THE USE OF MICROELECTRODES IN THE STUDY OF LOCALIZED CORROSION OF ALUMINUM 6111-LIKE ALLOYS

A Thesis in
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by
Aboubakr M. Abdullah

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We approve the thesis of Aboubakr M. Abdullah.

Howard W. Pickering
Distinguished Professor of Metallurgy
Thesis Co-Advisor
Co-Chair of Committee

Barbara A. Shaw
Associate Professor of Engineering
Science and Mechanics,
Thesis Co-Advisor
Co-Chair of Committee

Zi-Kui Liu
Assistant Professor of Materials Science and Engineering

Elizabeth Sikora
Research Associate

James P. Runt
Professor of Materials Science and Engineering
Associate Head for Graduate Studies in Materials Science and Engineering
ABSTRACT

This thesis is classified into four chapters. While chapter 1 is only an introductory chapter that summarizes the two mechanisms that are trying to explain localized corrosion of metals and alloys, Chapter 4 is the conclusions and future work chapter that presents the new achievements that have been added to the field of corrosion science by this work besides the proposed work to be done in the future. Chapters 2 and 3 are the core of this thesis and each of them has its own abstract, objective, and literature review, experimental, results and discussion, conclusions, and references list.

In chapter 2, Crevice corrosion of an experimental Al 6111-like alloy with 0.68% Cu has been studied using potentiodynamic and potentiostatic techniques in different concentrations of sodium chloride and in 0.1M nitric acid solutions. Potentiodynamic experiments show that the alloy has an active/passive transition in a saturated sodium chloride solution at elevated temperatures (90 and 70 °C). Also, a steep electrode potential gradient, $E(x)$, within the crevice has been measured using a microprobe connected to a SCE and controlled by a 3-D manipulator, and the observed locations of corrosion on the crevice wall are similar to the locations seen previously for systems in which it was clear that the shift of $E(x)$ into the active peak region of the polarization curve on the crevice wall stabilized the crevice corrosion process. The same active peak $E(x)$ relationship was observed for the Al 6111-like alloy in 0.1 M nitric acid solutions at room temperature.
In chapter 3, focuses on the corrosion of a peak aged aluminum 6111-like alloy of 1.47% copper using the artificial pit configuration (pencil electrode) with relatively larger specimens in the form of plates rather than wires. The sample which was flush with the surface of the epoxy resin mount was anodically polarized in neutral NaCl solutions of different concentrations and pH 6.9. The alloy dissolved uniformly at a certain rate to form a local cell with epoxy resin walls and the alloy surface as its bottom. Intergranular corrosion (IGC) also occurred and was recorded every 900 seconds using a stereo-microscope (through the transparent epoxy) connected to a PC uploaded with time-lapse software. IGC rate was in the order of 0.5 mm/day. The potential drop profile within the cavity was recorded on a daily basis. It showed that the total potential drop is in the order of 50 mV. The pH in the local cell was measured using a commercial mono pH microelectrode coupled with a homemade Pyrex (glassy) microprobe connected to a SCE and controlled by a 3-D manipulator. pH measurements showed the medium within the cavity is alkaline with a pH ranges from 9-12. Also, the chloride ion concentration within the local cell was measured using a mono Ag/AgCl microelectrode coupled with the same glassy microprobe, which is connected to a SCE. It showed that the chloride concentration within the cavity is at least one order of magnitude higher than that in the bulk solution. The study of the effect of the chloride ion concentration on the IGC rate showed that the increase in the chloride ion concentration increases only the initial rate of the IGC but the overall rate remained almost the same.
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I dedicate this work to my parents, my wife and my beloved daughters; Reem, Aaliah and Fareedah, and to all my brothers and sisters
CHAPTER 1

INTRODUCTION AND BACKGROUND

1.1. OBJECTIVE

The objective of this chapter is twofold; to introduce the objective of the whole work of this thesis and to summarize the two common theories currently used to understanding crevice corrosion of metals and alloys.

1.2. INTRODUCTION

The aim of the first half of this work (Chapter 2) was to study the crevice corrosion mechanisms and forms and of an Al 6111-like alloy (0.68% Cu), with a particular focus on the role of the IR voltage drop, to answer whether or not the IR voltage drop within the crevice is responsible for the stabilization of crevice corrosion for the systems that usually exhibit no active/passive transition in their measured polarization curves. To answer the aforementioned question, crevice corrosion behavior of the aluminum 6111-like alloy (0.68% Cu) was studied in solutions of different pH values and temperatures. Also, this study will encompass both kinds of polarizations on the alloy specimens; anodic and cathodic polarizations.
The goal of the second half of this work (Chapter 3) was to study the factors that affect the intergranular corrosion of a newly developed Al 6111-like alloy (1.47% Cu). This alloy was used in the as-received condition (peak-aged). Another parallel goal was to provide the potential profile, pH profile and the chloride ion concentration profile within cavities formed mainly due to intergranular corrosion for this alloy in both the as-received conditions (peak aged) and in an overaged condition. This data is required for developing a quasi static mathematical model for predicting the localized corrosion for this alloy and those of other compositions. Conclusions and future work will be represented in Chapter 4 and will be also followed by an appendix (Chapter 5).

1.3. BACKGROUND

Two main theories tried to explain crevice corrosion. The first mechanism is called the acidification and chloride ion accumulation mechanism while the other mechanism is the IR mechanism. Both mechanisms agree that the essential requirement of crevice corrosion is the separation of the anodic and cathodic reactions. The question that needs to be answered is why this separation takes place. Initially, uniform corrosion will take place inside and outside the crevice. Uniform corrosion means that the electrons, which are released from the corrosion of the metal or alloy, will be consumed locally (cathodic reaction) by the oxidants present in the solution. Oxidants will be depleted from the crevice electrolyte as time goes on due to the mass transfer restriction of oxidants (mainly oxygen) from the bulk electrolyte to the crevice electrolyte. The electrons, which are released by the formation of the oxidized metal atoms, will move through the
metal to an outer surface where oxidants are abundant, and will be consumed at that place. In other words, the cathodic reaction (oxidant reduction) starts to occur largely at the outer surface while the anodic reaction (metal dissolution) maintains itself within the crevice. Separation has now occurred at least to a limited extent. At this point, the two mechanisms start to have different pathways in explaining crevice corrosion.

The traditional mechanism (acidification-chloride ions accumulation mechanism), summarized by Fontana (1), proposes the following: due to oxygen depletion within the crevice (which means not enough cathodic reaction will take place within the crevice and not enough negative charges will be produced within the crevice) the metal ions concentration within the crevice will increase with time and in order to maintain the charge neutrality, anions including chloride ions will migrate from the bulk electrolyte to inside the crevice. A metal chloride complex will form and will undergo hydrolysis, which will lead to the formation of insoluble metal hydroxide and free acid within the crevice. The solution composition within the crevice will then become much more aggressive, which will result in increasing the rate of dissolution of the metal or alloy. The traditional mechanism is summarized in Figure 1.1. The role of potential gradient within the crevice electrolyte in the traditional mechanism is only understood as a driving force for the migration of ions. This mechanism fails to explain many observations in crevice corrosion. For example, Smith, et. al. (2), found that the crevice solution pH for an iron specimen increases from pH 2 to pH 4, instead of decreasing. Many research projects mostly during the last decade at Penn State University,
Figure 1.1. Schematic summarizing the acidification-chloride ion accumulation mechanism.
found that crevice corrosion can occur in buffered solutions as well as chloride-free solutions.\(^{(3-9)}\)

According to the \(IR\) mechanism, the separation between the cathodic and anodic reactions will lead to a current flow through the electrolyte. Because of the resistance of the electrolyte which impede the current flow, a potential drop will take place and lead to a new distribution of potential on the crevice wall. This potential distribution will follow Equation 1.1,

\[
E_x = E_{x=0} - IR_x \\
\text{Equation 1.1}
\]

where \(E_x\) is the potential at a distance \(x\) within the crevice. \(I\) is the current flowing in the solution. \(I\) is positive during anodic polarization (current flow from inside the crevice to outside the crevice) and negative during cathodic polarization (current flow from outside the crevice to inside it). \(E_{x=0}\) is the potential at the outer surface. \(R_x\) is the local resistance of the electrolyte. \(R_x\) can be calculated from Equation 1.2.

\[
R_x = \frac{\rho_x x}{A} \\
\text{Equation 1.2}
\]

\(\rho_x\) is the resistivity of the electrolyte at a certain distance \(x\). It changes due to many variables, e.g., the concentration of the different ions at that specific location, the
presence or absence of bubbles within the crevice electrolyte, and the temperature. \( A \) is the cross sectional area of the current path.

The main prerequisite condition for crevice corrosion to occur is that illustrated in Equation 1.3,

\[ IR > \Delta \phi^* \]

where \( IR \) is the potential drop and \( \Delta \phi^* \) is called the critical potential drop which is the minimum potential drop required in order to make the system exhibit crevice corrosion at a certain aspect ratio (AR). The aspect ratio is defined as the ratio between the length and the width of the crevice. For every system exhibits crevice corrosion there is a critical aspect ratio below which the system will not suffer from crevice corrosion. This concept is very important in the design of the metals or alloys parts that might suffer from crevice corrosion when they contact with certain electrolytes. If this condition \(( IR > \Delta \phi^* \) which means \( AR > AR_c \); \( AR_c \) is called the critical aspect ratio) is satisfied, the system will undergo immediate crevice corrosion. If \( AR < AR_c \), the system may undergo what is called delayed crevice corrosion. Figure 1.2 illustrates the two kinds of crevice corrosion and also introduces the concept of \( \Delta \phi^* \). Immediate crevice corrosion is represented in sketch a. Sketches b, c shows the crevice electrolyte composition changes (or temperature changes in some cases as will be shown in chapter 3) and how changes affect the active peak size of the polarization curve. Increasing the size of the active peak, means simply decreasing \( \Delta \phi^* \). Sketches d and e shows that once
the peak size is large enough to satisfy Equation 1.3, crevice corrosion starts. The time it takes until crevice corrosion starts is called the induction period or the initiation time for crevice corrosion to occur for a certain system (metal or alloy with a certain aspect ratio in a certain electrolyte). A Model was proposed to calculate the aspect ratio by Xu and Pickering. This model is very successful in predicting the critical aspect ratio needed for a system in order to exhibit crevice corrosion.

The IR will be discussed more in the introduction of the next chapter.
Figure 1.2. Schematic of the IR voltage form of crevice corrosion for the two classifications: immediate (sketch a), and delayed (d and e), the latter of which requires certain changes in the crevice solution resistance or in the polarization curve as shown here, e.g., due to a change in temperature or crevice solution composition.\(^{(10)}\) Also shown is the older composition-change mechanism where no consideration is given to the \(E_x\) distribution on the crevice wall (b and c). \(\Delta \phi^*\) is shown in (a).\(^{(11)}\)
1.4. REFERENCES


CHAPTER 2

CREVICE CORROSION OF ALUMINUM 6111-LIKE ALLOY

2.1. ABSTRACT

Crevice corrosion of an experimental Al 6111-like alloy with 0.68% Cu has been studied using potentiodynamic and potentiostatic techniques in different concentrations of sodium chloride and in 0.1M nitric acid solutions. Potentiodynamic experiments show that the alloy has an active/passive transition in a saturated sodium chloride solution at elevated temperatures (90 and 70 °C). Also, a steep electrode potential gradient, $E(x)$, within the crevice has been measured using a microprobe, and the observed locations of corrosion on the crevice wall are similar to the locations seen previously for systems in which it was clear that the shift of $E(x)$ into the active peak region of the polarization curve on the crevice wall stabilized the crevice corrosion process. The same active peak – $E(x)$ relationship was observed for the Al 6111-like alloy in 0.1 M nitric acid solutions at room temperature.

2.2. OBJECTIVE

The aim of this work was to study the crevice corrosion of an Al alloy, with a particular focus on the role of the IR voltage drop. This research will attempt to answer
whether or not the IR voltage drop within the crevice is responsible for the stabilization of crevice corrosion for the systems that usually exhibit no active/passive transition in their measured polarization curve. To answer this question, crevice corrosion behavior of an aluminum 6111-like alloy (0.68% Cu) was studied in solutions of different pH and temperature. Also, this study will encompass both kinds of polarizations on the alloy specimens; anodic and cathodic polarizations.

2.3. LITERATUR REVIEW

Corrosion, which is one of the greatest challenges facing all civilizations in the recent time, costs US only as much as 4.9 % of its Gross National Product (GNP) (1) which is equivalent approximately to $220 billion a year. (2) Although the economical effect of corrosion in general and crevice corrosion in particular was the most effective stimulant in fighting corrosion, the health and safety issues now are at least equal in importance. Regarding the health issues, crevice corrosion is one of main challenges in the surgical implantation field, where it affects both the biocompatibility and the biofunctionality of the material. Many authors have reported a significant increase in the metal ion concentration in association with a metal implant. (3-5) From the safety point of view, the danger of crevice corrosion, which is one of the most ubiquitous and damaging forms of corrosion, arises from its unnoticed occurrence within recesses that continues undetected to failure. (6) Generally, all metals and alloys e.g. Al and Al alloys, which rely upon oxide films or passive layers for corrosion resistance, are particularly susceptible to crevice corrosion. (7)
Crevice corrosion of Al and its alloys has many forms starting from staining which leads to a change in the color of the crevice wall, (8) pitting of the crevice wall, (9-11) which leads to perforation, attack of the crevice wall under atmospheric conditions, (9) and filiform corrosion (FFC), all of which are considered to be special cases of crevice corrosion. (12-14)

The first obstacle in studying crevice corrosion is finding an appropriate method. Ijsseling reviewed the electrochemical methods used in crevice corrosion testing that are reported in the literature up to the year of 1998. (15, 16) Besides the electrochemical methods, he reviewed the theory and modeling of the mechanisms of crevice corrosion, conditions, applications and experimental results of different alloy types. (16) Also he reviewed the protection against crevice corrosion. (16)

The electrochemical methods can be classified according to either the aims for which these techniques were designed or the stages of crevice corrosion (initiation, propagation, or repassivation). The linear polarization method was used to determine the crevice corrosion rate. (17) The AC impedance technique was used to study the role of oxygen, hydrogen ions and Al ions in initiating crevice corrosion in Al alloy 6061. (18) Electrochemical impedance spectroscopy, EIS, was used as a monitoring tool for studying passivation and localized corrosion of aluminum alloys. (19) Potentiostatic polarization of a sample assembled against a transparent artificial crevice using Plexiglas, which allows an in-situ documentation of the crevice wall with time, and
measurement both of the IR potential drop and the total current with time was founded in the late eighties of the last century.\textsuperscript{(20-22)} A digital speckle correlation method was used in 1995 as a nondestructive test for pitting, crevice corrosion and stress corrosion cracking.\textsuperscript{(23)} Electrochemical noise analysis, ENA, was used to study crevice corrosion of aluminum 6013 T6 alloy.\textsuperscript{(24)} ENA coupled with the scanning reference electrode was used for 304L stainless steel.\textsuperscript{(25)} An optical interferometry technique was developed for testing the initiation of crevice corrosion of Al brass and other metals.\textsuperscript{(26)} Open circuit potentials of an aluminum alloy 2024 (AA2024) coated with an organic coating that undergoes filiform corrosion was tested using the scanning Kelvin probe in aerated and deaerated conditions.\textsuperscript{(27)}

Besides the in-situ measurement of the potential drop within crevices and cracks, the solution composition (pH and [Cl\textsuperscript{-}]) measurements have represented an important part in the literature. Microprobes and microelectrodes, used for measuring potential drop, pH and [Cl\textsuperscript{-}] within crevices, have been always good tools in achieving this goal.\textsuperscript{(28-38)} Turnbull reviewed the solution composition and electrode potential measurements in pits, crevices and cracks up to the year of 1983.\textsuperscript{(39)} For Al alloys, the pH within an artificial pit (unknown depth) with and without galvanic coupling with a carbon rod was measured using a micro-antimony electrode.\textsuperscript{(40)} Evolution of hydrogen was observed from the pit but no precipitation of Al(OH)\textsubscript{3} was found. That was explained by the formation of a stable AlCl\textsubscript{3} solution more basic than that corresponding with the stoichiometric composition. Kitamura and Sato measured the potential and the pH change within the crevice of an Al alloy coupled to a free surface specimen in presence
of 0.5 M NaCl of pH 5. They found that both potentials (at the outer surface and within the crevice) changed to more negative values with time. Regarding pH, it decreased to pH 2.5 after 6 hours. This value increased to pH 7 after 150 hours.\(^{(41)}\) According to Shumming’s work\(^{(42)}\), the pH value within the Al crevices depends on the presence or absence of an external surface. In the presence of a low chloride concentration and the absence of an external surface, the pH inside the crevice becomes alkaline while in the presence of considerable concentrations of chloride ions and absence of an external surface, the pH inside the crevice becomes low at the crevice mouth and increases in the deeper regions. The change of pH from acidic to basic based upon the stress intensity factor was reported by Davis.\(^{(43)}\)

Because of crevice corrosion dangers, continuous efforts are done in order to inhibit or at least alleviate its detrimental effects in many metals and alloys. In the case of Al, inhibition was performed either by laser surface alloying\(^{(44)}\), by inhibiting the cathodic reaction via surface alloying with rare-earth salts\(^{(45)}\), by coupling to a more noble metal\(^{(46)}\), or by using aqueous inhibitors such as chromates which act according to some literature as repassivation promoter\(^{(47)}\) or as competitive adsorbsate to the aggressive ions in the media\(^{(48)}\) but not as an anodic inhibitor\(^{(49)}\).

