ON THE INTERGRANULAR CORROSION OF 7XXX ALUMINUM ALLOYS

DISSERTATION

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ABSTRACT

High strength 7xxx aluminum alloys used widely in aircraft structure are very susceptible to intergranular corrosion (IGC). From a practical point of view, it is important to understand IGC in these alloys. Measuring the kinetics of IGC is not only a way to evaluate corrosion susceptibility, but also very useful for a predictive model for corrosion. Several AA7075 and AA7178 plates were used in this work. The foil penetration technique was used to measure the localized corrosion kinetics of the alloys in a NaCl solution and a new approach was developed to quantify the growth rates of sharp IGC fissures in a humid environment. Electrochemical properties of the alloys were studied by measuring the polarization curves. Electron microscopy and analytical techniques were used to observe the corrosion morphology and to understand the IGC mechanism.

Localized corrosion kinetics were measured on several alloys with different grain aspect ratio to understand the influence of grain structure. Anisotropic corrosion kinetics were found on alloys with grain aspect ratio greater than 1; the localized growth rate in the short transverse direction (through-thickness direction of a rolled plate) was much slower than that in other directions. For equiaxed material (with grain aspect ratio = 1), the localized corrosion kinetics were found to be independent of orientation.
Metallographic cross-sections confirmed that the localized corrosion kinetics strongly depend on the IGC growth path, which was affected by the microstructural anisotropy of the material. It was also found that IGC morphology of AA7xxx in a NaCl solution was selective grain attack (SGA). A statistical model for corrosion in AA7xxx was developed based on the grain structure of the material and the foil penetration data. Scenarios for SGA mechanism were proposed according to the statistical method and simulations.

Heat treating AA7xxx changes its mechanical strength as well as its corrosion properties. Two breakdown potentials were found in AA7xxx-T6 and only one breakdown potential in AA7xxx-W and AA7xxx-T7. The difference of the localized corrosion rates for tempers became less at potentials higher than $-740$ mV SCE. W temper was found to have the fastest corrosion rate. At a potential of $-750$ mV SCE, the localized corrosion rate for AA7075-T6 was slower than that for AA7075-T7. However, AA7075-T7 has slower localized corrosion rate at OCP than AA7075-T6. The sharp IGC fissures, which grew in a humid environment, also show slower growth rate in T7 than in T6.

The sharp IGC fissure growth kinetics were found to be independent of the humidity from 96% to 58% RH due to little connection of the local sites to the external environment. The sharp IGC fissures were found to be filled with corrosion products that seem to drive fissure growth by an SCC mechanism.
Dedicated to my parents
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CHAPTER 1

INTRODUCTION

7xxx aluminum alloys are high strength light alloys that are used extensively as aircraft structural materials. However, corrosion is one of the main issues for aging aircraft and AA7xxx are susceptible to localized corrosion, such as pitting, intergranular corrosion (IGC), stress corrosion cracking (SCC), crevice corrosion and exfoliation corrosion. In particular, sharp IGC fissures have been found to initiate in plate through-holes and propagate long distances [1].

IGC often propagates parallel to the applied stress, which does not necessarily lead to a loss of strength. However, linking of different IGC sites can result in multi-site damage (MSD), which can lead to catastrophic failure. It is also possible that fatigue cracks can initiate at bends in IGC cracks, where the cracks can be perpendicular to the applied stress fluctuations. In order to assure that structural integrity is not compromised by corrosion problems, it is critical to understand the IGC on AA7xxx, including the effects of microstructure and environment on the corrosion progress.

Any model that incorporates corrosion into a prediction of structural integrity must accurately consider the propagation kinetics of localized corrosion. The aim of this dissertation is to measure the IGC kinetics in AA7xxx, considering the material
orientation, temper, applied potential and environment. AA7xxx is often used in the rolled or extruded condition, so that the microstructure is elongated and anisotropic. The corrosion kinetics would strongly depend on the orientation in such materials if the attack were intergranular in nature. It has been reported that AA2024-T3 exhibits anisotropic IGC kinetics due to the microstructural anisotropy of the material [2, 3]. Temper is another factor to affect the IGC kinetics in AA7xxx. It is well known that AA7xxx-T7 exhibits better SCC resistance than AA7xxx-T6 although its tensile strength is decreased [4-10]. It is interesting to know if IGC resistance (in the absence of stress) behaves similarly. The environment, whether at OCP, potentiostatically polarized in an aqueous solution, or exposed to atmospheric conditions in different RH, could also influence the IGC kinetics.

