,49], and monitor pit propagation using the single frequency EIS to relate the capacitance change to the pit fraction [50].

A detailed view of the dealloyed S phases as shown in Fig. 7.11 b demonstrates that it has nano-scale porous structure and large surface area, which will contribute the surface area changes of the whole sample. If the capacitance of dealloyed S phase is known and the total capacitance change is monitored by the single frequency EIS, the dealloying propagation rate of S phase can be determined based on the capacitance change. Fig. 7.12 a shows the capacitance evolution of dealloyed S phase after 1000s OCP measurement, which allows dealloying corrosion to occur. The capacitance is relatively stable, about 650 µF/cm², indicating the dealloying corrosion is completed and a Cu-rich layer has formed. If the exposure time is reduced to 15s, during which dealloying corrosion occurs, the capacitance increases slowly and reaches a stable value of 650 µF/cm² within 180s (Fig. 7.12 b). This stable capacitance value is used to estimate the extent of dealloying corrosion of S phase in a bulk alloy. The area fraction of S phase particle with a size larger than 0.5-0.7 µm in AA2024-T3 is 2.7% of the surface area[19], and the expected capacitance increases due to all dealloyed S phase is determined to 17.5 µF/cm². The
capacitance changes of bulk alloy upon exposure in the 0.1 M NaCl at 10 °C is measured by single frequency EIS, and the fraction of dealloyed S phase can be obtained via dividing the capacitance change of bulk alloy by 17.5 µF/cm². As shown in Fig. 7.13, the fraction of dealloyed S phase increases rapidly in the initial 900 seconds, and then reaches a plateau.

7.5 Conclusions

1. The impedances of IMCs and Al 4wt.%Cu in 0.1 M NaCl and chromate solution were characterized by FFT of an induced potential transient using a microcell method. The extracted impedance response of most samples was described by simplified Randles circuit.

2. The S phase showed high electrochemical reactivity in 0.1 M NaCl solution as indicated by the high equivalent capacitance and low polarization resistance. Reactivity was extinguished with the addition of chromate to an extent which is comparable to other noble particles (0.1 M NaCl). Other IMCs are passive in nature as indicated by low corrosion rate and high resistance, and their passivation behavior was improved by chromate addition as well.

3. All IMCs shows similar capacitance values in the chromate solution, about 10 µF/cm², and this is attributed to a protective surface film formed in the presence of chromate, which dominated the interfacial capacitor-like properties.

4. The B value of most IMCs and matrix in Stern-Geary equation is ranging from 4 mV to 52 mV, concentrated from 4 to 22 mV. These data were used for fast estimation and prediction of corrosion rate.
Fig. 7.1 Open circuit potential changes of S phase in 0.1 M NaCl solution at 30 °C.
Fig. 7.2 Current-time profile used to obtain potential transient: zero current at $t_0$ and $t_2$ regions and $I_1$ at $t_1$ region
Fig. 7.3 Potential transient of Al 4wt.%Cu in 0.1M NaCl after an injection of charge equivalent to 143.2 µC/cm$^2$
Fig. 7.4 Nyquist plots of a dummy cell \((R_1 + R/C)\) obtained by the FFT of potential transient and tradition EIS

\[
\begin{align*}
R &= 10k\Omega \\
C &= 100\mu F
\end{align*}
\]
Fig. 7.5 Nyquist plots of IMCs and matrix by FFT in 0.1 M NaCl and chromate solution obtained: a, Al$_2$CuMg; b, Al$_2$Cu; c, Al 4wt.%Cu; d, Al$_2$Cu$_2$Fe; e, Al$_{20}$Cu$_2$Mn$_3$; f, equivalent circuit used to fit the impedance spectra.
Fig. 7.6 Comparisons of equivalent capacitance in 0.1M NaCl and chromate solution: red solid horizontal line represented data in NaCl solution while black solid dots in chromate solution
Fig. 7.7 Comparisons of polarization resistance in 0.1M NaCl and chromate solution: red solid horizontal line represented data in NaCl solution while black solid dots in chromate solution.
Fig. 7.8 Average pitting potential and distribution of IMCs and Al 4wt.%Cu in 0.1M NaCl and chromate solution
Fig. 7.9 Corrosion rate of IMCs and Al 4wt.%Cu in 0.1M NaCl and chromate solution
Fig. 7.10 Relationship between $R_p$ obtained through fast Fourier transformed of potential transient data and $i_{corr}$ extrapolated from polarization curves in 0.1M NaCl and chromate solution.
Fig. 7.11 Optical profilometer of S phase (a, and SEM image (b)) and AlCuMnFe particles after 1 hour exposure in 0.1 M NaCl at 10 °C
Fig. 7.12 capacitance changes determined using single frequency EIS after different delay time: a, 960s; b, 15s.
Fig. 7.13 Dealloyed S phase propagation rate calculated based on the capacitance change of the bulk alloy and the dealloyed S phase
Table 7.1 Summary of the typical fit parameters obtained for IMCs and Al 4wt.Cu% in 0.1M NaCl and chromate solution

<table>
<thead>
<tr>
<th>Solutions</th>
<th>0.1 M NaCl</th>
<th>0.1 M NaCl + 1mM CrO$_4^{2-}$</th>
<th>0.1 M NaCl + 1mM CrO$_4^{2-}$</th>
<th>0.1 M NaCl + 1mM CrO$_4^{2-}$</th>
<th>0.1 M NaCl + 1mM CrO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_p$ (Ω·cm$^2$)</td>
<td>$C$ (µF/cm$^2$)</td>
<td>$\alpha$</td>
<td>$R_p$ (Ω·cm$^2$)</td>
<td>$C$ (µF/cm$^2$)</td>
</tr>
<tr>
<td>0.1 M NaCl</td>
<td>5015</td>
<td>349</td>
<td>1</td>
<td>32000</td>
<td>16.9</td>
</tr>
<tr>
<td></td>
<td>45253</td>
<td>121</td>
<td>0.87</td>
<td>336808</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>17642</td>
<td>275</td>
<td>1</td>
<td>67516</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>35182</td>
<td>167</td>
<td>0.98</td>
<td>115148</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>54983</td>
<td>122</td>
<td>0.87</td>
<td>153432</td>
<td>8.1</td>
</tr>
</tbody>
</table>
References