In fact, understanding the mechanism of crevice corrosion may be a shortcut to crevice corrosion inhibition. Then, one may choose the appropriate inhibitor, if any, and/or design, if possible, to avoid or at least mitigate against that form of corrosion.
Two general theories have been proposed to explain the mechanism of crevice corrosion in metals and alloys: the \textit{IR} voltage drop theory \textsuperscript{(22)} and acidification-chloride ion accumulation theory.\textsuperscript{(50-55)} In the case of aluminum, two more theories are proposed. The first is that the concentration of Al ions is the important parameter for the initiation of crevice corrosion. \textsuperscript{(56, 57)} The second is the chemical and electrochemical dissolution mechanism and it was proposed to explain the initiation of crevice corrosion.\textsuperscript{(58)} In summary, all papers in the literature explain crevice corrosion of Al and Al alloys in terms of compositional changes in the electrolyte within the crevice, while no papers have attempted to study, quantitatively, the role of the \textit{IR} voltage drop on the crevice corrosion of Al or Al alloys except for our earlier papers.\textsuperscript{(6, 59)}

The \textit{IR} theory, which is more comprehensive since it includes both potential distribution $E(x)$ and the effects of acidification and other solution composition changes, relates the crevice corrosion of metals and alloys to the voltage drop within the crevice electrolyte. Composition changes, in the \textit{IR} voltage drop theory, affect the shape of the polarization curve, mainly by changing the size of the active peak.

According to the \textit{IR} theory, the crevice corrosion mechanism is as follows: Oxidant/s depletion occur/s, not necessary completely,\textsuperscript{(60, 61)} within the crevice so that anodic and cathodic reactions became separated. Separation, of a certain amount of the anodic and cathodic reactions, allows for current flow and an \textit{IR} voltage drop in the crevice electrolyte. The latter causes, in the case of anodically polarized samples, (i) anion migration into, and cation migration out of, the crevice, (ii) instantaneous $E(x)$
distribution on the crevice wall ($E(x)$ profile), in which $E$ goes in the less noble direction as $x$ increases deeper within the crevice, and (iii) $i(x)$ distribution according to the polarization curve for the crevice electrolyte (Figure 2.1). In the case of cathodically polarized samples, anion migration out and cation migration into the crevice takes place. An $E(x)$ distribution will also take place but in this case, $E(x)$ will be nobler as $x$ increases and the $i(x)$ distribution will be in accord with the cathodic polarization curve of the crevice electrolyte.

Metals or alloys that undergo crevice corrosion can be classified into two categories according to their measured polarization curve, solution resistivity, crevice aspect ratio, and the applied or corrosion potential.

A- Immediate Crevice Corrosion

For systems that exhibit active/passive transitions in their measured polarization curves, e.g. Fe and Ni (in most electrolytes), stainless steel in strong acids,…etc, crevice corrosion has been well explained experimentally and theoretically using the $IR$ potential drop theory. Unlike the acidification–chloride ion accumulation mechanism, the $IR$ potential drop mechanism can explain crevice corrosion under conditions of constant electrolyte composition e.g. (chloride concentration and/or pH) within the crevice electrolyte.

B- Delayed Crevice Corrosion
Figure 2.1. Schematic illustration of the cross section of the crevice corrosion cell showing the passive region (Region 1) and active region (Region 2) areas of the internal crevice wall, and the IR-produced $E(x)$ and resulting $i(x)$ current density distributions (polarization curve) on the crevice wall.\(^{68}\)
For all spontaneously passive systems and for all other spontaneously active systems for which crevice corrosion doesn’t occur immediately, the onset of crevice corrosion by the IR mechanism can only occur after an induction period, but only then if certain changes occur in the system.\textsuperscript{(62, 63, 67)} Some spontaneously passive systems include Ti in most electrolytes, an exception being concentrated HCl,\textsuperscript{(74)} stainless steel in most neutral and alkaline solutions, Al and Al alloy systems which only rarely have active/passive transitions in their measured polarization curve for a wide range of conditions.\textsuperscript{(6, 75-87)} In these systems of delayed crevice corrosion, the mechanism of crevice corrosion is still unclear. The IR-voltage drop theory calls for an induction period (Figure 2.2) for these systems, during which time an active peak is formed. As the peak increases to a critical size (at t = end of induction period), the IR voltage just exceeds the critical value $\Delta \Phi^*$, and crevice corrosion starts.\textsuperscript{(62, 88-90)} In the most pronounced cases a cathodic peak will appear along with an anodic peak in the measured polarization curve, as schematically illustrated in Figure 2.2. Cathodic peaks have been reported in the literature e.g. stainless steel.\textsuperscript{(91)} Once the active peak is formed and the IR voltage exceeds the critical value, $\Delta \Phi^*$, then the system will be considered as a spontaneously active system and the IR theory parameters, e.g., $E_{P/A}$ (passive to active potential), $x_{P/A}$ (the boundary between the passive and the active regions on the crevice wall)… etc (see Figure 2.1) can be measured for every crevice whose aspect ratio, $AR$, is greater than the critical aspect ratio, $AR_c$. This IR voltage drop concept has been used to explain crevice corrosion in Alloy 625 in chlorinated seawater.\textsuperscript{(89)} Figure 2.3 is a schematic showing the logarithmic representation of the
Figure 2.2. Schematic diagram showing the development of an active peak for a spontaneously passive metal or alloy with time by illustrating the partial currents. The crevice corrosion starts once the induction period is over i.e. $IR \geq \Delta \Phi^*$ (c). The dashed lines are the partial currents while the solid lines are the measured (total) currents.

At Time = 0

At Time > 0

At Time = End of induction period

Crevice corrosion doesn’t occur at $t = 0$ by IR Mechanism

Crevice corrosion occurs at end of induction period by IR Mechanism
Figure 2.3. This schematic is a logarithmic representation of the measured current curve in Figure 2.2c. In this schematic, all the measured negative (cathodic) currents (regions 1, 3) are flipped in a mirror-like way. Positive (anodic) currents (regions 2, 4) remain the same.
measured current curve in Figure 2.2c. In this schematic, all the measured negative (cathodic) currents (regions 1, 3) are flipped in a mirror-like way. Positive (anodic) currents (regions 2, 4) remain the same.

2.4. EXPERIMENTAL

In this work, potentiodynamic and potentiostatic experiments were carried out using an EG&G-273 Potentiostat in an EG&G Greene cell of 1 liter volume. All potentials in this work are referred to the saturated calomel electrode (SCE). Two graphite rods were used as a counter electrode. Double distilled water was used to prepare all of the test solutions.

For the crevice experiments, Al 6111-like alloy (its chemical composition is summarized in Table 2.1) electrodes of dimensions 2 x 0.5 x 1 cm were used in this work. They were cut from sheet stock, embedded in epoxy resin, polished on two surfaces (one, 0.5 x 1 cm, is the outer surface to which the potential is applied and the other, 2 x 0.5 cm, is the crevice wall) using 600 grit silicon carbide paper, mechanically connected to a copper wire, and degreased using acetone. A lacquer was used to cover the connection and to close any gaps between the alloy and the epoxy resin. Plexiglas covers with different gap openings were attached to the crevice wall to create the artificial crevices. The $E(x)$ gradient on the crevice wall was measured using a Luggin capillary of a diameter of 0.15 mm connected to the SCE. The whole set up of the crevice experiments is described elsewhere.\(^{22}\)
Table 2.1. Chemical composition of the 6111-like Al alloys used in this study. They had been used in the as-received conditions (Naturally aged and a paint bake cycle for 30 minutes at 180 °C).

<table>
<thead>
<tr>
<th>Composition</th>
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<tbody>
<tr>
<td>Alloy #</td>
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<table>
<thead>
<tr>
<th></th>
<th>Si(%)</th>
<th>Cu(%)</th>
<th>Mg(%)</th>
<th>Mn(%)</th>
<th>Zn(%)</th>
<th>Ti(%)</th>
<th>Fe(%)</th>
<th>Al(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>749808</td>
<td>0.76</td>
<td>0.68</td>
<td>0.61</td>
<td>0.21</td>
<td>0</td>
<td>0.01</td>
<td>0.23</td>
<td>Bal.</td>
</tr>
<tr>
<td>749809</td>
<td>0.77</td>
<td>0</td>
<td>0.61</td>
<td>0.21</td>
<td>0.01</td>
<td>0.01</td>
<td>0.23</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
Experiments of Al alloy/electrolyte systems in this work are classified into two categories according to the electrolyte used; Al alloy in electrolyte with different chloride concentrations and Al alloy in 0.1 M nitric acid. For measuring the pH of the solution within the crevice, a specimen was extracted from the artificial crevice using a syringe and then the solution was flushed over a pH paper.

2.4.1 Al Alloy/Sodium Chloride Systems

Three different chloride systems are represented in this paper using the same alloy but with different chloride concentrations. Two of them are at elevated temperature (90 °C), conditions 1 & 2, and the third one, condition 3, is at room temperature (23 °C). Reagent grade sodium chloride was used to prepare the solutions without further purification. The temperature of the cell was controlled using a Dyna-Sense 1200-watt temperature controller with an error ± 1 °C. For systems at elevated temperature, conditions 1 & 2, the samples were preconditioned at −2.24V SCE for two minutes, the crevice was filled with sodium chloride crystals to maintain chloride ions at the saturation level within the crevice. The solution, either 1 mM ammonium nitrate (condition 1) or 1 mM ammonium nitrate saturated with sodium chloride (condition 2), was added to the cell, and the desired $E_{x=0}$ potential was applied to the outer surface, where $x = 0$ is at the top of the crevice. For the system at ambient temperature, the same preconditioning was done (−2.24V SCE for two minutes) but without a packing of NaCl crystals within the crevice.
Condition 1

A 1mM ammonium nitrate bulk solution (no chloride in the bulk solution, only within the crevice) was used for this system. A potential of +1.4 V SCE (higher than the pitting potential) was applied to the outer surface of the specimen with the Luggin capillary tip placed close to the crevice mouth \((x = 0)\) at the outer surface. The crevice gap was 0.5 mm. The location of corrosion on the crevice wall was photographically documented using an Olympus BX60M microscope interfaced with a monitor and a printer.

Condition 2

A 1 mM ammonium nitrate solution was saturated by sodium chloride crystals and used as a bulk electrolyte. For the crevice experiment, a potential of 1V SCE (higher than the pitting potential) was applied to the outer surface of the specimen. The crevice gap was 0.5 mm. This gap is filled by sodium chloride crystals. The \(E(x)\) potential profile within the crevice was measured using the method that has been developed previously.\(^{(69)}\) Also, the crevice corrosion behavior was documented using the same optical microscope and the camera mentioned above.

Polarization curves were measured using a normal scan rate (0.166 mV s\(^{-1}\)) on flat surface Al alloy electrodes each with a surface area of 1 cm\(^2\), at three different temperatures: 90, 70 and 23 °C. Pourbix diagrams for Al metal in 6M NaCl solution at
two different temperatures were constructed using HSC Chemistry Software version 2.03. Pourbiax diagrams were built to explore whether the change of the behavior of the polarization curves, as will be illustrated later, was due to the formation of new phases at elevated temperatures or not.

To study the stirring effect, the polarization curves for the same (alloy/solution) system were performed at 90 °C with and without stirring. Stirring was maintained using a magnetic stirrer at 1000 rpm to investigate whether the stagnant solution is the reason for the behavior observed in the polarization curves or not.

The effect of the Cu content of the alloy on the shape of the polarization curve was studied by including a Cu- free alloy (alloy # 9); its chemical composition is listed in Table 2.1.

Condition 3

The solution used for the ambient temperature system was 1M NaCl at pH 8.25 and the samples were polished to 1µm. The crevice gap was an unspecified few micrometers: a flat piece of Plexiglas was clamped against the crevice wall after the preconditioning for 2 minutes using Rozenfeld’s procedure of preconditioning the surface at –2.24 V SCE. A potential of -1.45 V SCE was applied to the outer surface of the specimen. For this system (aluminum alloy/1M NaCl at pH 8.25), the potentiodynamic polarization curve was obtained on flat Al alloy electrodes mounted in
epoxy resin of surface area 1 cm² (0.5 x 2 cm) each using Rozenfeld’s procedure of preconditioning the surface at −2.24 V SCE followed by a scan at a high scan rate immediately (after the preconditioning) in the anodic direction starting from the open circuit.\(^{76-79}\) According to Rozenfeld; the preconditioning increases the pH locally in front of the electrode surface and this reduces the oxide layer thickness.

For comparison, the polarization curve was measured on a Pt wire electrode of 1.6 cm² surface area using the same preconditioning technique. The number of coulombs under the peak in the case of the aluminum alloy was calculated and compared to a theoretical intact monolayer of hydrogen atoms covering the surface in an intact manner.

2.4.2. Al Alloy/0.1M Nitric Acid System at 23 °C

For the Al alloy/0.1M nitric acid system at 23 °C, specimens were polished to 1µm using alumina slurry. Reagent grade nitric acid and sodium nitrate were used without further treatment to prepare 0.1M nitrate solutions of pH 1, 2, and 5.4. The pH was adjusted using a few drops of nitric acid for the NaNO₃ solution at pH 2. The location of the corrosion on the crevice wall was photographically recorded using the same microscope mentioned above. The applied potential was −1.45V SCE and the crevice gap was 0.15 mm. Also, the potentiodynamic polarization behavior was evaluated using the Rozenfeld pretreatment procedure \(^{16-19}\) by preconditioning the surface of the electrode at -2.24 V SCE for 2 minutes before scanning the potential in the noble
direction starting from the open circuit potential. This was done in order to check the effect of pH in the bulk of the nitrates’ electrolytes on the electrochemical behavior of the alloy in these electrolytes.

2.5. RESULTS AND DISCUSSIONS

2.5.1. Al Alloy/Sodium Chloride Systems

Condition 1

Figure 2.4 shows the lightly pitted region (containing a low density of small pits) between the pitted top and the crevice-corroded bottom of the crevice wall after applying $E_{x=0} = +1.4 \text{ V SCE}$ to the sample for 3 hours. This $E_{x=0}$ value is a potential higher than the pitting potential, $E_{\text{pit}}$. $E_{\text{pit}}$ equals -420 mV SCE as can be seen from Figure 2.5. The crevice was filled with sodium chloride crystals and the bulk solution was 1mM ammonium nitrate at 90 °C (Condition 1). Similar distributions of attack on the crevice walls have been observed for iron/acidic Cl$^-$ at 23 °C systems which exhibit active-to-passive transitions in their bulk solution polarization curves, when a potential higher than the pitting potential was applied to the outer surface.\(^{70}\)

Figure 2.5 is the potentiodynamic curve of a flat Al 6111-like alloy specimen, embedded in an epoxy resin and positioned vertically, in a 1 mM NH$_4$NO$_3$ + 3 mM NaCl solution at 90 °C with a scan in the positive potential direction starting from + 200
Figure 2.4. (Condition 1) Optical micrograph (25x) shows the lightly pitted region between the attacked areas at the top and the bottom of the crevice wall of an Al 6111-like alloy specimen (0.68% Cu) at 90°C. The potential applied at $E_{e=0}$ is 1.4 V SCE for 3 hours. The micrograph was taken after the experiment was over.
Figure 2.5. Potentiodynamic polarization curve for the same alloy (0.68% Cu) in a 1 mM NH₄NO₃ + 3 mM NaCl at 90 °C with a scan in the positive potential direction starting from the corrosion potential (0.166 mV s⁻¹). The scan of the potential started from +200 mV above the open circuit potential (in the more noble direction).
mV above the open circuit potential corrosion potential (0.166 mV s⁻¹). The scan started at +200 mV above the open circuit potential (in the more noble direction) in order to avoid the instability of the measured current below this value due to the absence of any kind of supporting electrolyte. Choosing 3 mM NaCl in this experiment was considered to simulate the concentration of chloride ions in the bulk solution after the chloride ions being diffused from inside the crevice to the bulk solution. The diffusion happened because of the concentration difference of chloride ions between the bulk solution which is free of chloride ions and the crevice which is full of NaCl crystals.

Figure 2.6 is a micrograph shows the outer surface of the same sample represented in Figure 2.4. It shows large pits relatively to those found within the crevice. Pitting took place due to the diffusion of chloride ions out of the crevice as mentioned above.

The current transient of the crevice experiment shown in Figure 2.4 is represented in Figure 2.7. The current increase until it reached 1 mA then dropped to 450 µA/cm². This maximum in the current appeared at the time at which the chloride concentration achieved its maximum at the outer surface due to the diffusion of chloride ions from inside the crevice. The current measured in this transient can not be considered as the crevice corrosion current because of the high current coming from the top of the crevice wall (pitted region) besides the outer surface due to pitting corrosion.
Figure 2.6. (Condition 1) Optical micrograph (25x) shows the pitted region on the outer surface of an Al 6111-like alloy specimen (0.68% Cu) at 90 °C. This pitting took place due to the diffusion of chloride ions out of the crevice. The potential applied at $E_{x=0}$ is 1.4 V SCE for 3 hours. The micrograph was taken after the experiment was over.
Figure 2.7. The current transient for the same experiment represented in Figure 2.4.
The question arises: Does this morphology of attack on the wall appear because of the flux of chloride ions out of the crevice, which led to a concentration gradient of chloride ion within the crevice or is it due to the \( IR \) voltage drop within the crevice?