The second chapter of this thesis is a literature review. Chapter 3 through 6 are written as stand-alone papers, including the details of the technical findings with individual introduction, experimental, results, discussion and summary. The contents of the chapters are summarized below to provide a roadmap for the rest of the thesis.

Chapter 2 reviews the metallurgy of 7xxx aluminum alloys, including heat treatment and alloying elements effects, which are related to their corrosion behavior. IGC, SCC and hydrogen embrittlement are three different types of attack that mainly occur at grain boundaries and are addressed separately for their mechanism in AA7xxx. The foil penetration technique, which is a non-electrochemical method to measure localized corrosion kinetics, is also reviewed.

Chapter 3 describes the influence of the grain structure on the localized corrosion kinetics in AA7075-T6 and AA7178-T6. The grain size of the materials were first
measured and analyzed. An equiaxed plate as well as two other plates with different grain aspect ratio were used to study the anisotropic localized corrosion kinetics. The localized corrosion kinetics were measured by the foil penetration technique on these materials in different orientations. Polarization curves from these materials were also compared and discussed. Anisotropic localized corrosion kinetics were observed on rolled plates due to the microstructural anisotropy and equiaxed material had localized corrosion kinetics independent of orientation.

Chapter 4 is an extension of the work from Chapter 3. The experimental results in Chapter 3 were used to develop a statistical model for IGC in AA7xxx. The model was based on a 2-dimensional brick-wall description of the microstructure. IGC growth in different orientations was considered in this model. The goal is to use statistical method and simulations to predict IGC growth in AA7xxx and to understand the IGC mechanism. Two possible IGC mechanisms were proposed based on the corrosion morphology and the simulations of the statistical model.

Chapter 5 describes the effects of temper and potential on the localized corrosion kinetics of AA7075. The material was heat treated to obtain three different temper conditions, W, T6 and T7. The localized corrosion kinetics according to each temper were measured by the foil penetration technique under several potential conditions, and were used as a criteria to determine the effects of temper and potential on the corrosion resistance of AA7075. The current density measured during the experiments was also recorded and compared to support the findings. W temper was found to have the fastest localized corrosion rate in all potential conditions. The localized corrosion rate in T7 was
faster than that in T6 under potentiostatic conditions, but slower than that in T6 under open circuit conditions.

Chapter 6 is a study of sharp IGC attack found in KC-135 wing structures. A method to duplicate similar sharp IGC fissures in the laboratory was first described. The kinetics of the sharp IGC attack could not be obtained by the foil penetration technique so a new approach was developed to quantify the rates of this attack. The procedure involves electrochemical pre-treatment of thin samples in a chloride solution, followed by exposure in a humid environment to form sharp IGC. The pre-treatment initiates localized corrosion sites that contain corrosion products and aggressive environments. This condition develops into sharp IGC during the subsequent exposure in humidity. Such initiating environments can be found in crevices and through-holes in aircraft. The back sides of the thin samples were monitored by a digital camera to determine the time for the fissures to penetrate the sample. It is then necessary to serial section the sample to determine the depth of the sharp IGC fissure, which is needed for quantification of the growth kinetics. Samples were tested in different humid environments to evaluate the effect of humidity on the kinetics of sharp IGC attack. 3-D images of the sharp IGC were successfully reconstructed from the serial sections to reveal the geometry of IGC propagation inside the material. FIB, XPS, SEM and TEM were used to understand the mechanism of sharp IGC. It is suggested that the sharp IGC fissure could be a form of SCC.

Chapter 7 summarizes the findings of this work on the IGC of 7xxx aluminum alloys. The effects of microstructure, temper, potential and environment on the IGC
kinetics in AA7xxx are concluded. This chapter also makes suggestions for future work on certain unresolved issues.