Chapter 8 Conclusions and Future Work

8.1 Conclusions

In this work, the electrochemical properties of secondary phases commonly found in AA2024-T3 were characterized in 0.1 M NaCl and in the presence of rare earth metal and vanadate inhibitors at ambient and elevated temperature conditions. The electrochemical data collected have been related to localized corrosion morphology characterized by secondary electron microscopy. The inhibition performance of vanadate on AA2024-T3 at high temperature was examined and the inhibition mechanism was explained. The following are the key findings:

1. Increasing temperature on the range of 0-80 °C increases the corrosion rate of secondary phases including the dealloying kinetics of S phase. The relationship can be described by an Arrhenius Equation. Activation-controlled reaction becomes dominant factor in the localized corrosion at above 50 °C.

2. Both oxygen solubility and diffusion coefficient are strongly temperature-dependent in the range of 0-80 °C. Calculations indicate and measurements support a maximum in oxygen reduction reaction rate at around 50 °C.

3. Rare earth metals dissolved in solution are cathodic inhibitors for secondary phases. REM inhibition results from the hydroxide precipitation on cathodic sites due to local a pH increase. The pH increases occur as a results of local corrosion
cell action. This makes rare earth metal inhibitors slow to act. Precipitation of REM hydroxides occurs preferentially on the dealloyed S phase due to its ability to support oxygen reduction reactions at high rates.

4. The thickness of rare earth metal precipitation formed on the S phase is a few hundred nanometers, and once this precipitation layer forms, its thickness growth rate slows as the corrosion of S phase is inhibited.

5. The ‘slow’ nature of rare earth metals inhibition is magnified at high temperature. Cerium shows some inhibition at 50 °C on both secondary particles and matrix, especially on the S phase, where only small pits are observed and the surrounding trenching corrosion is suppressed. But inhibition is only observed on the secondary phases and no inhibition on the matrix at 70 °C. Dealloying corrosion of S phase will penetrate half the particle depth, but the hydroxide layer that forms is very stable even under vacuum conditions.

6. Vanadate inhibitors can form a vanadate film on the surface at high temperature (> 50 °C), and film thickness increases with temperature. Vanadate film formation is attributed to the chemical reduction of vanadate by Al or Mg. This reduction reaction was confirmed by XPS, which showed that vanadate can be reduced to a 4+ state in the solution and reoxidized to 5+ by exposure to air. This reduction reaction is strongly affected by the dissolved oxygen in the solution, which will compete with vanadate species for the reduction, especially at 50 °C. Treated samples show residual corrosion protection in NaCl without vanadate inhibitor after exposure to vanadate solution at 80 °C. This residual protection can be
enhanced if the reduced vanadium is allowed to be reoxidized to 5+ by contact with air or aerated solutions.

7. The interfacial impedance of most secondary phases in NaCl solution with and without chromate could be described by simplified Randles circuit. The polarization resistance and capacitance were obtained from impedance data derived from Fast Fourier Transform of an induced potential transient. These data were compared to the corrosion rate determined from anodic polarization curves. Chromate additions to solution enhanced passive film properties and made the active S phase possess a similar corrosion resistance to that of AlCuMnFe particles observed in NaCl, thereby increasing overall alloy corrosion resistance.

**8.2 Future work**

During this research, several interesting points arose for potential future study.

1. In aerated solutions, a theoretical calculation demonstrates that the limiting current density of the oxygen reduction reaction is highest at 50 °C, and then drops at 70 °C. However, the corrosion rate on a number of IMC was found to increase with temperature exponentially. Some bubbles were observed on the surface during the exposure test at 70 °C, and this was attributed to hydrogen evolution. It seems that both oxygen reduction and hydrogen evolution contribute to the cathodic reactions, but how to separate their contributions is an interesting topic that has a bearing on how to deploy corrosion inhibitors at elevated temperatures.
2. Cerium shows strong inhibition on the active S phase particles at 50 °C in CeCl₃ solution, which can effectively suppress dissolution of S phase. But trenching around the S phase is still observed. It seems there is a synergistic effect of aluminum hydroxide and cerium hydroxide, which could provide enhanced protection. The detailed reason is not clear, and deserves further study.

3. Vanadate films formed at high temperatures are mixed V⁵⁺/V⁴⁺ analogous to the mixed Cr⁶⁺/Cr³⁺ film in chromate conversion coating. However, vanadate films are not as protective as this chromate counter parts. In this work, only one vanadate species is characterized, but there are other 15 species that have not been explored. There is a possibility that some or combined vanadate species possesses comparable oxidizing ability to chromate at high temperature.

4. Vanadate shows little inhibition in acid solution since it will polymerize to form decavanadate, which is not an effective inhibitor species. In this work, it is found that complex vanadate species will decompose to monovanadate at high temperature. It remains to be determined if decavanadate can also decompose into metavanadate or monovanadate at high temperature. If decavanadate can also decompose into metavanadate or monovanadate at high temperature, which are effective inhibitor species, vanadate could be a temperature-sensitive inhibitor under acidic conditions.
Bibliography