**Condition 2**

To answer the above question, another experiment was carried out (condition 2) in which a sodium chloride-saturated bulk solution was used (to ensure that there is no chloride concentration gradient within the crevice). All other conditions were the same as condition 1 except that the applied voltage was +1.0 V SCE (which is also above \( E_{\text{pit}} \) of the saturated NaCl bulk solution) and the duration of the experiment is only 6 minutes.

Figure 2.8 shows the same result on the crevice wall as in Figure 2.4. The only difference is the extent of the attack on the crevice wall of the sample. Crevice corrosion started immediately at \( t = 0 \) after the potential is applied in both conditions (1 & 2). In another word, pitting takes place at the top then relatively lightly pitted region and heavy crevice corrosion at the bottom of the crevice. The difference in the extent of corrosion on the crevice wall can be easily understood from the big difference in the chloride concentration in the bulk solution and within the crevice and consequently in \( E_{\text{pit}} \) and pitting density between those two experiments. The difference in the chloride concentration within the crevice comes from the depletion of chloride ions from inside the crevice to the bulk solution due to diffusion (condition 1) but this does not exist in
Figure 2.8. Optical micrograph (8x) shows a lightly pitted region between the attacked areas at the top and the bottom of the crevice wall of an Al alloy sample (0.68% Cu) at 90 °C in saturated chloride solution. This result also was obtained at 70 °C. The potential applied at $E_{x=0}$ is 1 V SCE for 6 minutes. The micrograph was taken after the experiment was done.
condition 2 where the both the bulk and crevice electrolytes are saturated with NaCl. Thus, this distribution of attack (lightly pitted region between the heavily pitted top and the crevice corroded bottom) is not a function of the concentration of the chloride ions within the crevice.

Figure 2.9 shows the current transient for this experiment represented in Figure 2.7. The measured current also cannot be considered as the crevice current where the top of the crevice wall has a potential higher than the pitting potential. This can be understood from the measured current. The measured current is three times higher than the maximum current of the active peak (the limiting current) as shown in Figure 2.9. This can be explained from the contribution of the current coming from the region which undergoes pitting at the top of the crevice wall.

In the measured polarization curves of the alloy in a still and agitated saturated sodium chloride solution at 90 °C, shown in Figure 2.10, the Al alloy samples were flat and embedded in an epoxy resin of surface area 1 cm². These samples were oriented vertically. They show an active nose with a current density difference of more than one order of magnitude between the peak current, in the active region, and the passive current, \( i_{\text{pass}} \). \( i_{\text{pass}} = 10 \text{ mA/cm}^2 \) which means a high rate of corrosion in the passive region. The appearance of this active/passive transition was not affected by whether or not there was stirring during the measurement of the polarization curve which indicated that the transition from the active peak to a passive region is not due to salt film formation at the electrode surface.
Figure 2.9. The current transient for the experiment represented in Figure 2.6.
Figure 2.10. Potentiodynamic polarization curves for the same alloy as in Fig. 5 (0.68\% Cu) in a saturated solution of NaCl at 90 °C with a scan in the positive potential direction starting from the corrosion potential (0.166 mV s\(^{-1}\)). (a) Agitated solution and (b) Still solution.
Thermodynamically, the formation of an AlCl$_3$ salt film is even more favorable to be formed at ambient temperatures than at elevated temperatures. This can be seen in Figures 2.11 and 2.12. Figures 2.11 and 2.12 are the Pourbix diagrams for the aqueous Al-Cl-90 °C and Al-Cl-23 °C systems respectively. As can be shown in these $E$-pH stability diagrams, the stability area of AlCl$_3$ phase is even higher at the ambient temperature (23 °C) than at the elevated temperature (90 °C) for the same bulk chloride solution concentration. This is another confirmation, beside there is no effect of agitation on the shape of the polarization curve, that the salt film is not the reason of the active to passive transition at the elevated temperature.

In the case of still solutions, the visual observations of the surface of the sample from the beginning of the scan through the active region indicated that the dissolution starts with a high density of pits which are soon connected to each other to give a nominally uniform attack of the surface. This phenomenon of initiating pitting in the active region was not observed in the case of agitated solution. Smialowska$^{(92)}$ reported pitting at the beginning of the active peak, when the surface of the metal is inhomogeneous and contains some areas more active than others, e.g. mild steel (with sulfide inclusions) in neutral chloride solution. Passive film break down occurs at different locations on the surface at the beginning, followed by a uniform corrosion. Also Isaacs$^{(11)}$ reported a similar situation for stainless steel where the active peak (within a crevice) started with a pit which grew laterally to encompass the whole
Figures 2.11. Pourbax diagrams for the aqueous Al/6M NaCl at 90 °C system. This Pourbax diagram was constructed by HSC Chemistry Software version 2.03.
Figures 2.12. Pourbix diagrams for the aqueous Al/6M NaCl at 23 °C system. This Pourbix diagram was constructed by HSC Chemistry Software version 2.03.
surface and that was documented by a video camera and a VCR. He justified this by the mass transfer limitations.

Figure 2.13 illustrates the measured electrode potential profile, \( E(x) \), inside the crevice for Al 6111-like alloy (0.68% Cu) with sodium chloride crystals packed inside the crevice gap (condition 2). The bulk solution is 1mM ammonium nitrate saturated with sodium chloride at 90 °C. Insert shows an enlargement of the plot in the vicinity of \( E_{\text{pit}} \) and \( E_{A/P} \). The gradient was measured immediately after applying the constant potential and it lasted for 30 minutes. It shows that a very large \( IR \) voltage drop existed inside the crevice during the experiments conducted under condition 2. The voltage drop, Figure 2.13, which is the same magnitude as the difference in \( E(x) \) from \( x = 0 \) to \( x = L \), is almost 1.8 V. The measured electrode potential within the crevice matched well with the polarization curve in terms of the pitting, \( E_{\text{pit}} \), and active/passive potentials, \( E_{A/P} \), potentials, see Figure 2.13.

Figure 2.14 is potentiodynamic polarization curves for the same alloy (0.68% Cu) represented in Figure 2.13 in a quiescent saturated solution of NaCl at 90, 70 and 23 °C. Scan rate is 0.166 mV/s. The scanning starts from the open circuit potential and proceeds forward in the more noble direction. It indicates that the minimum temperature for this active nose to appear is 70 °C. The reason for that might be attributed to the change in the nature of the oxide layer, in aqueous solutions, from bayerite to boehmite around 75 °C. \(^{93}\)
Figure 2.13. Measured electrode potential profile, $E(x)$, inside the crevice for Al 6111-like alloy (0.68% Cu) with sodium chloride crystals packed inside the crevice gap (condition 2). The bulk solution is 1mM ammonium nitrate saturated with sodium chloride at 90 °C. Insert shows an enlargement of the plot in the vicinity of $E_{\text{pit}}$ and $E_{\text{A/P}}$. The gradient was measured immediately after applying the constant potential and it takes 30 minutes.
Figure 2.14. Potentiodynamic polarization curves for the same alloy (0.68% Cu) in a quiescent saturated solution of NaCl at 90, 70 and 23 °C. Scan rate is 0.166 mVs⁻¹. The scanning starts from the open circuit potential and proceeds forward in the more noble direction.
The Cu content in the alloy was not responsible for the appearance of the active nose in the polarization curve. Figure 2.15 is the potentiodynamic polarization curves for alloy # 09 (0% Cu) in a still saturated solution of NaCl at 90 °C with a scan starting from the corrosion potential at a rate of 0.166 mV s⁻¹. It shows that the active nose and the active-to-passive transition also appear for the Cu-free alloy. The only difference in the polarization curves for the two alloys is the ~ 30 mV shift of the open circuit potential in the less noble direction for the Cu-free alloy.

The effect of chloride concentration in the bulk solution is shown in Figure 2.19, which shows three potentiodynamic polarization curves for the same alloy in three different chloride bulk solution concentrations at 90 °C with a scan starting from the corrosion potential at a rate of 0.166 mV s⁻¹. It shows that only an active passive transition for the saturated solution (6 M) while 4M and 5M NaCl only show passive to active behavior. Figures 2.17 and 2.18 are Pourbiax diagrams for aluminum metal in 4M NaCl and 5M NaCl solutions at 90 °C. These diagrams were constructed and compared with the aluminum metal in 6M NaCl solution (Figure 2.11) in order to find out whether a different phase was formed at the 4M or 5M NaCl solutions that was not formed at the 6M NaCl solution (saturated NaCl Solution) or vice versa. Pourbiax diagrams for aluminum in different NaCl solution concentrations at 90 °C (2.11, 2.17 and 2.18) are almost the same with an AlCl₃ stability area lower than that found at 23 °C (Figure 2.12) which make the elucidation of the sharp change of the polarization curve behavior hard.
Figure 2.15. Potentiodynamic polarization curves for alloy # 09 (0% Cu) in a still saturated solution of NaCl at 90 °C with a scan starting from the corrosion potential at a rate of 0.166 mV s⁻¹.
Figure 2.16. Potentiodynamic polarization curves for alloy # 8 (0.68% Cu) samples in three different NaCl solutions of different chloride concentration at 90 °C. Scan rate is 0.166 mVs\(^{-1}\). The scanning direction was the more noble direction starting from the open circuit potential.
Figures 2.17. Pourbix diagrams for the aqueous Al/4M NaCl at 90 °C system. This Pourbix diagram was constructed by HSC Chemistry Software version 2.03.
Figures 2.18. Pourbix diagrams for the aqueous Al/5M NaCl at 90 °C system. This Pourbix diagram was constructed by HSC Chemistry Software version 2.03.
**Condition 3**

At room temperature, in 1M NaCl at pH 8.25 and a crevice gap of a few microns, the corrosion of the crevice wall was revealed by staining. This staining can be seen clearly from Figure 2.19 for a sample polarized at –1.45 V SCE (passive region) for 50 minutes and from the corresponding polarization curve shown in Figure 2.20. The preconditioning at –2.24 V SCE for 2 minutes is thought to reduce the oxide layer\(^{16, 17}\) to a reproducible state on the alloy surface and allows the reproducible demonstration of the active nose. Polarization curve measured using a scan rate of 30 mV s\(^{-1}\), shows an active peak and a transition to a lower current density region, Figure 2.20.

The limiting current of this active peak represented for the Al alloy in Figure 2.20 is almost 10 mA/cm\(^2\). What was expected from the crevice experiment represented by Figure 2.19 is to find an extensive corrosion within the crevice instead of staining. This argument can be discussed within the linear sweep voltammetry (LSV) equations for a reversible system.\(^{94}\) For the same conditions, the peak current, \(i_p\), is related to the scan rate, \(\nu\), the following equation can be derived;

\[
(i_p)_1/(i_p)_2 = [(\nu_1)/(\nu_2)]^{1/2} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots 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Figure 2.19. Optical micrograph (8x) shows another crevice corrosion form (stain). Al 6111-like alloy (0.68% Cu) at room temperature had been polarized at – 1.45V SCE for 50 minutes in 1M NaCl solution of pH 8.25. The crevice gap was only a few µm (“tight crevice”).
Figure 2.20. Potentiodynamic polarization curves of Pt and 6111-like alloy (0.68 Cu\%) in 1M NaCl solution at 23 °C after reducing the oxide layer by conditioning the surface at –2.24 V SCE for 2 minutes. Scans are from negative to positive potentials at a rate of 30 mV s\(^{-1}\).
current, the mass transportation limitations of the aluminum ions within this very tight
crevise play a significant role in the inhibition of the crevice corrosion.

Another question rises here; is this active peak due to H atom oxidation or Al
dissolution? To answer this question, the area under the peak was integrated to find out
the number of coulombs passed and compared to the number of coulombs required to
oxidize an intact monolayer of H atoms over 1 cm². The answer was totally supporting
that this peak was due to Al dissolution where the number of coulombs actually passed
was 137.5x10⁻⁴ coulombs, while in order to oxidize an intact monolayer of H atoms,
which is a hypothetical situation, it is only enough to pass 4 x 10⁻⁴ coulombs which is
almost 35 times lower than what is actually passed under the peak of the Al alloy curve.

For more confirmation on this point, this behavior (active peak and a transition to a
low current density) is confirmed by carrying out the same experiment on a platinum
electrode. Figure 2.20 shows the polarization curves for the alloy and the Pt electrode.
The absence of an active nose or even a depression of the cathodic current in the Pt
curve in the potential region of the anodic peak indicates that the current peak on the Al
alloy curve is caused by the anodic dissolution of the Al alloy rather than by some other
reactions (involving bulk solution species). An increase in pH (due to the HER \cite{18, 19})
near the surface is assumed to be responsible for the appearance of the anodic peak.
2.5.2. Al Alloy/0.1M Nitric Acid System

The Al alloy/0.1M nitric acid system undergoes crevice corrosion under cathodic polarization. The importance of this point arises from the fact that crevice corrosion of aluminum and aluminum alloys samples with no outer surfaces is accompanied, if not due to, an increase rather than a decrease in the pH especially in the absence of chloride ions.\(^{(42)}\) So, the samples were cathodically instead of anodically polarized as an accelerated test in order to increase the pH within the crevice. The increase in the pH within the crevice by cathodic polarization was addressed before by Peterson and Lennox when they studied the effect of cathodic polarization on stainless steel in seawater.\(^{(29)}\)

Nitric acid and ammonium hydroxide at pH 1 and 13, respectively, provide an exceptional stability for the protective aluminum oxide layer\(^{(95)}\) where the dissolution, in contrast with thermodynamics, is kinetically very slow. For this reason, 0.1N nitric acid (pH 1) was used as the electrolyte in this series of crevice experiments at room temperature.

Figure 2.21 is a micrograph that shows crevice corrosion occurred within the crevice when applying a cathodic potential, \(-1.45\) V SCE, to the outer surface of the sample for four hours. In these experiments, the crevice gap was 0.15 mm. The boundary between the non-attacked cathodically protected region and the crevice-corroded active region is very clear. The non-attacked region on the crevice wall was the same in appearance as
Figure 2.21. Optical micrograph of the active/passive transition region of the crevice wall after 4 hours in 0.1M HNO₃ at –1.45 V SCE. Crevice gap is 0.15 mm. Sketch shows the whole crevice wall and the different regions. The other sketch shows the cross section of the crevice wall.
the outer surface and extended from the crevice mouth at $x = 0$ into the crevice to the boundary with the attacked region. The boundary between the active and the passive regions, $x_{A/P}$, is not shown in the micrograph but was observed to be sharp. The potential applied at the outer surface (-1.45 V SCE) is well below the open circuit potential for the alloy in the solution even after preconditioning the surface for 2 min at $-2.24$ V SCE (see Figure 2.23 later).

Figure 2.22 shows the **IR** potential drop measured after 4 hours using the Luggin microprobe. The potential drop is almost $+1.1$ V. The schematic insert in this figure shows that the location of crevice corrosion on the crevice wall matched exactly with the potential of the active peak measured in the polarization curve (see Figure 2.22 where $E_{oc} \approx 1.050$ V SCE and $E_{A/P} \approx 0.92$ V SCE). The hydrogen evolution within the crevice due to cathodic polarization increases the pH, allowing for a decrease in stability of the passive film, and formation of an active peak in the polarization curve and the observed corrosive attack on the crevice wall. The measured pH with the crevice using a pH paper was 3. This pH measurement is an average measurement for the solution’s pH within the crevice.

The formation of the active peak, as the pH increases, was confirmed by studying the polarization behavior of the alloy at different pH of the nitric acid-sodium nitrate solutions as can be seen in Figure 2.23. It shows that the active peak is present at pH 2 and increases at pH 5.4 but it does not appear at pH 1 in the polarization curves (Figure 2.23). By applying a potential $E_{x=0}$ lower than the open circuit potential to the outer
Figure 2.22. Measured electrode potential profile, $E(x)$, inside the crevice for the Al 6111-like alloy (0.68% Cu) in 0.1M HNO3 (bulk solution) after 4 hours of conditioning the surface at – 1.45 V SCE.
Figure 2.23. Effect of pH on the formation of an active peak in the polarization curve of Al 6111-like alloy in 0.1M nitrate solution at different pH. Scan is from negative to positive potentials at a rate of 40 mV s$^{-1}$. 