There are five appendixes in the end of this dissertation. Appendix A is a study of the variation of corrosion susceptibility across AA7178 wingskin plates. The localized corrosion kinetics were measured by the foil penetration technique and were compared with the microstructure and breakdown potentials. Appendix B is a work on evaluating corrosion susceptibility in two AA7178 wingskin plates. These two plates exhibit very different corrosion susceptibility. The localized corrosion kinetics, microstructure and polarization curves of these materials were measured and discussed. Appendix C is a discussion of the localized corrosion morphology in AA7075 and AA7178. The shortcomings of utilizing Optical Microscopy (OM) to observe the corrosion morphology were also addressed. Appendix D is a work on evaluating the temper effect on equiaxed AA7178. Appendix E includes some results of temper effects on AA7075 that were not shown in Chapter 5.
REFERENCES


CHAPTER 2

LITERATURE REVIEW

AA7xxx alloys have been widely used in aircraft applications because of their high strength and low weight [1]. For the KC-135, AA2024-T3 is used in the fuselage structures and AA7075-T6 in the wing structures. Although they have good mechanical properties, they can be very susceptible to localized corrosion. As the aircraft ages, the effect of corrosion can become more pronounced. Different forms of localized corrosion, such as pitting corrosion, crevice corrosion, intergranular corrosion (IGC), exfoliation corrosion and stress corrosion cracking (SCC), were found in different locations of wing structures made of AA7xxx [2]. These localized corrosion attacks can initiate at small sites and accelerate failure of a structure, leading to catastrophic damage.

Much work has been put into giving a protective coating to metal surfaces to separate the alloys from their environment. This is one approach to improve the corrosion resistance. On the other hand, an understanding of the electrochemical characteristics of the material can provide important information to increase its corrosion resistance. Many alloying elements are added to aluminum to increase its strength, but some of them can be harmful to its corrosion performance. By way of different heat treatment cycles, the
microstructure of the alloys can be changed and is possible to enhance the corrosion resistance without losing too much of their mechanical properties.

It was reported that corrosion of aircraft structures was one of the most costly maintenance problems for the aging aircraft fleet of the US Air Force [3]. While scientists put a lot of effort into corrosion prevention, it is also important to examine the corrosive attack and repair it before it causes catastrophic failures. The difficulty of detection of localized corrosion makes the maintenance of the aircraft more difficult. From a practical point of view, it is important to develop a model to predict the corrosion attack. Measuring the corrosion rate in the lab can provide useful information for the predictive model.

The physical metallurgy of AA7xxx alloys as well as possible IGC and SCC mechanisms in AA7xxx alloys will be reviewed in this chapter. Heat treatment also plays an important role on the corrosion resistance in AA7xxx alloys. A fundamental understanding of localized corrosion kinetics, including the effects of microstructure, potential, temper, and environment on the progress of localized corrosion, is the current issue.

2.1 Physical Metallurgy of AA7xxx

7xxx aluminum alloys are heat treatable. Zn and Mg are the principle alloying elements. They offer the highest potential for strengthening through age hardening (precipitation hardening), but also lead to high susceptibility to stress corrosion cracking (SCC) [1, 4]. Al-Zn-Mg alloys were first introduced in 1901 [5]. High strength Al-Zn-Mg-Cu alloys were primarily developed for aircraft construction, most of which have
very limited weldability. Cu is added in these alloys to improve the age hardenability as well as increase the resistance to SCC [6].

Age hardening involves the decomposition of a supersaturated solid solution (SSSS) to form finely dispersed precipitates, which hinder the movement of dislocation and thus increase the strength [1, 4, 6-13]. The precipitation scheme of AA7xxx alloys is as follows:

Solution Heat Treatment (SHT) → quench → SSSS → GP zones → η’ → η

The GP zones are spherical [6]. η’ and η are hexagonal MgZn₂ [6]. The most commonly used heat treatments in AA7xxx alloys are T6 and T7 tempers.

T6 temper is the peak aged condition and has the maximum strength [1]. It is achieved by SHT and quench, followed by a single heat treatment at temperatures ranging in between 120-135 °C for 24 hours [14]. The tensile strength can reach 550–610 MPa, depending on the alloy composition [1]. Unfortunately, AA7xxx alloys in T6 temper have a relatively low resistance to SCC. To improve the SCC resistance, a duplex heat treatment (or the over-aged condition), T7 temper, was developed. The T7 temper involves two steps of artificial aging treatment. The first aging step is at 107-120 °C for a few hours to nucleate GP zones [14]. The second aging step is at 160-170 °C and produces a refined dispersion of η’ (or η) particles from pre-existing GP zones [14]. The refined dispersion of η’ (or η) particles reduces the strength by about 15% from the T6 temper, but was reported to increase resistance to SCC [1]. The T7 temper provides a choice if SCC is a concern.

Another heat treatment, which enables AA7xxx alloys to exhibit high tensile strength like the T6 temper as well as maintaining similar resistance to SCC like T7
temper, is called retrogression and re-aging (RRA) temper [15]. RRA temper consists of three steps of aging treatments, i.e., T6 temper treatment, retrogression and re-aging steps. The T6 temper treatment was described above. The retrogression step is a very short treatment at a higher temperature, usually 200-260 °C, that dissolves some of the precipitates responsible for age hardening [16]. The re-aging step is similar to the T6 temper. During the re-aging stage, the solute re-precipitates and the mechanical strength increases again [16]. It was reported that an optimum combination of mechanical properties and resistance to SCC could be achieved by RRA temper [17].

Viana et al. observed the microstructure of AA7075-T6 with TEM and found a very fine precipitation distributed homogeneously inside the grains [18]. Coarser and continuous precipitates were seen at the grain boundaries. Puiggali et al. [19] and Rampogal et al. [20] found the precipitates of AA7010-T6 and AA7150-T6 to be up to 50 nm in the matrix and from 50 to 120 nm at the grain boundaries. The width of the precipitate free zone (PFZ) at the grain boundaries is about 30 nm [19, 20].

In T7 temper, the precipitates at the grain boundaries are coarser and more spaced than that in T6 temper, while inside the grains the precipitates are rather coarse and uniformly distributed [18]. It is suggested that the precipitates in the T7 temper are essentially \( \eta \), with a smaller amount of \( \eta' \) precipitates. The elongated \( \eta \) precipitates in AA7150-T7 alloys were reported to be up to 70 nm and 250 nm in the matrix and at the grain boundaries, respectively [19]. The width of PFZ at the grain boundaries is between 40 and 50 nm [19].

After retrogression but before the re-aging process, Viana et al. observed that the precipitation of AA7075 inside the grains is similar to that of the T6 temper, while the
grain boundaries showed very coarse precipitates well apart, which is similar to the T7 temper grain boundary precipitation [18]. They concluded that retrogression is responsible for the dissolution of the less stable precipitates, such as GP zones and the finer particles of $\eta'$ inside the grains [18]. Other researchers have made the same observation [21]. After RRA, Viana et al. observed a very dense precipitation inside the grains while the grain boundary precipitates continue the growth process initiated during retrogression [18]. They described the microstructure after RRA as similar to T6 temper inside the grains, but a little coarser and denser, while the precipitation at the grain boundaries is similar to T7 temper [18].

In summary, it can be pointed out that T6 temper maximizes the tensile strength of AA7xxx alloys while T7 and RRA tempers have improved SCC resistance. Fine precipitates inside the grains of T6 temper are responsible for the high mechanical strength while the coarser and more spaced grain boundary precipitates in T7 and RRA alloys seem to enhance the SCC resistance.

**2.2 Alloying Elements and Impurities in AA7xxx**

Different compositions of commercial AA7xxx alloys are now available and AA7075 is perhaps the best known. A higher strength modification, AA7178, with a tensile strength of 600 MPa when peak-aged, was introduced in 1951 [5]. Alloying elements are added mainly for precipitation hardening [1]. They may present as solid solutions with aluminum, or precipitate out to form another phase. They can have great effects on the corrosion properties.
Zn, Mg and Cu are important alloying elements in AA7xxx. Effects of Zn, Mg and Cu on the corrosion properties of Al solid solution are discussed in binary Al-Zn, Al-Mg and Al-Cu alloys separately.