Current $i$, mA cm$^{-2}$
surface, the electrode potential, $E(x)$, in the crevice will be more noble (positive) with increasing distance into the crevice (since current flows into crevice at these cathodic potentials), and at some distance, $x_{oc}$, it will enter in the region of the active peak which is bounded by the open circuit potential, $E_{oc}$, at around $-1.0$ V SCE and the potential of the active/passive transition, $E_{A/P} \approx -0.9$ V SCE. With the applied potential in the cathodic part of the polarization curve, rather than in the passive region, the outer surface is cathodically, rather than anodically, protected. Thus, crevice corrosion also occurs for this condition if the $IR$ voltage is sufficiently large for $E(x)$ to be in the active peak region on some part of the crevice wall. This system also shows the $IR$ voltage drop causes $E(x)$ values to be in the potential range of the anodic peak, which itself is created by the increase in pH. This situation during localized corrosion under cathodic polarization conditions has been studied and discussed before.\(^{(63, 67, 96, 97)}\)

Another question can be raised about whether the pH or the potential drop or both are responsible for crevice corrosion in that case where the pH increased inside the crevice. The increase in pH could occur either by cathodic polarization or at open circuit potential due to the absence of an outer surface so the hydrogen evolution reaction occurs locally within the crevice. The answer for this can be easily understood from the distribution of the crevice corrosion on the crevice wall which is illustrated in the sketch in Figure 2.21. Crevice corrosion occurred as a region of the wall between the open circuit, $x_{oc}$ boundary and the active/passive, $x_{A/P}$, boundary on the crevice wall. This is consistent with the measured $E_x$ distribution on the crevice wall where in the region of the cathodic polarization, $x = 0$ to $x_{oc}$, there was no corrosion, then crevice
corrosion between $x_{oc}$ and $x_{A/P}$, then no corrosion again at $x > x_{A/P}$. What happened is that the increase in the pH allows for the appearance of the active state and the active to passive transition. The former was the reason for the horizontal boundary seen in Figure 2.21 and the latter for the $x_{A/P}$ boundary (not shown in the micrograph in Figure 2.21). The shape of crevice corrosion is matched with the shape of a polarization curve with an active peak. The situation, in some way, is similar to iron in basic medium. In the later case the decrease in the pH to pH 4 allows the formation of the active to passive transition and crevice corrosion occurs immediately. If only pH is responsible, so the corrosion should be high near the top of the crevice wall where pH is higher where HER near the top of the crevice wall is beefed up by high overvoltage (-1.45 V SCE). Going deeper in the crevice should have a lower pH, so corrosion should be less and so on. This is quite different from actual situation described above.

2.6. CONCLUSIONS

From the above experiments, it can be concluded that:

The active peak that formed for this alloy in saturated sodium chloride solution at high temperature was not due to salt film formation.

(i) The Cu content doesn’t affect the alloy’s polarization behavior.

(ii) Different forms of crevice corrosion were observed in chloride media which is more than has been previously proposed where the nature of crevice corrosion is described as only pitting.\(^{(10)}\)
(iii) The chloride concentration within the crevice does not change the mechanism of the crevice corrosion of an experimental 6113-like Al alloy (with 0.68% Cu) only the susceptibility and the rate of the attack are affected by chloride concentration.

(iv) Also, it is clear that the increase in the pH (not the oxidation of H atoms adsorbed on the surface) due to either prior cathodic polarization (conditioning), as in the case of the chloride solution experiments conducted in this research or during the cathodic polarization in the case of the nitric acid experiments, creates an active peak in the polarization curve. It is obvious from these results that this active peak combined with the IR drop to stabilize crevice corrosion for at least the Al alloy studied in this work.
2.7. REFERENCES


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CHAPTER 3

INTERGRANULAR CORROSION OF UNDERAGED Al 6111-LIKE ALLOYS

3.1. ABSTRACT

This study focuses mainly on the corrosion of a peak aged aluminum 6111-like alloy of 1.47% copper using an artificial pit configuration (pencil type electrode configuration with a rectangular cross section) with relatively larger specimens in the form of plates rather than wires. The sample which was flush with the surface of the epoxy resin mount was anodically polarized in neutral NaCl solutions of different concentrations and pH 6.9. The alloy dissolved uniformly at a certain rate to form a local cell with epoxy resin walls and the alloy surface as its bottom. Intergranular corrosion (IGC) also occurred and was recorded every 900 seconds using a stereo-microscope (through the transparent epoxy) connected to a PC uploaded with time-lapse software. The IGC rate was in the order of 0.5 mm/day. The potential drop profile within the cavity was recorded on a daily basis and this profile showed that the total potential drop was on the order of 50 mV. The pH in the local cell was measured using a commercial mono pH microelectrode coupled with a homemade Pyrex (glassy) microprobe connected to a SCE and controlled by a 3-D manipulator. Measurements of pH showed the solution within the cavity was alkaline with a pH that ranged from 9-12. Also, the chloride ion concentration within the local cell was measured using a mono Ag/AgCl microelectrode.
coupled with the same glassy microprobe, which is connected to a SCE. These measurements showed that the chloride concentration within the cavity was at least one order of magnitude higher than that in the bulk solution. The study of the effect of the chloride ion concentration on the IGC rate showed that the increase in the chloride ion concentration increased only the initial rate of the IGC but the overall rate remained almost the same.

3.2. OBJECTIVE

The goal of this work was to study the intergranular corrosion of an as-received (peak-aged) Al 6111-like alloy with 1.47%Cu addition and to measure the intergranular corrosion propagation rates. Another parallel goal is to provide the potential profile, pH profile and the chloride ion concentration profile within cavities formed mainly due to intergranular corrosion. This data is required for developing a mathematical model for predicting the localized corrosion for this alloy and those of other compositions.

3.3. LITERATURE REVIEW

Pure aluminum is very corrosion resistant in general but is typically not used in structures because of its low strength. The addition of strengthening elements improves the mechanical properties but decreases the corrosion resistance at the same time. Al alloys can be classified according to the major alloying elements into eight series starting from the 1XXX to the 8XXX. Al-Mg-Si alloys are of the 6XXX family. They
are classified as moderately high strength alloys. They are suitable for building, marine, machinery, and process equipment applications.\(^{(1)}\) The aerospace industry started to depend upon aluminum alloys a while ago.\(^{(2)}\) Recently, automakers have even more interest in using the high strength aluminum alloys where they are up to 40% lighter than their corresponding steel parts. One of the infamous forms of corrosion of the Al 6xxx series alloys is intergranular or intercrystalline corrosion (IGC).

Aluminum 6111-like alloys are hardened by the formation of metastable precursors of one or more of the following phases: \(\text{Mg}_2\text{Si} (\beta)\), \(\text{Al}_2\text{Cu} (\theta)\), \(\text{Al}_2\text{CuMg} (S)\) and/or \(\text{Al}_{x}\text{Cu}_y\text{Mg}_z\text{Si}_w (Q)\) phases and develop a complex microstructure upon ageing.\(^{(3)}\) The type and the amount of the precipitation of different phases relies upon the ratio between the Si and Mg and also the amount of Cu in that alloy. According to the Mg:Si ratio, the Al-Si-Mg commercial alloys can be classified into three groups. The first group is that which contain balanced ratios between Mg and Si which is 1.73:1. The other two groups have unbalanced ratio between the Mg and the Si.\(^{(4)}\) The alloy presented in this study is of the category which has excess Si. It contains 0.41-0.42 wt. % excess Si which means that the ratio between Mg and Si is 1.73:1.41 rather than 1.73:1. Also the alloy contains 0.96-0.99 wt. % of \(\text{Mg}_2\text{Si}\) in the peak aged condition.

Blanc and Mankowski\(^{(5)}\) described the precipitation sequence for Al-Mg-Si Al-6056, a French version of Al-6013. The described sequence is as follows: Mg and Si enriched spherical GP zones\(\rightarrow\)Clusters of Mg and Si atoms\(\rightarrow\)co-clusters of both Mg and Si
Besides the dispersed $\beta''$ precipitates, Shi et. al.,$^{(6)}$ reported some precipitation along the grain boundaries of an Al 6111-like alloy with a distribution less in density than that within the grain. Initially they did not find any precipitate free zones (PFZs). They supposed that the copper-containing precipitates existing at the grain boundaries may be composed of the quaternary $\text{Al}_x\text{Cu}_y\text{Mg}_z\text{Si}_k$ phase. But, in a recent scanning transmission electron microscopy (STEM) study of him,$^{(7)}$ he proved the existence of Cu-Mg-Si rich secondary phase at the grain boundaries with a Cu depleted region adjacent to the grain boundaries. Also, it is likely according to his research, that these secondary phase particles might contain aluminum since the aluminum signals could be either originated from the matrix or the secondary phase itself. The width of the Cu depleted regions is in the order of 30 nm. The Cu-Mg-Si precipitates could act as cathodes relative to the regions just adjacent to them. The later point was also reported previously by Mankowski et. al., elsewhere on their study on a similar alloy.$^{(8, 9)}$  

Many mechanisms have been proposed to explain intergranular corrosion in aluminum and its alloys. Galvele and De Micheli$^{(10)}$ studied the intergranular corrosion of Al-4%Cu in chloride solutions. Figure 3.1 is a schematic shows the microstructure of an aged Al-4%Cu alloy. They found that that the presence of chloride ions is necessary for intergranular corrosion to happen. In another word, the potential difference between the Cu depleted regions (Region 2 in Figure 3.1) and both the matrix (region 1 in Figure
3.1) and the grain boundaries (Region 3 in Figure 3.1) is not the only reason for intergranular corrosion to take place. To study this, pure aluminum, pure Al$_2$Cu alloy (representing the intermetallics) and Al-0.2\%Cu (representing depleted regions) special samples were prepared by Galvele and De Micheli and the coupling between them was studied by them in the 1970’s.$^{(10)}$ Their study resulted in a conclusion that intergranular corrosion of the Al-4\%Cu alloy occurred because of the differences in the breakdown potential between the pure aluminum and the intermetallics at the grain boundaries. This opposes the commonly proposed theory regarding the influence of differences in the potential between grain boundaries and the matrix.$^{(3, 4, 8, 9, 11, 12)}$

Mankowski and Guillaumin$^{(8)}$ studied the mutual relation between pitting and intergranular corrosion of 6056-T6 which is the French version of alloy 6013 in 1 M NaCl. They found that pits nucleated at coarse intermetallic Al-Si-Mg-containing particles within the grains, and then developed through microscopic tunnels while the intergranular corrosion nucleated on the pits walls and spread from them. It was proposed by them that the mechanism of the intergranular corrosion was based upon the preferential dissolution of the anodic Si and Cu depleted zones along the grain boundaries. Cu-Si-Mg rich intergranular precipitates worked as local cathodes and stimulated the dissolution of the depleted zone. They also studied the influence of the T78 overaging treatment on the corrosion behavior of the same alloy in the same solution.$^{(9)}$ They found that Al 6056-T78 coarse intermetallic Al-Mg-Si-containing particles were found to be even more reactive than those in the Al 6056-T6 alloy.
Figure 3.1. Schematic representation of the microstructure of an aged Al-4\%Cu alloy illustrating three phases: I-the intermetallic compound $\theta$, II-the copper depleted region along the grain boundaries, and III-the matrix.\(^{(10)}\) $\delta$ is average size of the precipitate.
Burleigh\textsuperscript{(13, 14)} studied also the intergranular corrosion of two Al-Si-Mg-Cu alloys. For one heat-treated alloy, the intergranular corrosion was investigated using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). For the other alloy, Al 6013-T6, it was found that the alloy is immune to exfoliation and stress corrosion cracking but it shows severe and shallow intergranular corrosion during long-term seacoast exposure which is quite similar to the other 6XXX alloys, notably alloy 6061-T6. The results in both indicated, according to the author, that IGC of this alloy occurred because the depleted region adjacent to the grain boundaries corroded rapidly in acidic solutions within the pits. He proposed the presence of pits with corrosion chimneys, or some type of occluded cells, must have maintained the acidic environment, which caused intergranular corrosion. These results lead Burleigh to the conclusion that intergranular corrosion would not take place without the occluding nature of the pit covers. Additional work was carried out\textsuperscript{(13, 14)} to measure the actual rate of local corrosion that took place by the galvanic coupling of the Al-6013 matrix with the depleted grain boundary region. In this work, the alloy was compared with pure aluminum. The pure aluminum worked as a depleted grain boundary region, and dissolved at a rate of almost three orders of magnitude higher than that of the alloy. Because of the low quality of the in situ microscopy performed in his study, all measurement and study of the intergranular corrosion was necessarily performed after the completion of the experiment. These results reveal some of the problems of traditional microscopy of an immersed surface.
The segregation of the excess Si at the grain boundary was discovered by Bhattamishra and Lal.\(^{(4)}\) These segregated Si precipitates are cathodic with respect to the bulk alloy and result in a depleted zone adjacent to the grain boundary. These depleted zones act anodically relative to both the matrix and the Si precipitates and this consequently results in the intergranular corrosion susceptibility.

Buchheit et. al.,\(^{(15)}\) studied the role of microstructural heterogeneity on the intergranular corrosion of Al 2090 alloy in 3.5% NaCl solutions. A mechanism was proposed for the intergranular corrosion of these kinds of alloys. According to this mechanism, preferential precipitation at the grain boundary or sub-grain boundary takes place. Grain boundary precipitates (Al\(_2\)CuLi) undergo active dissolution. Due to the dissolution of these precipitates, the pH decreased and an aggressive occluded environment developed. The later maintained the process and dissolution propagated along the grain boundaries.

Another mechanism was proposed for alloy 2017 by Izu et. al.\(^{(16)}\) They attributed intergranular corrosion to the difference in pitting potentials between the areas close to the grain boundaries and the matrix.

Yamaguchi and Tohma\(^{(17)}\) attributed the intergranular corrosion of Al-Mg-Si-Cu alloys to the selective dissolution of the Mg\(_2\)Si phase that precipitated in the grain boundaries and also to the galvanic phenomenon induced between the less noble Mg\(_2\)Si and the noble Cu-containing grain matrix.
For the Al-Mg and Al-Mg-Zn, Cherkasov et. al.,\textsuperscript{(18)} found that annealing at 200 °C caused the formation of an unstable $\beta$ phase ($\text{Mg}_2\text{Al}_3$). This precipitation of $\beta$ along grain boundaries was in the form of relatively continuous chains which made the alloy susceptible to intergranular corrosion.

The processing parameters and the chemical compositions effects on the intergranular corrosion of Al 5182 alloy were studied by Tsuchida and Tanaka.\textsuperscript{(19)} Ohsaki, et. al.,\textsuperscript{(20)} studied the effect of stretching before the peak-aging on the intergranular corrosion of Al 2090 and 2091 alloys. Stretching prior the peak aging improved the corrosion resistance to the intergranular corrosion of these two alloys in general but more noticed in case of Al-2090. This was attributed to the uniform precipitation of Cu-rich phases within grains because of the stretching. Ohsaki and Takahashi\textsuperscript{(21)} related the susceptibility of stress corrosion cracking (SCC) to the intergranular corrosion. They found that cracks nucleated at the intergranular corrosion pits. The correlation between stress corrosion cracking and intergranular corrosion was also investigated on 2017 alloy with various aging structures by Izu et al.\textsuperscript{(16)} They also found that the pitting potential close to the grain boundaries was totally different from those grains. Maitra and English\textsuperscript{(22)} studied the effect of the same environments on the difference between the pitting potentials of the grain boundaries and the matrix for alloy 7075-T7351. Chaudhuri, et. al.,\textsuperscript{(23)} compared the fatigue life of 6013 bare, Alclad 2024, and 2024 bare aluminum alloy sheet materials. They attributed the low fatigue life of Al-6013 alloy to the intergranular corrosion. Posada, et. al.,\textsuperscript{(24)} studied the exfoliation...
of the materials used in aircraft bodies (alloy KC-135). Their study showed that the anodic sites do not play a significant role in the nucleation or the propagation of the exfoliation.

Intergranular corrosion can not be explained only by theories which talk about precipitation at or close to the grain boundaries for certain alloys. Also, it can not be explained in terms of the difference in the pitting potential between the matrix and the secondary phases since it has been reported that the IGC takes place in a zone-refined aluminum and zone refined iron.\textsuperscript{(25, 26)}

Many facilities, equipment and methods have used to study intergranular corrosion. Atomic Force Microscope (AFM) was used for the nanoscopic visualization of initiation and growth of intergranular corrosion in the 7XXX aluminum alloys.\textsuperscript{(27)} Also, transmission electron microscopy (TEM), scanning electron microscope (SEM) and energy-dispersive X-Ray analysis (EDAX) techniques have been used to study the intergranular corrosion of aluminum alloys.\textsuperscript{(3, 7, 13, 24, 28, 29)} Phase shift microscopy has also played a role in studying the behavior of the intermetallic particles in different electrolytes.\textsuperscript{(30, 31)}

Electrochemical techniques have been used to a small extent for investigating the intergranular corrosion of aluminum alloys. The reason for this is that IGC is mainly a non faradic process. For instance, Cherkasov, et. al.,\textsuperscript{(18)} used a potentiostatic method to enhance the dissolution kinetics to study the intergranular corrosion of Al-Mg and Al-
Mg-Zn alloys in solutions of 3% NaCl and 1% HCl. On the other hand, Tohma et. al.,\textsuperscript{(32,33)} worked on the estimation of the intergranular corrosion of Al--Mn, Al--Zn--Mg, Al--Si and Al--Mg--Si alloys by surface observations of the alloy in solutions of different chloride concentrations after polarizing the alloy galvanostatically. To test whether the material had unnoticeable intergranular corrosion, Prikhod'ko, et. al.,\textsuperscript{(34)} used eddy-current Dynamic Defectoscope to detect IGC in the initial stages. Eddy current is an electromagnetic technique and is completely non-destructive. It works on the principles of Electro Magnetic induction. Eddy Current is limited to testing metallic materials and works best on non-magnetic alloys. It can be applied to magnetic materials, such as ferritic stainless steels using magnetic saturation techniques. The new eddy current defectoscope having two microprocessors allows defects 30 and more microns to be detected in real time domain. Its sensitivity is comparable to that of ultrasonic defectoscopes.

McCosby\textsuperscript{(2)} significantly contributed to the study of the IGC in general, and to the study of the IGC of three Al 6111-like alloys with different Cu content in particular. He combined electrochemical techniques with in-situ optical microscopy to study IGC propagation. In order to obtain clear propagation rate measurements, he developed a new specimen arrangement that was also employed in the research presented in this thesis.

Pizzo and Daeschner \textsuperscript{(35)} used the phenomenon of a change in the mechanical properties for the materials (due to the IGC) to evaluate the susceptibility of aluminum
alloys to IGC. They compared the extension rates of Al-Li-Cu alloys before and after immersion in chloride solutions and found that the extension rate was higher after the immersion due to the intergranular corrosion.

Inhibition of IGC of aluminum alloys was studied by many groups using different techniques. Laser surface melting (LSM) technique was used by Ferreira et. al.,(36) to alter the localized corrosion resistance of Al-2024-T351. They compared the immersion test results before and after melting the surface with a carbon dioxide laser. Ferriera, et. al.,(36) found that IGC was totally suppressed and the pitting corrosion resistance was significantly enhanced as a result of LSM in 3% deaerated NaCl solutions. The reason of this was attributed, according to Ferriera et. al., to the production of a modified microstructure consisting of fine α-Al dendritic subgrains with Al2Cu precipitates in the subgrain boundaries. Also, Chan, et. al.,(37) used an excimer laser under two different gas environments (air and nitrogen) to treat the surface of an Al 6013-T651 alloy for the sake of improving its intergranular corrosion behavior. Excimer stands for excited dimer; a diatomic molecule usually of an inert gas atom and a halide atom, which are bound in excited states only. These diatomic molecules have very short lifetimes and dissociate releasing the excitation energy through UV photons. They found that the excimer laser surface treatment significantly increased the pitting potential and the intergranular corrosion resistance; especially, when the treatment conducted under the nitrogen gas environment. The high pitting corrosion resistance was attributed to the formation of an AlN phase on the alloy’s surface. The improved intergranular corrosion resistance was primarily attributed to the reduction of large harmful intermetallics.
within the grains at the surface and the absence of precipitate free zones and Al-Cu-Si bearing needle like precipitates at the grain boundaries.

Also, Alloying elements played an important role in the inhibition of the intergranular corrosion of Al alloys. The effect of Zn addition, for instance, on suppressing under-paint film corrosion and intergranular corrosion of Al-Mg-Si-Cu alloys was studied by Yamaguchi and Tohma.\textsuperscript{(17)} They noticed that small quantities of Zn decreased the intergranular corrosion. This can be explained in terms of minimizing the corrosion potential of the matrix with respect to the precipitates at the grain boundaries. This, in return, will decrease the potential difference between the matrix and the grain boundaries, which means decreasing the local galvanic coupling between the precipitates near the grain boundaries and the matrix. Also Sinyavskii, et. al.,\textsuperscript{(38)} found that additions of Zr and Sc improved the intergranular corrosion resistance of Al-Mg alloys. The intergranular corrosion resistance of Al-4.5%Mg was improved by aging as was reported by Dif et al.\textsuperscript{(39)} Ce additions have been used to inhibit the intergranular corrosion of Al 1430 alloy (Al-Li).\textsuperscript{(28)} The addition of Ce coarsened the grains and Al 1430 containing Ce showed better intergranular corrosion resistance when compared to the same alloy without Ce additions. Lal and Bhattamishra\textsuperscript{(40)} studied the effect of Cr and Si additions on the intergranular corrosion of Al-Mg-Si alloys. They observed that the degree of intergranular attack increased with increasing aging time with a maximum at the peak aged condition, and a decline after it. They also found that small additions of Cr improved the alloy’s resistance to intergranular corrosion.
Wu, et. al.\textsuperscript{(41)} studied the inhibition of intergranular corrosion of Al 7075 in NaCl solutions using sulfate ions. They found that the inhibitive effect increases with increasing the relative amount of sulfate ions in the chloride solution. They attributed the inhibition effect to both of the competitive adsorption and migration of the sulfate ions with the chloride ions. McIntyre and Dow\textsuperscript{(42)} studied the intergranular corrosion of Al-7075 alloy in artificial seawater in the presence of nitrate ions under room and elevated temperature conditions. They observed a unique synergism between the seawater and the nitrate ions where the seawater-nitrate environment accelerated the intergranular corrosion of the Al 7075 alloy. On the other hand, the aforementioned environment was very kind towards AA 6061, PM7XXX, IN9052, and IN905XL alloys. Al-Zn sacrificial anodes in hot seawater show intergranular corrosion. The higher the temperature, the more severe the intergranular corrosion. The same conclusion about the detrimental effect of the nitrates on the intergranular corrosion resistance of Al-7075 was reported earlier by Maitra and English.\textsuperscript{(22)}

Gatenby, et. al.\textsuperscript{(43)} studied the heat treatment effect on both the intergranular corrosion and the mechanical properties Al-5XXX alloys with 4.5% Mg. They found that annealing at a temperature higher than 623K reduced the intergranular corrosion while annealing at a temperature lower than 423K increased the intergranular corrosion sensitivity. They attributed the intergranular corrosion at low temperature to the precipitation of beta Mg\textsubscript{5}Al\textsubscript{8} (sensitization) which led to an extensive intergranular corrosion. Onda, et. al.\textsuperscript{(44)} studied the effect of different Mg and Si contents in Al-Mg-Si alloys. They found that the precipitation of Mg\textsubscript{2}Si at the grain boundaries for a
certain combination of temperature and composition was responsible for the intergranular corrosion. For alloy 7075, Rajan, et. al.,\(^{(29)}\) used a heat treatment (known as retrogression and reaging) to inhibit stress corrosion cracking without sacrificing the high yield strength through formation of large grain-boundary precipitates and coherent matrix precipitates. Dubost, et. al.,\(^{(45,46)}\) attempted to prevent the intergranular corrosion and the stress corrosion cracking of alloy 2214 through a “high-low” precipitation aging process. After solution heat treatment and cooling, the specimen was heated for a short time above 220 °C, cooled and then heated for a long period at less than 180 °C. They showed that this process, through increasing the volume fraction of the precipitates, inhibited the intergranular corrosion without sacrificing the hardness.

It could be easily deduced from the literature survey introduced above that most of what presented in the literature concerns microgalvanic effects in the vicinity of the grain boundaries. There is a significant shortage of information available in the literature concerning the chemical composition (pH and [Cl\(^-\)]) of the solution around the grains, the potential drop associated with IGC, and the rate of the IGC. The study presented in this chapter provides a novel view of the intergranular corrosion of an Al 6111-like alloy. In the present study, intergranular corrosion was studied in-situ while pH, chloride ion concentration, and potential drop measurements were being made.


3.4. EXPERIMENTAL

The intergranular corrosion form is one of the most difficult forms of corrosion to study. The measured current from polarizing the sample at a certain potential (or during the scanning of potential within a predefined potential window) in an accelerated corrosion test does not reflect the actual deterioration of the material under investigation. From this perspective, a combination of electrochemical and microscopic studies is very helpful in terms of quantifying the degree of the intergranular corrosion under a certain set of experimental conditions. This information can then be used in the development of a life-time prediction model for the alloy.

The chemical composition of the alloy is listed in Table 3.1. In this work all the samples were used in the as-received condition (underaged with a paint-bake cycle at 180 °C for 30 minutes) except of two specimens which were peak aged at 180 °C for 11 hours.

In every experiment, intergranular corrosion propagation rate, $IR$ potential drop within a cavity, and either pH profile within this cavity (see pH electrode specifications: Section 3.4.3) or chloride ion concentration profile within the same cavity (see Ag/AgCl electrode preparation: Section 3.4.4) were measured. In order to understand how the cavity was formed within which these measurements took place, the specimen configuration needs to be comprehended first. A well polished specimen (using 1 µ
Table 3.1 Chemical composition of the Al 6111-like alloy. The alloy was fabricated by ALCOA, Inc. and used in the as-received conditions. In this case, the as-received condition was naturally aged and then paint-baked for 30 minutes at 180 °C.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Type</th>
<th>Si (%)</th>
<th>Cu (Si)</th>
<th>Mg (%)</th>
<th>Mn (%)</th>
<th>Zn (%)</th>
<th>Ti (%)</th>
<th>Fe (%)</th>
<th>Al (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>749810</td>
<td>High Copper</td>
<td>0.78</td>
<td>1.47</td>
<td>0.63</td>
<td>0.21</td>
<td>0</td>
<td>0.01</td>
<td>0.24</td>
<td>Bal.</td>
</tr>
</tbody>
</table>
alumina slurry) with dimensions of 0.7x2.4x14 mm³ was embedded in an epoxy resin while a scale was fixed in front of the specimen (see specimen preparation: Section 3.4.5). The bulk solution contacted this specimen only at one of the two 0.7x2.4 surfaces while the opposite surface was connected to the potentiostat that was used in applying the desired constant potential, in the potentiostatic experiment, at the surface that was contacting the solution using a Hg/Hg₂SO₄ reference electrode. The other four surface of this specimen were totally embedded in the epoxy resin. At the beginning of the experiment there was no cavity but as time proceeded, corrosion took place and an IGC band was formed which later on changed to loose grains and a new IGC band was formed at a lower location which means that a cavity was formed. The cavity’s four walls in this case were of epoxy while the bottom of the cavity was the specimen with its IGC band at its top. The IGC band was dynamic where its location and thickness were changing with continuously with time.

The IGC propagation rate was measured in every experiment using: (i) the aforementioned specimen to which the desired potential was applied and (ii) a digital microscope that was connected to a PC which was loaded with software that allows capturing a single picture every 900 seconds, during the 7-days averaged experiment, for the 2.4x14 mm-surface (lateral surface) in front of which the scale was fixed. These pictures (around a 1000 single pictures for every experiment that were also, used to make a 1-minute movie) were analyzed after the experiment was finished. The pictures’ analysis was based on determining the change of both the IGC band thickness (h) and the cavity’s depth (H) with time. The feature that helped in determining h and H was the
different way that the three regions (loose grains, IGC band and non-attacked region) reflect the light of the microscope. These loose grains looked shiny while the IGC band looked darker than the region lower to it (the non-attacked part of the specimen). Using the scale fixed in front of the lateral side of the specimen, \( H \) and \( h \) values (in mm) can be determined at any time. Both of \( H \) and \( h \) were plotted on two different y-axes in one graph as a function of time (in days) on the x-axis. The total corrosion (\( h + H \)) at any day can be calculated from any IGC graph by adding the two corresponding points at that day. The current response to the applied potential at different times (\( i-t \) curve) was recorded using a PC. By comparing the actual current (after getting it from changing molar volume corresponds to the total corrosion \( H + h \)) to the average of the measured current, a new parameter was calculated which is the IGC index. IGC propagation rates were measured, besides the three specimens for the as-received alloy, for a peak aged specimen.

pH profiles within the cavity were measured, for two as-received specimens and one peak aged specimen, every day starting from the day at which there was a cavity that had a considerable depth (\( \geq 0.5 \) mm) and plotted as a function of distance within this cavity using a mono Sb/Sb\(_2\)O\(_3\) microelectrode (see pH electrode specifications: Section 3.4.3) which was coupled with a Pyrex microprobe (see Pyrex microprobe preparation: Section 3.4.2). That microprobe was connected to a SCE. Both of the Pyrex microprobe’s tip and the pH microelectrode’s tip were kept in the same plane to avoid errors that might rise from the \( IR \) drop in solution.
Chloride ion concentration profiles within the cavities, for three as-received specimens and a peak aged specimen, were measured every day starting from the day at which there was a cavity that had a considerable depth ($\geq 0.5 \text{ mm}$) and plotted as a function of distance within that cavity using a Ag/AgCl microelectrode coupled with a Pyrex microprobe. Both of the Pyrex microprobe’s tip and the Ag/AgCl microelectrode’s tip were kept in the same plane to avoid errors that might rise from the IR drop in solution.

For the IR potential drop profile measurements, both of the Pyrex microprobe, which was connected to a SCE, and the working electrode, were connected to a high impedance voltmeter. This set up was used to measure the potential drop profile as function of distance within the cavity daily starting from the day at which there was a cavity that had a considerable depth ($\geq 0.5 \text{ mm}$). IR potential drop measurements were carried out for three as-received specimens besides a peak aged specimen. The insertion of the electrodes and the microprobe within the cavity was done using a micromanipulator in a very slow manner in order to minimize the mixing effect.

Three solutions with different chloride concentrations were used in this study to characterize the effect of the bulk solution chloride concentration on both the concentration of chloride ion within an occluded cell (cavity), for an as-received specimen and the rate of the propagation of the intergranular corrosion. The chloride ion concentrations were 5, 50 and 100 mM prepared from the analytical J. T. Baker NaCl salt. The NaCl was used without further purification. For the pH measurements, only
one chloride concentration was used which was 50 mM NaCl. De-ionized water (with a conduc-tance of 9.5 µ siemens) was used to prepare the different solutions. In all experiments, a constant potential of +150 mV vs OCP (-824 mV Hg/Hg₂SO₄) was applied at the top of the specimen.

### 3.4.1. Experimental Set up

Figure 3.2 illustrates schematically the set up used in these experiments. The set up consists of: an alloy specimen of dimensions 2.4x7x14 mm³ embedded in an epoxy resin (its preparation will be mentioned below), an electrochemical cell (half of a standard flat cell), a carbon rod acting as a counter electrode, a Hg/Hg₂SO₄ reference electrode, a saturated calomel electrode (SCE), a potentiostat, a high impedance voltmeter/pH meter, a high impedance voltmeter, a Pyrex microprobe connected to the saturated calomel electrode (SCE) by TYGON polyethylene tube, a pH or Ag/AgCl microelectrode, and a stereo-microscope. Figure 3.3 presents a close up view of the digital photo showing an overview for the whole set up and manipulator fixed above the cell and tied to the base of the microscope using rubber connectors. This configuration was used to collect the images from the digital microscope. Note that the images that are collected and stored are inverted with respect to their actual orientation.

The microelectrode (pH or Ag/AgCl) and the microprobe (SCE) are held together using hot glue while their tips are in the same X-Y plane using a MM-33 micromanipulator purchased from Sutter Instruments Company. Keeping the tips in the
Figure 3.2. Schematic diagram showing the set up used in the intergranular corrosion study.
Figure 3.3. Digital photos showing (a) an overview of the entire experimental set up and (b) manipulator fixed above the cell which is tied to the base of the microscope using rubber connectors.
same X-Y plane is necessary to avoid any $IR$ potential drop between the Pyrex probe (which is connected to a SCE) and the microelectrode (either the pH or the Ag/AgCl). Thus it is not necessary to correct for the $IR$ potential drop for the pH or chloride ion concentration measurements. Also, for pH and Ag/AgCl microelectrodes, the exterior of the microelectrode was covered with a Red Glyptal lacquer except its tip and as a result, the tip, only, was in contact with the solution. This arrangement allowed measuring the gradient of the pH and the chloride ion concentration as a function of depth ($x$) within the cavity.

Since the two potentiostats and the high impedance voltmeter are connected to the same working electrode, all of them need to be grounded. Failing to ground all of them properly to an earth ground, not to a floating ground, will result in large errors in the measured potential difference. The EG&G potentiostat was used to apply the desired potential ($\pm 150$ mV OCP in all the experiments) relative to a Hg/Hg$_2$SO$_4$ reference electrode. Hg/Hg$_2$SO$_4$ electrode was chosen purposely in order to avoid any Cl$^-$ ions leaking from the reference electrode when the experimental time averaged more than a week. The Gamry potentiostat was used to double check both the EG&G potentiostat and the high impedance voltmeter/pH meter readings.

A high impedance voltmeter-pH meter was used to measure the potential difference between the Pyrex microprobe (SCE) and the Hg/Hg$_2$SO$_4$ reference electrode to measure the potential drop within the cavity. An additional function of the high impedance voltmeter is to measure the potential difference between the Pyrex
microprobe (SCE) and the pH or the Cl⁻ microelectrodes in order to measure the pH or the [Cl⁻]. In other words, in every experiment, the data collected were either pH and potential drop measurements or [Cl⁻] and potential drop measurements. The pH electrode was calibrated before each experiment using three buffer solutions of pH values 2, 7 and 10. During the experiment, pH was measured directly using the pH meter while the chloride ion concentration was translated from the potential difference measurements with the aid of the calibration curve which is constructed before the experiment starts (see calibration curves in the Ag/AgCl preparation section: Section 3.4.4)

A Boreal Digital/Analog USB stereo-microscope was purchased from Science Kit & Boreal Laboratories and connected to a PC uploaded with Motic software version 1.2. This version was updated lately to 2.0. The software was set to capture a single frame every 900 seconds during the experiment. The average time for each experiment was 7 days. The frames were collected together in a 1-minute movie after the experiments were completed. Capturing the single frames allowed the overall corrosion rate to be determined. Also, it helped in allowing one to determine the rate of intergranular corrosion since the intergranular corrosion band appears brown in color while the loose grains reflected the light in different directions and looked very shiny as mentioned before.

In addition to the stereomicroscope light, another light source (from Cambridge Instruments) was used in order to improve image quality. The additional light source
was set at an angle of 45° in order to minimize the reflections from the surface of the sample within the epoxy. Lights in the laboratory were kept on during the entire test period in order to minimize the effect of the absence of day light during the night on the image quality.