Muller and Galvele studied the binary Al-Zn alloys with Zn content ranging from 1.07 to 4.85% [22]. They measured the breakdown potential of these alloys by performing polarization experiments in a chloride solution and found that the shapes of the polarization curves were similar to those found for pure aluminum. However, the breakdown potential decreased when Zn was present [22]. Other authors observed similar results [23-25]. Sato and Newman further investigated the effect of Zn content (up to 2%) on the mechanism of pitting corrosion of Al-Zn alloys. They concluded that Zn acts as an activator for aluminum in pitting corrosion and enhances the dissolution kinetics in the local environment [23, 24]. During the metastable pitting stage, Zn makes metastable pits grow faster and for a longer time before they repassivate, although the pit nucleation frequency is independent of Zn content. Ramgopal and Frankel studied of Al-Zn alloys of up to 5.86 wt% Zn content, and suggested that Zn might not be as efficient an activator of pitting in aluminum beyond a certain concentration and that there may be fine second-phase precipitation that would alter the electrochemical response of the alloy [25]. This is consistent with Muller and Galvele’s suggestion that further increases in the Zn content did not affect the breakdown potential of the alloy [22].

Muller and Galvele also measured the breakdown potential of Al-Mg alloys in chloride solution [22]. Their results showed that the breakdown potential is independent of Mg content and is close to that of pure aluminum. Inside the pits, they measured only
Al content. Therefore, they suggested that Mg would be expected to dissolve preferentially from Al-Mg alloys.

It is reported that the addition of Cu to aluminum has the opposite effect of adding Zn. The corrosion potential of solution treated Al-Cu alloys in a chloride environment was found to increase with increasing Cu content [26]. It is also noted that increasing the Cu content beyond the solubility of Cu in the aluminum should have little effect on the breakdown potential of the alloys [26, 27]. Rampogal and Frankel measured the repassivation potential of binary Al-Cu alloys and observed that even an amount as small as 0.022 wt% Cu in solid solution can raise the repassivation potential by 30 mV relative to that of pure Al [25]. Cu additions were found to ennoble the dissolution kinetics because the potential required to achieve a given current density increased with Cu content.

In addition to the changes in electrochemical behavior, Cu also plays an important role in the microstructure. It increases the volume fraction of η′ and also alters the kinetics of the precipitation reaction [28]. In the presence of Cu, the development of semi-coherent η′ from GP zones is accelerated and the η′ precipitate persists to much longer aging times. Moreover, Muller and Galvele observed Cu enrichment inside the pits in Al-Cu binary alloy [28]. This means that Al is preferentially dissolved and Cu stays in the alloy. This will cause an increase in Cu concentration locally and affect the corrosion mechanism.

From the above discussion, it is believed that in a chloride environment, Zn lowers the breakdown potential of aluminum and Cu increases the breakdown potential of aluminum; however, Mg has little effect on the breakdown potential of aluminum. It was
reported that Mg would be dissolved preferentially from the Al-Mg alloys and Al would be dissolved preferentially from Al-Zn and Al-Cu alloys [22]. Therefore, an enrichment of Zn and Cu would be expected inside the pits of Al-Zn and Al-Cu alloys. This was confirmed by various researchers [22, 26, 29]. It is believed that either the change of Zn concentration inside the pits or Cu being plated onto the pit walls, affects the dissolution mechanism of aluminum. Since Zn and Cu have opposite effects on the dissolution of aluminum, it is possible that there is competition between these two alloying elements, which makes the corrosion morphology of AA7xxx alloys irregular and multiform. However, the relationship is still not clear.

Second phase particles usually exhibit different electrochemical characteristics and have different effects on the corrosion behavior of the surrounding matrix [30]. They can be cathodic or anodic to the matrix of the alloy. Usually, second phase particles can lead to non-uniform attack at specific areas of the alloy surface and are the source of most of the problems with electrochemical corrosion [1].