3.4.2. Pyrex Microprobe Preparation

Pyrex glass tubes were purchased from Fisher Scientific (Catalog # 11-365A) with an outer diameter of 3mm. These Pyrex tubes are characterized by low coefficient of expansion and great mechanical strength. Its softening point is 821 °C while the working point is 1252 °C. Small sizes of these Pyrex tubes (like those used in this work) can be bent after heating over a blast burner using gas and compressed air. Pyrex microprobes were prepared by cutting 25 cm pieces of the Pyrex tubes and bend the two ends of each piece in an opposite direction. One end then was used to hang the tube and to the other end a weight of 16 gm was fixed. A blast burner flame then was directed at the middle of the 25 cm-bent tube. The Pyrex tubes, because of the softening happened by the flame plus the added weight, were elongated and their diameters at the middle decreased significantly. After the elongation, the outer diameter at the middle was 0.06 mm. Using a scissor, the elongated tube was cut from the middle to create two microprobes. The formed Pyrex microprobe was connected to a SCE using TYGONE polyethylene tubes of different diameters and coupled with either a pH microelectrode or Ag/AgCl microelectrode as mentioned before. The Pyrex microprobes usually could not be used twice.
3.4.3. pH Electrode Specifications

Different pH microelectrodes have been reported to work efficiently within crevices and cracks.\(^{47-57}\) For the pH measurements in this work, a commercial pH mono microelectrode (PHM-146) was purchased from Lazar Research Laboratories, Inc. It consisted of a Sb/Sb\(_2\)O\(_3\) wire 1-mm in diameter) with an epoxy body covered with a Teflon tube. The epoxy body and the Teflon tube covered all the wire except for one inch which is called the cap. The cap was covered with a very thin layer of Delrin leaving only the tip bare. The pH electrode was calibrated before each experiment and also checked after each one. Four solutions of pH 2, 4, 7 and 10 were prepared using commercial buffer solutions purchased from Micro Essential Laboratories. They were used in calibrating the pH microelectrode. Calibration of the pH electrode was done within a cavity similar to the one that forms during the experiment.

3.4.4. Ag/AgCl Microelectrode Preparation

Measuring the chloride ion concentration locally has been reported in the literature by many groups.\(^{47, 49-51, 56, 58}\) For the chloride ion concentration measurements in this work, commercial and home-made Ag/AgCl microelectrodes were used. The commercial one was purchased from Lazar Research Laboratories, Inc. The electrode’s model number is ISM-146Cl. It consists of Ag/AgCl wire of 1 mm diameter embedded
in epoxy and covered with a Teflon tube except for one inch (the cap). In order to be able to measure the concentration gradient of the chloride ions within the cavity, the entire cap was lacquered, using Red Glyptal purchased from Alltronics, except for the tip of this cap. This allows measurements at different locations within the occluded cell rather than an averaging the different chloride concentrations in the entire volume.

For preparing the home-made Ag/AgCl microelectrode, a pure silver wire of 1 mm diameter was purchased from Alfa Aesar. A 25 cm long piece was cut from this Ag wire and polarized potentiostatically at 2 V SCE in a 0.1 M NaCl solution until the current reached 300 microamps/cm². The electrode then was soaked for one day in the same solution. After soaking, the whole wire was lacquered with Red Glyptal except its tip. Calibration of the electrode was done in both the bulk solution and in the same environment as the experiment (i.e., in a small cavity (2.4x7x6 mm³) connected to the bulk solution). The electrode was calibrated using different chloride solutions. The home-made chloride electrode showed a slope of 58 mV/decade of chloride concentration when it was calibrated in the bulk solution but only a 42 mV/decade of concentration when the calibration was done within the small cavity. This can be easily seen by comparing the two calibration curves represented in Figures 3.4 and 3.5. Figure 3.4 shows the calibration curve for the Ag/AgCl electrode in the bulk solutions while Figure 3.5 shows the calibration curve within a cavity similar to the one that always formed during the experiment. The reason for this discrepancy is unclear, but similar differences have been reported in the literature before. This difference in slope happened in the case of the chloride measurements, but not in the case of the pH
Figure 3.4. A calibration curve for the home-made Ag/AgCl electrode in the Bulk solution. Calibration curve for each experiment was carried out before each experiment and checked after each one.
Figure 3.5. A calibration curve for the home-made Ag/AgCl electrode within the cavity. Calibration curve for each experiment was carried out before each experiment and checked after each one.
measurements. In order to overcome problem, measurements were carried out after a pause of the potentiostat (temporarily stopping allows one to resume the experiment from the stopped point) and disconnect the working electrode from the potentiostat. This raised the slope to 50 mV/decade. The Ag/AgCl microelectrode worked in concentrations higher than 1 mM up to 2 M of chloride ions without showing deviations from the straight line behavior of its calibration curve. The Ag/AgCl microelectrode was calibrated before and after each experiment. A calibration curve for each experiment was carried out before each experiment and checked after each one.

3.4.5. Specimen Preparation

Figure 3.6 shows an actual specimen after preparation. This electrode is similar in concept to a pencil electrode, except in this case the alloy is in the form of plate rather than a wire. Samples of dimensions 2.4 \((a)\) x 7 \((w)\) x 14 \((height)\) mm\(^3\) were cut from sheet then polished to 1 micro using alumina slurry. The specimens were always oriented in the rolling direction oriented along the 14 mm face.

The quality of the specimen surface finish is very important for the quality of the images captured during the experiment. The higher the quality of the surface finishing the better the quality of the digital image and the better the contrast between the loose grains and the intergranular corrosion band. Surface finishing was carried out using an alumina slurry of particles with an average size of 1 µm. Following polishing, the
Figure 3.6. (a) Horizontal view of an actual specimen before the experiment (b) Sketch representing the specimen a few days after the start of the experiment showing loose grains and IGC band and (c) Top view of the specimen. During the course of the experiment, the contact between the alloy and the solution was in the vertical direction.
specimen was fixed to a rectangular base at its bottom using silver paste purchased from TED PELLA, Inc. This base was used to connect the sample to the potentiostat.

A scale was fixed in front of the sample with quick-dry glue to follow the rate of the IGC. This scale is in half millimeters. The sample, the scale, and the electrical contact disk were then imbedded in a clear epoxy resin and exposed to vacuum for two 5-minute intervals, separated by a 10 minute period in which the sample was removed from the vacuum chamber, to dislodge any bubbles that might have formed within the epoxy. The use of continuous vacuum results in embedded bubbles in the epoxy since the curing of the epoxy is an exothermic reaction. The heat dissipation rate in the vacuum is very small. As the polymerization reaction proceeds (more cross linking between chains takes place), more heat is released. This process ends up with boiling of the epoxy resin and the epoxy resin becomes semitransparent rather than transparent which makes the specimen unsuitable for capturing any images. After the second vacuum interval was completed, the specimen was left to cure for 24 hours before testing. The final step in the specimen preparation process was to polish the top (which will be in contact to the solution) and the bottom (which will be connected to the potentiostat by a Cu conductive tape) of the specimen to a 600 grit finishing and the bottom of the sample.
3.5. RESULTS AND DISCUSSIONS

In the following subsections, the collected intergranular corrosion measurements data for the as-received alloy (with 1.47% Cu) will be presented and discussed in detail. These results and discussion of the as-received alloy will be classified to four categories: IGC for as-received, potential drop for as-received, pH measurements during IGC measurements for as-received and chloride ion concentration measurements during IGC measurements for as-received alloy specimens. Following this, results and discussion for the overaged alloy will be presented.

3.5.1.1. Intergranular Corrosion Measurements For the As-Received Alloy

While Figure 3.7 shows in-situ pictures that represent the short-term development of the IGC in the first day after the as-received specimen (1.47% Cu) was polarized at –824 mV Hg/Hg₂SO₄ in 50 mM NaCl, Figure 3.8 displays in-situ pictures for the same specimen represented by Figure 3.7 for the long-term development (at different days). Figure 3.7 shows that the IGC propagation rate is fast. The pictures in Figure 3.8 show that the overall corrosion rate was 0.5 mm/day under these experimental conditions. Figure 3.9 presents SEM (scanning electron microscope) micrographs at different magnifications of the intergranular corrosion and the intergranular corrosion
Figure 3.7. In-situ pictures represent the short-term development of the IGC after the specimen (1.47% Cu) was polarized at -824 mV Hg/Hg₂SO₄ in 50 mM NaCl solution.
Figure 3.8. In-situ pictures represent the long-term development of the IGC after the specimen (1.47% Cu) was polarized at -824 mV Hg/Hg2SO4 in 50 mM NaCl solution. Pictures in Day 4 and Day 8 show an Sb/Sb2O3 within the cavity.
Figure 3.9. SEM micrographs at high and low magnifications show the intergranular corrosion and the intergranular corrosion band thickness for an as-received sample after being polarized in 50 mM NaCl at – 824 mV Hg/Hg₂SO₄ for 12 days.
band thickness of an as-received specimen (1.47% Cu) after being polarized in 50 mM NaCl for 12 days at – 824 mV Hg/Hg₂SO₄. The grooves’ width is approximately 2 µm. These SEM micrographs were taken after the experiment was completed. Then the sample was cross sectioned vertically, polished and dried. The low magnification SEM micrograph verifies that no crevice corrosion occurred between the epoxy and the embedded specimen. This can be deduced from the shape of the IGC band at low magnification. If crevice corrosion (between the wall and the specimen) is the reason for intergranular attack or is leading the IGC, then the location of the IGC band would not be the same. If that is the case, then the IGC band should be seen at a deeper location when it is closed to the epoxy walls compared to the band’s location when it is away from the epoxy. As can be seen from the low magnification micrograph in Figure 3.12, the thickness of the IGC band is the same in the middle of the specimen (middle of the micrograph) as it is close to the edges of the specimen (edges of the micrograph). In another word, the intergranular corrosion that occurred close to the epoxy walls was of the same magnitude and at the same location as what occurred in the middle of the specimen. Since there was no curvature in the IGC band, crevice corrosion was not the reason for the IGC.

The development of the intergranular corrosion behavior of the as-received alloys (1.47% Cu) as a function of time was shown in Figure 3.10. Figure 3.10 illustrates how the IGC band’s thickness (h) and the cavity’s apparent depth (H) change with time for an as-received sample (1.47% Cu) in 50 mM NaCl under a potential of -824 mV Hg/Hg₂SO₄. The apparent depth (H) was formed due to removal of the grains while and
Figure 3.10. Plot of both the intergranular corrosion band’s thickness (h) and the apparent cavity’s depth (H) as a function of time for the as-received alloy (1.47% Cu) specimen represented in Figures 3.7 and 3.8. At the beginning of the experiment, the sample was polarized at -824 mV Hg/Hg₂SO₄ (+ 150 mV vs OCP) and the bulk solution was 50 mM NaCl at 23 °C.
the IGC band thickness (h) was formed due to IGC. The total depth which is the apparent depth plus the intergranular corrosion (IGC) band can be calculated (ignoring the tortuosity factor) by adding the corresponding points on the two curves at the same time. The apparent depth of the cavity always increases with time. On the other hand the IGC band thickness passes through a maximum. This behavior was confirmed via repeating the same experiment. The data of the replicate experiments are presented in appendix of this thesis. The effect of the chloride ions in the bulk solution on the intergranular corrosion of this alloy will be discussed in the chloride concentration measurements section.

3.5.1.2. Potential Drop Measurements For The As-Received Alloy

Figure 3.11 shows the potential drop measured within the growing cavity after 6 and 12 days for an as-received alloy specimen (1.47% Cu). The bulk solution is 50 mM NaCl of pH 6.9 and a temperature of 23 °C. The applied potential at the surface is -824 mV Hg/Hg2SO4 (+150 mV vs OCP). The applied potential at the surface is lower than the pitting potential, \(E_{\text{pit}}\), (-300 mV SCE which corresponds to -674 mV Hg/Hg2SO4) as was reported by McCosby.(2) Figure 3.11 shows that the potential drop at the same distances within the cavity decreased with time as can be deduced from the slope of the two curves. The reason for this can be discussed within the IR potential drop theory frame\(^{(59-74)}\) where the potential drop is affected by the total resistance, \(R\), the current or by both of them.
Figure 3.11. Potential drop measurements within the cavity formed after 6 days and 12 days for an as-received alloy (1.47% Cu) specimen. At the beginning of the experiment, the sample was polarized at -824 mV Hg/Hg$_2$SO$_4$ (+ 150 mV vs OCP) and the bulk solution was 50 mM NaCl at 23 °C.
The resistance, $R$, of the solution is controlled by three parameters according to ohms law;

$$R = \rho \frac{l}{(a)w}$$

Where $\rho$ is the resistivity of the solution; $l$ is the current path’s length, and $a$ and $w$ are dimensions of the rectangular cross sectional area of the electrolyte for current flow (see Figure 3.6c).

The total resistance in the IGC measurements, $R$, is the algebraic sum of three resistances connected in series; $R_1$, $R_2$, and $R_3$. Figure 3.12 is a schematic that shows these resistances. $R_1$, the bulk solution resistance, is considered to be constant; $R_2$ (the cavity solution resistance); and $R_3$ (the resistance associated with the IGC path).

$R_2$ is the resistance of the solution within the cavity. The cavity is formed by removing the grains from the matrix of the alloy sample. This resistance is only controlled by two factors. It is controlled by the resistivity of the solution within the cavity and the depth of the cavity but the cross sectional area ($a \times w$) is constant in this case and equals 0.17 cm$^2$. The resistivity of the solution within the cavity decreases with time because the resistivity of the solution within the cavity and the bulk solution decreases with time due to the dissolution of the aluminum alloy components and the
Figure 3.12. Schematic diagram showing the different resistances existing in every IGC experiment. $R_1$ is the resistance of the bulk solution, $R_2$ is the resistance of the solution within the cavity and $R_3$ is the resistance of the solution trapped within the grain boundary grooves.
increase of the pH and chloride ion concentration within the cavity as will be discussed later. On the other hand, the apparent depth of the cavity (H) increases with time as shown in Figure 3.10. But, the dominant factor affecting $R_2$ is the resistivity. The reason for this is the huge ion build up (several orders of magnitudes) within the cavity. The ions build-up will be discussed later. $R_2$ is also affected by the hydrogen evolution which takes place within the cavity. Hydrogen bubbles increase the resistance significantly. Also, the presence of the loose grains is a factor that should be considered. These loose grains decrease the cross sectional area which, in turn, increases $R_2$.

$R_3$ is the resistance of the solution trapped within the attacked grain boundary grooves. $R_3$ is controlled by the resistivity of the solution along the grain boundaries, the width of the grain boundaries grooves, $\delta$, ($\approx 2 \mu$m as was shown in SEM micrographs in Figure 3.9) and the average depth of the intergranular corrosion band. The tortuosity factor for the intergranular path should also be considered. Both the depth of the grooves along the grain boundaries and their width are varying with time. The width of these grooves, $\delta$, passes through a maximum. It starts very small then increases gradually and decreases sharply once the grain is separated from the matrix. This resistance could not be measured because of the experimental difficulties or even calculated because of the lack of information about the solution trapped within the grain boundary grooves. Another factor that affects $R_3$ is the hydrogen gas bubbles that evolve at the grain boundary grooves. These bubbles increase $R_3$. In fact, the total resistance contribution in the $IR$ potential drop in this case is very complicated and its quantification is beyond the scope of this work.
The current-time behavior for this alloy (with 1.47% Cu in the as received condition) in 50 mM NaCl solution is presented in Figure 3.13. The potential applied was -824 mV Hg/Hg$_2$SO$_4$. As can seen in Figure 3.13, the total current is at its maximum value which is almost 3 times higher than that at 12 days. The ratio between the current at these two different times is 3:1 which is almost equal to the measured $IR$ potential drop ratio, at the same two times. This explains, in a simple way, the reason for the decrease in the measured potential drop as a function of depth at these two different times, as shown in Figure 3.11.

In brief, the potential drop measurements indicated that the measured $IR$ potential drop varied with time and it ranged from 50-250 mV. Tying between the IGC and the measured potential drop was difficult because of the lack of information about the $IR$ potential drop along the grain boundary grooves due to experimental difficulties.

### 3.5.1.3. pH Measurements For the As-Received Alloy

The pH measured within the cavity as a function of distance for an as-received alloy sample polarized in 50 mM NaCl at 6 and 12 days at – 824 mV Hg/Hg$_2$SO$_4$ is presented in Figure 3.14. At the beginning of the experiment, the bulk solution’s pH was 6.9 and at the end of the experiment the bulk solution’s pH was 5.9. Twenty minutes after the beginning of the experiment, the pH at the surface of the sample was 4.3. As time proceeded and the cavity formed, by intergranular corrosion (mainly) and uniform
Figure 3.13. Current vs time plot for the same as-received alloy # 10 (1.47% Cu) specimen which is represented in Figures 3.8 and 3.10. The experiment, the specimen was polarized at -824 mV Hg/Hg\textsubscript{2}SO\textsubscript{4} (+ 150 mV vs OCP) and the bulk solution was 50 mM NaCl at 23 °C.
Figure 3.14. Graph of pH measurements as a function of distance within the cavity which is formed during the polarization of an as-received alloy (1.47% Cu) specimen at -824 mV Hg₂/Hg₂SO₄ (+ 150 mV vs OCP) in a 50 mM NaCl solution.
corrosion, the hydrogen evolution reaction (HER) and the oxygen reduction (OR) reaction took place within the cavity. The first reaction (HER) was documented in-situ using the microscope and in a 1-minute movies (consisting of about 1500 single frames) which show the continuous bubble evolution from the bottom the cavity. Figure 3.16 consists of two single frames out of 1500 frames collected in a prescribed order to create the 1-minute movie. Figure 3.15a shows a lower hydrogen evolution rate three days into the experiment. Figure 3.15b is another frame that shows the pH microelectrode inserted within the cavity and hydrogen bubbles evolving at the same time (after 6 days). The second reaction (the oxygen reduction reaction) has been reported in the literature elsewhere. Because of the absence of an outer surface and consequently both of the HER and the OR reactions occurring within the cavity, a significant increase in the pH was expected.

An interesting phenomenon was observed within the cavity as the experiment proceeded. It had been noticed that the HER increased with time as can be noticed from the rate of the bubbles evolved. Figure 3.15a shows low rate of hydrogen evolution after 3 days. The HER rate was even considerably higher in the case of the as-received alloy samples than in case of the peak-aged sample. In fact, according to the thermodynamics, this reaction, HER, should be unfavorable to occur rather than increasing with time. The increase of hydrogen evolution with time is the increase in the pH value of the medium within the cavity. For example, the pH measured at the bottom of the cavity on Day 12 was 9.3 as shown in Table 3.2.
Figure 3.15. Photomicrograph showing an as received alloy (1.47% Cu) specimen (a)
low rate of bubbles evolution after 3 days. The potential applied at the beginning of the
experiment is -824 mV Hg₂/Hg₂SO₄ (+ 150 mV vs OCP) and the bulk solution is 50
mM NaCl. (b) the pH microelectrode inserted within the cavity and that hydrogen
bubbles evolving after 12 days.
Table 3.2. pH measurements at top, middle and bottom of the cavity for alloy # 10 (with 1.47% Cu) on different days. The potential applied at the beginning of the experiment was -824 mV Hg₂/Hg₂SO₄ (+ 150 mV vs OCP). The bulk solution was 50 mM NaCl and its pH is 6.9.

<table>
<thead>
<tr>
<th>Days</th>
<th>pH at the top of the Cavity</th>
<th>pH at the middle of the Cavity</th>
<th>pH at the bottom of the Cavity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 4</td>
<td>7.0</td>
<td>12.4</td>
<td>9.6</td>
</tr>
<tr>
<td>Day 5</td>
<td>7.8</td>
<td>12.6</td>
<td>9.2</td>
</tr>
<tr>
<td>Day 6</td>
<td>8.6</td>
<td>12.2</td>
<td>9.5</td>
</tr>
<tr>
<td>Day 7</td>
<td>7.3</td>
<td>10</td>
<td>8.4</td>
</tr>
<tr>
<td>Day 8</td>
<td>7.4</td>
<td>10.5</td>
<td>9.2</td>
</tr>
<tr>
<td>Day 9</td>
<td>7.4</td>
<td>9.8</td>
<td>9.3</td>
</tr>
<tr>
<td>Day 10</td>
<td>8.0</td>
<td>10.1</td>
<td>9.2</td>
</tr>
<tr>
<td>Day 11</td>
<td>8.3</td>
<td>11.2</td>
<td>9.3</td>
</tr>
<tr>
<td>Day 12</td>
<td>8.9</td>
<td>11.8</td>
<td>9.3</td>
</tr>
</tbody>
</table>
Consequently, the reversible potential for the HER at pH 9.3 is \(-1.16\) V Hg/Hg\(_2\)SO\(_4\). The potential measured, at the bottom of the cavity, was only \(-0.884\) V Hg/Hg\(_2\)SO\(_4\) at Day 12 which is above the equilibrium potential for the HER. This phenomenon could be explained in terms of both, the potential drop within the grain boundaries grooves (the driving force for the HER) and the exchange current densities (kinetics parameter) of the HER on both Al and Cu.

The first thing to be introduced here before addressing the potential drop change is; it was only possible to measure the potential drop at the bottom of the cavity which is formed by removing the loose grains from the matrix. It was not experimentally possible to measure the potential drop along the grooves between the grain boundaries that form due to intergranular corrosion while they are still stuck to the matrix. The reason of this is that the insertion of a glass probe between the grains while they are still stuck to the bulk of the matrix is not possible since the grain boundary groove thicknesses are in the range of 1-2 \(\mu\)m while the diameter of the glass probe is in the range of 50-150 \(\mu\)m.

For aluminum and aluminum alloys, the increase in the pH, shifts the open circuit potential in the less noble direction.\(^{(70)}\) According to the IR potential drop theory, the limiting potential, \(E_{lim}\) (the crevice’s mixed potential), can be changed if the equilibrium potential or the open circuit potential is changed. This in return, allows more potential drop to happen within the grooves of the corroded grain boundaries, especially since the current path thickness (the grooves thickness) is very small as mentioned before. This
argument was explained before in the literature by Pickering et al.(76) If the potential drop is enough to make the potential of the alloy to shift below the reversible potential of the HER, then HER will take place. This, in fact, was expected to happen but was not measured because of the experimental difficulties mentioned above. Another possibility for the HER to take place is the decrease of the pH to a value less than 4 but this possibility collapsed in front of the experimental finding that the measured pH at the bottom of cavity is about 9.5 on average which in turn totally excludes this possibility.

Another phenomenon was noticed regarding the HER rate. It was observed that the HER rate was very slow in the first three days, even though the potential drop existed along the grain boundaries. As time proceeds, Cu enrichment by plating at the surface of the IGC takes place. It is well known that the exchange current density for the HER on Cu is more than three orders of magnitude higher than that on Al.(77) Consequently, the HER rate increases with time as a result of the increase of the surface area of Cu due to the replating of the dissolved Cu$^{2+}$ ions during the Cu redistribution and enrichment process on the Al alloy surface. The later was proven by the unique copper coloration as can be shown in Figure 3.16. Figure 3.16 shows a distinguishable difference in the Cu-coloration (due to Cu-redistribution) between an as-received alloy specimen and the peak aged one in a 50 mM NaCl bulk solution. This can be noticed at the bottom of the two specimens. The as-received specimen shows dark Cu-coloration at the bottom of the cavity (see right specimen) while the heat treated one shows slight Cu coloration
Figure 3.16. Photomicrographs showing the difference in the Cu-coloration (due to Cu-redistribution) between an as-received alloy sample and the peak aged one in a 50 mM NaCl solution. The two specimens are of the same depth. The potential applied at the beginning of the experiment is -824 mV Hg/Hg$_2$SO$_4$ (+ 150 mV vs OCP) and the bulk solution is 50 mM NaCl.
at the IGC band at the bottom of the cavity. The two specimens are of the same depth. The potential applied at the beginning of the experiment was -824 mV Hg₂/Hg₂SO₄ (+ 150 mV vs OCP) and the bulk solution is 50 mM NaCl. For confirming this assumption, a back scattered SEM micrograph (Figure 3.17) and an energy dispersive X-ray (EDS) spectrum (Figure 3.18) were taken for the loose grains after the experiment was completed. In Figure 3.17, the grains which are covered with an element of a high atomic number (Cu) look lighter than the grains with an element of lower atomic number (Al). Also in EDS spectrum (Figure 3.18), the Cu peak indicates the presence of a high amount of Cu. The reason that the Al peak appears is that the EDS beam penetrates the surface of the grains. Cu redistribution indicates the reason why the pH did not reach high values within the cavity in case of the heat treated alloy (no Cu-redistribution took place) where the kinetics of HER on aluminum are much slower than on copper. The presence of oxygen for the Cu redistribution process is very vital and its presence increases significantly the amount of the replated Cu²⁺ ions as was reported by Buchheit et al.\(^{(75)}\) This can be explained by the higher over potential for the oxygen reduction reaction relative to the hydrogen evolution reaction, HER, at the applied potential (-824 mV Hg/Hg₂SO₄). Cu-enrichment is higher in basic media because of the low solubility of Cu in alkaline mediums.\(^{(78)}\) Consequently, it can be mentioned that replating of the Cu²⁺ ions on the IGC band surface, after the dissolution of Cu, can be considered as an autocatalytic process where Cu²⁺ ion plating catalyzes the HER and the latter decreases the plated Cu dissolution.
Figure 3.17. Back-scattered SEM micrograph for as-received alloy (1.47% Cu) loose grains. Grains were collected after the experiment was completed. The specimen was polarized for 12 days at -824 mV Hg/Hg$_2$SO$_4$ in 50 mM NaCl solution. The lighter regions are the elements with high atomic numbers.
Figure 3.18. EDS spectrum for the loose grains that were collected after the IGC experiment for an as-received alloy (1.47% Cu) grains was completed. The specimen was polarized for 12 days at -824 mV Hg/Hg₂SO₄ in 50 mM NaCl solution.
A third interesting behavior was found during the pH measurements. The pH always went through a maximum at the middle of the cavity for an as-received alloy (1.47% Cu) specimen regardless the time or the depth of the cavity at which the measurements were taken. This can be clearly seen in Figure 3.14. This behavior was confirmed in one experiment for the same specimen in different days (see Table 3.2) and in different experiments using different specimens at the same day as can be seen in Figure 3.19. Figure 3.19 shows the reproducibility of the pH measurements of the as-received alloy (1.47%Cu) after 6 days. Finding a lower pH at the top of the cavity (close to the bulk solution) can be easily understood from the mixing effect of the bulk solution and the solution within the cavity but the question that needs to be answered is why the pH decreases significantly at the bottom of the cavity. The answer to this question can be addressed within the frames of the IGC and the Cu dealloying and redistribution mechanisms in the Al-Cu alloys.

Figure 3.20 is a schematic that shows the several regions that are present within the cavity due to the IGC and the pH electrode placement within the cavity for taking measurements. The Al-Cu-Mg-Si phase will dissolve close to the grain boundaries leading to the formation of Cu\(^{2+}\) and Al\(^{3+}\) ions. Part of the dissolved Cu\(^{2+}\) will be plated out in the IGC region and the other part will be plated on the loose grains which are still in contact with the matrix. The loose grains are totally plated with a very thin layer of Cu. HER takes place within the grooves that are formed due to intergranular corrosion and also between the loose grains as long as the potential is less than the equilibrium potential for the HER in this medium. Al\(^{3+}\) ions, which dissolution is responsible for
Figure 3.19. Graph of pH as a function of depth within the cavity for two as received alloy specimens (1.47% Cu). The specimens was polarized at -824 mV Hg/Hg$_2$SO$_4$ (+150 mV vs. OCP) for 6 days in 50 mM NaCl solution.
Figure 3.20. Schematic diagram showing the different regions that are formed due to the IGC and also the position of the pH electrode during the pH measurements.
the IGC, will undergo hydrolysis in the IGC region leading to the consumption of the hydroxide ions in the IGC region which in turn will decrease the pH in the IGC region and the region of the loose grains which is close to the IGC region.

3.5.1.4. Chloride Concentration Measurements For the As-Received Alloy

The reproducibility of the chloride ion concentration measurements as a function of distance within the cavity is presented in Figure 3.21 which shows three chloride concentration measurements within three different cavities after 4 days from the beginning of the experiment. In these three experiments, the bulk solution concentration was 50 mM NaCl. Figure 3.21 indicates that the reproducibility of the measurement is good. Figure 3.21 shows that the concentration of chloride ion increases as a function of distance within the cavity. Chloride ion concentrations at the bottom of the cavity are at least one order of magnitude higher the chloride concentration in the bulk solution. Figure 3.22 shows the concentration of chloride ions as a function of depth within the cavity of an as-received alloy for three different bulk solutions concentrations, 5, 50 and 100 mM NaCl. It shows that chloride ion concentrations within the cavity vary slightly as the bulk solution concentration changes. The lower the bulk solution concentration, the greater is the difference in the chloride ion concentration between the bulk and the cavity. It was found that the chloride ion concentration at any distance within the cavity $C_{Cl}(x)$ can be calculated approximately from this empirical equation:

$$C_{Cl}(x) = ax + b.$$

\[3.2\]
Figure 3.21. Graph of [Cl\textsuperscript-] vs distance within cavity showing the reproducibility of the three separate chloride measurements for as-received alloy (1.47\% Cu) specimens in the same bulk solution concentration, 50 mM NaCl solution, after 4 days. The potential applied at the beginning of the experiment was -824 mV Hg/Hg\textsubscript{2}SO\textsubscript{4} (+ 150 mV vs OCP).
Figure 3.22 Graph of $[\text{Cl}^-]$ vs distance within cavity showing the chloride concentrations as a function of depth within the cavity of as-received alloy # 10 (1.47% Cu) specimens. The bulk solution chloride concentrations were 5, 50, and 100 mM sodium chloride. The potential applied at the beginning of the experiment is $-824 \text{ mV Hg/Hg}_2\text{SO}_4$ (+ 150 mV vs OCP).
where $x$ is the distance within the cavity in cm, $a$ and $b$ are constants ($b = 0.2$ while $a$ depends on the bulk solution concentration).

For a chloride bulk solution concentration, $C_b$, higher than zero, $a$ can be calculated from this empirical equation;

$$a = 1.044C_b + 0.2$$

Figure 3.23 shows the effect of time on the measured chloride concentration as a function of depth within the cavity. Measurements were taken after 4 and 6 days, respectively, for a bulk solution concentration of 50 mM NaCl. It shows that chloride ions build up as time increases in a linear way.

The effect of chloride concentration on the IGC was also investigated using two different bulk solutions concentrations of 5 and 50 mM NaCl, respectively. Figure 3.24 shows the effect of changing of the bulk solution chloride concentration on the apparent depth of the cavity. After one day, grains start to dislodge from the matrix in the case of the specimen that is in contact with the 50 mM NaCl bulk solution. For the other solution it takes 4 days for this to happen. At 6 days both cavities had the same depth. It means that the concentration in the bulk solution affects only the rate of propagation.
Figure 3.23. Graph of [Cl\textsuperscript{-}] vs distance within cavity showing the effect of time on the measured chloride concentration as a function of distance within the cavity. Measurements were taken after 4 and 6 days. The bulk solution concentration is 50 mM NaCl. The potential applied at the beginning of the experiment is -824 mV Hg/Hg\textsubscript{2}SO\textsubscript{4} (+150 mV vs OCP).
Figure 3.24. Graph of [Cl⁻] vs distance within cavity showing the effect of the bulk solution chloride concentration change on the cavity’s apparent depth (H). Two chloride solutions were used in the bulk, 5 and 50 mM of NaCl respectively. The potential applied at the beginning of the experiment is -824 mV Hg/Hg₂SO₄ (+ 150 mV vs OCP).
3.5.2.1. Potential Drop Measurements For Peak-Aged Alloy

The measured potential drop for the peak-aged specimen is shown in Figure 3.25. The potential drop is almost the same for the as-received sample at Day 12 (Figure 3.11). The current-time profile for this experiment is presented in Figure 3.26. It shows that the current for the peak aged specimen is almost four times higher than that of the corresponding as-received specimen (as was shown previously in Figure 3.13). However, this does not mean that the intergranular corrosion is higher. Only the initial rate of the IGC was higher but the overall IGC rate was the same as the as-received specimen as will be described in the next section (compare Figure 3.10 and 3.28).

3.5.2.2. Intergranular Corrosion For Peak-Aged Alloy

Figure 3.27 is a scanning electron microscope (SEM) micrograph of the intergranular corrosion and the intergranular corrosion band thickness of a peak aged specimen (1.47% Cu) after being polarized in 50 mM NaCl for 6 days at – 824 mV Hg/Hg2SO4.