MgZn$_2$ (η) is the strengthening phase in AA7xxx alloys. The corrosion potential of MgZn$_2$ in 1M NaCl was measured between –1035 and –1100 mV SCE, which was more negative than the corrosion potential of aluminum [31, 32]. Therefore, the MgZn$_2$ phase is active with respect to the matrix. It is usually considered that the η phase is in the form of Mg(Zn,Cu,Al)$_2$ because of substantial solid solubility for Cu and Al [20]. In the presence of Cu, the development of semi-coherent η′ from GP zones is accelerated and the η′ precipitate persists much longer [33]. Ramgopal et al. studied the η phase as a function of Cu, Zn and Al concentration by using the flash evaporation technique to generate thin film compositional analogs of the intermetallics [20]. For the MgZn$_2$ with
no Cu content, they observed a sharp current increase at a potential which is close to the reversible potential of Zn/Zn\(^{2+}\) while the reversible potential of Mg/Mg\(^{2+}\) is very low in comparison [29]. Therefore, they suggested that the breakdown potential of the \(\eta\) phase is associated with the dissolution of Zn. Adding a small amount of Cu up to 8 at % does not change the breakdown potential of MgZn\(_2\); however, addition of 17 at % and 27 at % Cu increases the corrosion potential by 250 mV and 300 mV respectively and raises the breakdown potential by 150 mV and 210 mV respectively [20]. They did not observe any significant change when adding up to 10 at % Al to MgZn\(_2\).

Iron and silicon are reported to be the dominant impurities in commercial grade aluminum alloys [27]. The solubility of silicon decreases from 12.6% in molten aluminum to 1.65% in solid aluminum [34]. Similarly, the solubility of iron is high in molten aluminum, but is low in solid aluminum (~0.04%) [34]. Therefore, most of the iron will precipitate out during solidification and form large second phase particles. The iron-rich particles, such as Al\(_3\)Fe, usually act as cathodes in local cells on the surface of the metal, providing points at which the surface oxide film is weak, thereby promoting electrochemical attack. Murray et al. reported that the presence of copper ions in the solution would cause metallic copper to plate onto the iron-rich particles [35]. If the matrix adjacent to the iron-rich particles has copper content, aluminum will be dissolved and the copper will remain inside the pits and plate onto the iron-rich particles, which makes the particles more cathodic with respect to aluminum [35].

Overall, second phase particles can be noble, active or neutral with respect to the matrix. Iron-rich particles are more noble to the matrix and act as cathodes. MgZn\(_2\) phases are more active to the matrix and are usually dissolved preferentially. While
adding Al to the MgZn$_2$ phase has little effect on the corrosion potential and breakdown potential of the MgZn$_2$ phase, adding Cu into the MgZn$_2$ phase will increase its corrosion potential and breakdown potential. Some of the elements of the active parts will leave the pits after being dissolved, but some will stay. The concentration change inside the pits will affect the further corrosion mechanism. It is clear from the discussion above that the presence of various second phase particles in AA7xxx alloys affects their corrosion behavior extensively.

### 2.3 Intergranular Corrosion

IGC is a type of localized corrosion that preferentially attacks grain boundaries. It occurs when either the thermodynamic driving force or the kinetic rate for corrosion at grain boundary regions is greater than in the grain interiors [36]. IGC of austenitic stainless steels probably is the best-known form. When heating austenitic stainless steel between 425 and 815 °C, noble chromium carbides (Cr$_{23}$C$_6$) precipitate at the grain boundaries, which form a Cr-depleted zone at the grain boundary region. The noble chromium carbides will enhance the dissolution of the active Cr-depleted zone at the grain boundaries and lead to IGC in acidic solutions.

IGC in aluminum alloys has been studied since the 1940’s. Generally speaking, IGC occurs in the following situations: active precipitates form at the grain boundary and dissolve, a beneficial element, normally in solid solution, is depleted from the grain boundary region, or detrimental elements segregate near the grain boundary and dissolve [36]. Composition, microstructure and heterogeneity of a material are all related to IGC [36].
Grain boundaries usually act as a sink for the annihilation of the supersaturated concentration of vacancies [36]. Precipitation of supersaturated solute usually depletes the zone near the grain boundary of solute. If a beneficial element is depleted from the regions adjacent to the grain boundaries, it will become more susceptible to corrosion than the matrix and cause IGC.

Based on the galvanic coupling theory, the region with a lower corrosion potential will be corroded and the other region with a higher corrosion potential will be protected. Therefore, when exposed to certain environments, the more active solute depleted zones will dissolve and lead to IGC. Dix et al. studied the corrosion behavior of Al-4%Cu in a NaCl-H₂O₂ environment [37, 38]. Precipitates of Al₂Cu were found along the grain boundaries and the Cu-depleted zones were observed adjacent to the grain boundaries. They measured the corrosion potential and found that the corrosion potential of the Cu-depleted zone was 44 mV more active than that of the grain matrix. They concluded that IGC in Al-Cu alloys is caused by the difference in the corrosion potential between these regions.

In AA7xxx, such as AA7075 and AA7150, both Zn and Cu were found to be depleted in the PFZ [20, 39]. It was discussed earlier that Zn and Cu have opposite effects on the dissolution of aluminum. While depletion of Cu makes the PFZ more susceptible than the matrix, depletion of Zn could be beneficial to the PFZ. Therefore, it is more complicated to determine the role of the PFZ in the process of IGC in AA7xxx than in binary alloys.

Another possible mechanism for IGC is anodic dissolution of grain boundary precipitates. If the precipitates form continuously at the grain boundary and corrode more
readily than the grain matrix, the dissolution of grain boundary precipitates will cause IGC. Continuous $\beta$ ($\text{Mg}_5\text{Al}_8$) is known to form along the grain boundary in Al-Mg alloys with $\beta$ more active than Al-Mg solid solution matrix [40, 41]. This can result in a high susceptibility to IGC. For AA7xxx, grain boundary precipitates of $\eta$ were also reported to be active than the solid solution matrix [29, 31, 32]. However, $\eta$ typically does not form a continuous structure at the grain boundary like the precipitates in Al-Mg alloys. Therefore, active grain boundary $\eta$ could be preferentially dissolved but this does not directly result in IGC in AA7xxx.

It has been observed that the IGC morphology in AA7xxx alloys in NaCl solution is irregular and complicated and the matrix near the grain boundary is also dissolved. This is probably due to the acidic and crevice environment that Buchheit et al. described in the IGC mechanism in Al-Cu-Li alloys [42]. In this case, which is in an aqueous environment, the solution inside the pits become severe enough to attack the matrix near the grain boundary while it dissolves the grain boundary preferentially. If the solution inside the pits is limited, it is likely that this critical condition to dissolve the matrix is not available and the attack is only along the narrow grain boundaries. It has been observed in this thesis that sharp IGC formed in AA7xxx alloys when samples were pretreated in NaCl solution to initiate corrosion and then moved to a humid environment.

From the discussion above, it can be concluded that the composition change at the grain boundary, either precipitates or PFZ, changes the electrochemical properties. The potential difference among grain boundary precipitates, PFZ and grain matrix makes AA7xxx susceptible to IGC.
2.4 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is the synergism between mechanical stress and corrosive attack acting on a susceptible alloy in a critical environment [2]. In aluminum alloys, SCC is reported to be almost exclusively intergranular [2, 44, 45]. Transgranular cracking is generally associated with mechanical fractures resulting from fatigue, creep rupture, tensile overload, etc [5].

Intergranular stress corrosion cracking (IGSCC) usually refers to stress-assisted IGC because most alloys that show such failures also show IGC without stress [2]. The corrosive attack at the grain boundary regions initiates the crack and tensile stress promotes the failure. In AA7xxx alloys, pitting of MgZn₂ serves as an initial crack site for further cracking. The dissolution of MgZn₂ which caused pitting in active crack tips was confirmed by Sedriks et al. [32] Both the size of MgZn₂ precipitates and the mean free path between the precipitates along the grain boundaries increased with aging time [32]. Therefore, the distance between the most anodic and the more rapidly dissolving regions increases with aging time, which would be expected to decrease crack advance [32].