The development of the intergranular corrosion as a function of time is shown in Figure 3.28, which also shows both the apparent depth (H) and the IGC band thickness (h). The overall behavior has some similarity as for the as-received alloy where the IGC
Figure 3.25. Potential drop measurements within the cavity formed after 6 days of a peak-aged alloy (1.47% Cu). At the beginning of the experiment, the sample was polarized at -824 mV Hg/Hg₂SO₄ (+ 150 mV vs OCP) and the bulk solution was 50 mM NaCl. Peak-aged condition was achieved by heating the specimen for 11 hours at 180 °C.
Figure 3.26. Plot of current - time after polarizing a peak-aged alloy # 10 (1.47% Cu) sample at -824 mV Hg/HgSO₄ (+ 150 mV vs OCP) in a 50 mM NaCl solution. Peak-aged condition was achieved by heating the specimen for 11 hours at 180 °C.
Figure 3.27. SEM micrographs at high and low magnifications showing the intergranular corrosion and the intergranular corrosion band thickness for a peak aged sample (180 °C for 11 hours) after being polarized in 50 mM NaCl at – 824 mV Hg/Hg₂SO₄ for 6 days.
Figure 3.28. Plot of both the intergranular corrosion band’s thickness and the apparent cavity’s depth as a function of time for a peak-aged alloy (1.47% Cu). The potential applied at the beginning of the experiment is -824 mV Hg/HgSO₄ (+ 150 mV vs OCP) and the bulk solution is 50 mM NaCl. Peak-aged condition was achieved by heating the specimen for 11 hours at 180 °C.
band thickness passed through a maximum. However, there is no step-wise growth for
the apparent cavity’s depth. IGC didn’t disappear with time as was shown in Figure
3.28. The circled points proved to be wrong. This was done by cutting the sample after
the experiment was completed. Also, the initial rate of the IGC is very fast compared to
the as-received specimen as can be revealed form the slopes of the two curves shown in
Figure 3.29 which shows a comparison between the total corrosion penetration depth as
a function of time for an as-received and a heat treated specimen in a 50 mM NaCl and
a potential of -824 mV Hg/Hg₂SO₄ (+ 150 mV vs OCP) was applied. Peak-aged
condition was achieved by heating the specimen for 11 hours at 180 °C. The decrease of
the IGC resistance due to heat treatment was also reported for a similar alloy by
Mankowski et. al. (9) The reason for this decrease in the IGC resistance could be
attributed to coarsening of the precipitates at the grain boundaries which means an
increase in the cathodic area next to the anodic depleted zone. This increase in the
cathodic area increases the cathodic current which needs to be compensated by more
anodic current. The increase of the anodic current from the depleted zone close to the
grain boundaries simply means a faster dissolution close to the grain boundaries. This
explanation (microgalvanic cell around the grain boundaries) which follows the
concepts of galvanic corrosion, might not always be valid since it was reported that
intergranular corrosion occurs in zone-refined aluminum and iron (99.99999% purity). (25, 26) This means that there are almost no impurities that can act as cathodic or
anodic regions relative to the grain boundaries or to the areas next to it. Another
explanation can also be introduced here. The intergranular corrosion might be attributed
to the reorientation of the grain boundaries’ geometry in the direction of increasing
Figure 3.29. Total corrosion penetration depth for an as-received and a heat treated specimen in a 50 mM NaCl and a potential of -824 mV Hg/Hg₂SO₄ (+ 150 mV vs OCP) was applied. Peak-aged condition was achieved by heating the specimen for 11 hours at 180 °C.
\[ \Sigma \text{ CSL (coincidence site lattice) due to the heat treatment (peak aged at 180 °C for 11 hours) which means increases the free energy at the grain boundaries and makes them more susceptible to corrosion than the matrix. This was illustrated by Kim, et. al.}^{(26)} \]

They showed that for \( 1 \leq \Sigma \leq 3 \) the grain boundaries are totally resistant to the intergranular corrosion while for \( \Sigma \geq 29 \) (random boundaries), the sample is susceptible to intergranular corrosion. \( \Sigma \) is defined as the ratio between the volume of the CSL and the volume of the unit cell. Orientation Imaging Microscopy (OIM) can be used in determining this ratio. OIM is based on automatic indexing of electron backscatter diffraction patterns (EBSP) which can be produced in a properly equipped SEM. OIM provides a complete description of the crystallographic orientations in polycrystalline materials. The higher the value of \( \Sigma \), the more random the grain boundaries are and hence the more susceptible to intergranular corrosion. Also, there is a strong dependency of the segregation of elements in an alloy on the CSL. Chaturvedi, et. al.,\(^{(79)}\) studied this on a Ni-B alloy. They found that the higher the value of \( \Sigma \), the more segregation of B to the grain boundary. Also, Kim, et. al.,\(^{(80)}\) found for stainless steel that the lower the value of \( \Sigma \), the lower the chromium segregation and the higher the intergranular corrosion resistance.

3.5.2.3. pH Measurements For Peak-Aged Alloy

Figure 3.30 shows the pH measurements as a function of depth within the cavity for an alloy (1.47% Cu) specimen that was heat treated before at 180 °C for 11 hours. The
Figure 3.30. Graph of pH as a function of depth within the cavity for an alloy (1.47% Cu) specimen that was heat treated before at 180 °C for 11 hours. The sample then polarized at -824 mV Hg/Hg_2SO_4 (+ 150 mV vs. OCP) for 4 days in 50 mM NaCl solution.
specimen then polarized at -824 mV Hg/Hg$_2$SO$_4$ in 50 mM NaCl solution for 6 days. In this case, the pH increased gradually with distance into the cavity. In other words, the maximum in the pH value was at the bottom of the cavity not in the middle as was seen for the as-received specimens. This can be explained by the same concept used before to explain the maximum in the pH for the as received specimens. In the heat treated case, Cu plating was much less than in the case of the as-received samples (based upon a visual observation of the Cu-coloration intensity). The decrease in the amount of the replated copper after heat treatment might be attributed to the change of the Cu content of the Cu precipitates due to the heat treatment which, in turn, will decrease the dissolved amount of Cu$^{2+}$ ions and consequently, the amount of replated Cu$^{2+}$ ions will be smaller than that in the corresponding case of the as-received sample.\textsuperscript{(81)} As the amount of replated Cu on the loose grains was small, a lower HER rate took place in the loose grain region. In other words, the HER occurred mainly within the IGC band where the majority of the Cu$^{2+}$-ion plating takes place. This, in turn, will make the pH relatively high in the IGC band and lower as $x$ decreases.

\textbf{3.5.3. Discussion Summary}

Generally, as was seen in the previous sections that the as-received alloy resistance to IGC is not high. Tying the results collected from the IGC propagation rates, potential drop measurements, pH measurements and chloride ion concentration measurements within the cavity of as-received alloy (1.47% Cu) specimens might throw some light on the way by which IGC progressed. Chloride ions started attacking the as-received alloy,
anodic reaction, randomly which resulted in the formation of aluminum ions due to the formation of pits. The oxygen reduction reaction rate, the cathodic reaction, at the grain boundaries is expected to be much higher than that of the matrix due to the presence of the Cu-precipitates at the grain boundaries which have high exchange current density for the oxygen reduction reaction compared to the aluminum matrix. This led to a local alkalinity at the grain boundaries which results in a preferential dissolution of the areas near the grain boundaries where it is close to the cathodic reaction. Once the grooves were formed due to the dissolution of aluminum near the grain boundaries, the resistance increased because of the narrow path of the current within the grooves and consequently more potential drop took place which increased the HER rate. The HER increased the alkalinity within the grooves. This increase in the alkalinity shifted the open circuit potential to a lower value and increased the potential drop within the grooves.\cite{73}

Beside their role in initiating the intergranular corrosion, chloride ions played another important role in the propagation of the IGC. Chloride ions migrated, because of the IR potential drop, from the bulk solution to the grain boundary grooves. The high concentration of chloride ions forced the copper atoms in the dislodged copper-containing precipitates within the cavity to dissolve through the formation of CuCl$_2^-$ complex.\cite{82} Later on, this complex will form the soluble CuCl$_2$ compound which will be reduced mainly at the IGC band leading to the Cu plating.
3.6. CONCLUSIONS

The alloy under study, Al 6111-like (1.47% Cu), suffers from intergranular corrosion. Aging, initially, increases the rate of the intergranular corrosion while the overall depth of the attack was almost the same as the as-received alloy (0.5 mm/day). A large $IR$ drop took place along the grain boundary grooves. This large $IR$ potential drop was not measured because of the tiny size of the grain boundary grooves. An evidence of that $IR$ potential drop was the hydrogen evolution reaction which took place while the potential at the surface was not enough to allow HER to take place. This $IR$ potential drop is expected to play an important role in the IGC by allowing the HER to take place which increased the local alkalinity. This local alkalinity allowed the propagation of the IGC.

For the as-received alloy, the pH increased from 5.9 in the bulk solution to 12 in the middle of the cavity then decreases back again to 9.3 at the bottom of the cavity. This maximum phenomenon was attributed to the Cu enrichment and redistribution. The increase in pH occurs because the hydrogen evolution reaction and oxygen reduction reactions are taking place within the cavity. In the case of the peak aged samples, pH gradually increased from 5.9 in the bulk solution to 10.3 at the bottom of the cavity. Peak aging affected the Cu enrichment and redistribution where it decreased the amount of the replated copper.
Chloride ion concentration in the bulk only affects the initiation of intergranular corrosion. This conclusion is very important in the intergranular corrosion inhibition where the concentration of the chloride ions is not a critical factor as was thought before. Chloride ion concentration in the bulk solution only affects the progress of the removal of the intergranularly corroded grains. At high chloride ion bulk solution concentration, the removal was in a step-wise way. At low chloride ion bulk solution concentration, IGC developed for a long time before the removal of the grains starts.
3.7. REFERENCES


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CHAPTER 4

CONCLUSIONS AND FUTURE WORK

4.1. CONCLUSIONS

This section summarizes the new achievements that have been added to the field of corrosion science by the work that is presented in this thesis.

4.1.1. Crevice Corrosion

Regarding crevice corrosion of aluminum and its alloys, it has been proved that aluminum has an active peak in its polarization curve in electrolytes that have never been studied before, or that have been studied superficially without being able to reach these conclusions. The electrolytes used were at different temperatures starting from the ambient temperature up to 90 °C. It has been established in this thesis that the active peak “nose” is not due to salt film formation or because of the presence of Cu in the alloy. The existence of an active peak opposes what was reported in most of the literature about crevice corrosion of aluminum and its alloys, namely, that aluminum and/or its alloys only go from passive to active as the potential is scanned from the open circuit potential in the more noble direction.
This work also developed the relation between the critical crevice corrosion temperature (CCCT) and the $IR$ potential drop mechanism which was first presented by Pickering$^{(1)}$. This work provided the evidence required for explaining the CCCT using the $IR$ mechanism (see Figure 2.11) for the passive systems that undergo delayed crevice corrosion. Temperature changes the polarization curve of the alloy/electrolyte system in the way that makes $IR > \Delta \phi^*$ which is the condition that once is satisfied, the induction period is completed and crevice corrosion starts immediately.

It is also documented in this thesis that the nature of crevice corrosion, which is unclear in the literature on Al and its alloys, ranges from staining to regular crevice corrosion and not only restricted to the pitting form of corrosion that has been reported in the literature regarding aluminum and its alloys.

The presence of the aggressive ions (chloride ions) does not change the mechanism through which aluminum alloys undergo crevice corrosion but $\text{Cl}^-$ do change the susceptibility and the rate of that crevice corrosion attack.

This thesis shows for the first time examples of crevice corrosion of Al alloy/electrolyte systems in which, crevice corrosion were stabilized by the $IR$ potential drop. This was confirmed by direct measurement of the $E(x)$ profile. A huge $IR$ potential drop (+1.8 V) was measured and the locations of crevice corrosion on the crevice wall matched well with the polarization curve of these alloy/electrolyte systems.
Furthermore, this result (measured \( E(x) \) proving the role of the \( IR \)) was also obtained for the first time in case of crevice corrosion when the alloy was cathodically polarized. The latter has a significant importance since it resembles in some way an important case that happens in the field when aluminum alloys do not have enough outer surface area. Absence of an enough outer surface area results in an increase in the pH within the crevice since most of the cathodic reaction takes place within the crevice. The increase in the pH will shift the limiting potential to a less noble value and forming an active peak. Due to this partial separation of anodic and cathodic reactions, the \( IR \) potential drop takes place and crevice corrosion starts once \( IR > \Delta \phi_c \) where \( \Delta \phi_c \) is the difference between \( E_x = 0 \) and the Al equilibrium potential, \( E^\text{rev}_{Al/Al^{3+}} \). This concept was documented for the first time in this thesis by the formation of the active peak due to the pH increase that was measured. It was proved for the first time that the peak was not due to the oxidation of adsorbed hydrogen atoms. Also, the location of crevice corrosion on the wall in the crevice corrosion experiment when a cathodic potential was applied at the outer surface was shown for the first time to match well with the polarization curve of that system.

4.1.2. Intergranular Corrosion

With respect to the intergranular corrosion behavior of an aluminum 6111-like alloy (alloy # 10 with 1.47% Cu addition), a novel system has been developed in this thesis to collect comprehensive data about the intergranular corrosion parameters of the alloy mentioned above, e.g., potential drop, pH and chloride ions concentration. Also the rate
of corrosion attack was documented for the first time using a microscope which is the same method that was used previously in this research group. This study came out with new results as follows:

Firstly, it was proved that there was a large potential drop that occurs along the grain boundary grooves. This was documented by the hydrogen bubbles that were observed to evolve from these grain boundary regions, where these bubbles can not be formed on the outer surface where the electrode potential was too noble for the HER.

Copper enrichment and the redistribution process which took place during the intergranular corrosion of this alloy was an autocatalytic process. The high rate of the HER due to the high exchange current density on Cu increases the pH while the alkalinity decreases the solubility of the plated copper. The pH values reached their maximum at 12.3 and minimum at 9 within the cavity that had been formed by intergranular corrosion. The bulk solution pH was 6.9 at the beginning of the experiments. This is contrary to what was thought before, that only acidification is responsible for the intergranular corrosion.

It was shown in this thesis for the first time that peak-aging of this alloy increases the initial IGC rate but the overall corrosion rate remains the same. This was documented by an in-situ digital optical microscope supported by time-lapse software.
In addition, measurements in this thesis show primarily for the first time that the chloride ion concentration in the bulk solution only affects the initiation rate (the induction period) of the intergranular corrosion while the overall rate remains the same. The measured chloride concentration reached a value of 1M at the bottom of the cavity for a bulk solution that was only 50 mM NaCl.

Also, this work offered experimental data to help in creating a mathematical model to predict the localized corrosion of aluminum alloys.

4.2. Future Work

For narrow crevices (< 0.1 mm) a new set-up can be designed (see Figure 4.1). This design will help in collecting data within narrow crevices. Quantitative information about the narrow crevice is totally absent from the literature. This will help not only in studying crevice corrosion but also can be extended to study intergranular corrosion which is very similar in terms of grain-boundary-grooves dimensions (2 µm). This set up can provide information about the potential drop, pH and aggressive ion (chloride ions) concentration. Also it can provide valuable information about the $E-i$ behavior of this alloy in contact with this stagnant solution to study the presence or absence of an active peak. In other words, if $IR$ stabilized the crevice corrosion does or does not occur in these narrow crevices.
For the potential profile measurements, Ag sheets of dimensions 5 x 10 x 0.1 mm will be stacked as shown in Figure 4.1. Only one face of dimensions 5 x0.1 mm (which will oppose the alloy crevice surface) will be in contact with the solution. The other three faces will be lacquered. Between every successive sheet, there will be an insulator. All the Ag sheets will be connected to a switch box (every sheet will have its own key so it can work separately) and the switch box will be connected to a high impedance voltmeter. This unit, which is called a multireference electrode, will be working as the opposite wall to the crevice wall and using a 3-D manipulator, it can be positioned with respect to the alloy crevice wall. Before assembling the multireference electrode unit, a layer of AgCl should be deposited on every face of the twenty faces that oppose the aluminum alloy crevice surface. This will be carried out by connecting the whole unit using the sun key (see Figure 4.1) to a potentiostat and applying 2V SCE (higher than the equilibrium potential), so a layer of AgCl will be deposited on every single face. Every single Ag/AgCl face (electrode) will be checked against each other and against a SCE to confirm that all of them are working perfectly. After assembling this multireference electrode the potential at every mm depth will be measured using one single electrode of For chloride profile measurements, the voltage difference between every successive microelectrode in the multi reference unit will be measured, then using the following equation (equation 3), the chloride concentration can be determined using equation 4.1.

\[ \Delta E = 0.0591 \log[\text{Cl}^-] \]  

4.1
Figure 4.1. Schematic diagram for the experimental set up that will be used in case of narrow crevices (< 0.1 mm).
Every microelectrode in the multi reference unit will be calibrated in different concentrations of Cl⁻ using a commercial Ag/AgCl electrode. A calibration curve will be plotted between the $\Delta V$ and log[Cl⁻].

For pH profile measurements, the same unit shown in Figure 4.1 will be used except Ag sheets where Pd sheets will be used instead. Then, the whole unit will be charged with hydrogen for 10-15 hours under the same procedure described for the Pd wire in the case of the wide crevices. Here also, every two successive sheets will work as a concentration cell and the difference in voltage will correspond directly to the difference in [H⁺] in the crevice solution. A calibration curve will be constructed before assembling the unit, i.e. a relation between $\Delta V$ and pH will be created.

The advantage of this unit is (i) measurements can be done in a very narrow crevice, (ii) no convective mixing occurs due to moving the probe within the narrow crevice, and (iii) easier in handling than the probe. The disadvantage is that the unit needs to be calibrated twenty reference electrodes before every single set of measurements.
4.3. REFERENCES


Figure A1. Plot of both the intergranular corrosion band’s thickness (h) and the apparent cavity’s depth (H) as a function of time for an as-received alloy # 10 (1.47% Cu). At the beginning of the experiment, the sample was polarized at -824 mV Hg/Hg$_2$SO$_4$ (+ 150 mV vs OCP) and the bulk solution was 50 mM NaCl at 23 °C.
Figure A2. Plot of both the intergranular corrosion band’s thickness \( h \) and the apparent cavity’s depth \( H \) as a function of time for an as-received alloy # 10 (1.47% Cu). At the beginning of the experiment, the sample was polarized at -824 mV Hg/Hg\(_2\)SO\(_4\) (+ 150 mV vs OCP) and the bulk solution was 50 mM NaCl at 23 °C.
VITA

The author was born in April 19, 1972 in Giza, Egypt. In June 1989, he got his high school diploma from Ahmad Lotfy El-Sayed High school that is located in the Pyramids area in Giza, Egypt. In June 1993, the author achieved his bachelor degree with distinctive honor from the Chemistry Department at The University of Cairo, Giza campus. In September 1997, the author was awarded his Master of Science degree in Electrochemistry from the same department. His Master thesis was entitled “Metal-Complex Modified Conducting Polymer Electrode, Characterization and Sensory Application”. In October 1998, the author was invited by Dr. Howard Pickering and Dr. Barbara A. Shaw to pursue his doctorate degree in the Materials Science and Engineering Department at The Pennsylvania State University. In May 17, 2003, the author was awarded his Doctor of Philosophy degree in Materials Science and Engineering with high distinction.