Gest and Troiano anodically polarized stressed AA7075-T6 specimens in a NaCl solution [46]. They interrupted the test, increased the stress to fracture the specimens, and examined the fracture surface. Three regions were observed: a corroded zone, a non-corroded brittle zone and a ductile region. The non-corroded brittle zone was just ahead of the corroded zone. The corroded zone and the non-corroded brittle zone were believed to occur during testing, and a more ductile type of fracture was due to the forced rupture of the specimen. From their observation, it is possible that cracks were initiated by the
dissolution of active particles and continue to grow by brittle fracture until the next active particle is reached. Once the crack tip reaches the next active particle, the process is repeated again [46].

Since SCC is related to anodic dissolution, limiting the localized anodic dissolution should theoretically delay the formation of critical defects and improve SCC resistance. In order to understand this effect, Najjar et al. tested AA7050 alloys in a deaerated 3% NaCl solution [47]. The corrosion potential in an aerated solution is usually close to the breakdown potential, which is higher than the corrosion potential in a deaerated solution. Therefore, reduced rates of anodic reaction can be achieved by applying the corrosion potential in a deaerated solution. In this case, they observed an improvement in SCC resistance which they believed to be due to the delayed formation of dissolution sites [47].

It can be concluded that the main role of anodic dissolution is to produce critical defects, which corresponds to the first stage of the SCC process in AA7xxx alloys. It has been reported that the subsequent stages of SCC may possibly be localized hydrogen discharge, entry and embrittlement [47].

2.5 Hydrogen Embrittlement

Hydrogen embrittlement is one of the main factors causing SCC in steels. It is generally assumed that hydrogen acts to weaken interatomic bonds in the plane strain region at the crack tip [2]. Hydrogen is small and it migrates readily through the crystal structure of most metals and alloys [2]. In aluminum alloys, localized corrosion is always accompanied by hydrogen evolution. The corrosion potential for aluminum alloys is low
compared to steels and is close or below the reversible potential of hydrogen evolution, depending on the pH. Inside pits, the pH is lower owing to cation hydrolysis and the potential is lower due to ohmic potential drop. So the potential inside a pit or some other form of localized corrosion in aluminum alloys is well below the reversible potential for hydrogen evolution. Furthermore, the dissolving aluminum alloy surface is very catalytic, especially relative to the oxide covered outer surface. As a result of the favorable thermodynamic and kinetic factors, hydrogen evolution inside Al pits occurs at high rates, even during high rate localized dissolution of the alloy. The hydrogen evolution reaction is a cathodic reaction that consumes some portion of the electrons generated by localized corrosion. This portion has been measured to be about 20% [48] and even higher in some cases [49]. The hydrogen, in the form of nascent or atomic hydrogen can result in a loss of ductility and brittle cracking either at a crack tip or after transport into the alloy ahead of the crack tip [2] [32]. The volume diffusion of hydrogen in aluminum alloys was reported to be less than $10^{-9}$ cm$^2$/s compared to $10^{-5}$ cm$^2$/s in iron [50, 51].

Even though the diffusivity of hydrogen in aluminum alloys is low compared to that in iron, proof of hydrogen embrittlement in aluminum alloys was observed by several scientists. A decreased reduction of area in a tensile test and the occurrence of intergranular fracture usually indicates the loss of ductility [27]. Albrecht et al. performed a series of tensile tests on equiaxed AA7075 and observed a significant embrittling effect as manifested by a decreased reduction of area when precharging with hydrogen, especially in the underaged specimens [50]. When the cathodic charging was combined with the straining electrode test, a dramatic increase in the extent of the intergranular
fracture was observed. They interpreted the embrittlement as a result of the presence of cathodically charged internal hydrogen and the further straining enhanced the transport of additional hydrogen by the movement of dislocations. Therefore, a large amount of hydrogen can be transported by dislocation deep into the interior of the alloys. This provides a more rapid transport mode than the lattice transport of hydrogen in aluminum alloys and thus explains the existence of hydrogen embrittlement.

In order to cause embrittlement, hydrogen must be present at the crack tip [27]. The absorption of hydrogen is reported to be favored in regions where the highest stress intensity exists [52]. In materials susceptible to IGSCC, like aluminum alloys, grain boundaries are the locations of preferred hydrogen accumulation [52]. The extent and degree of brittle fracture was reported to be controlled by the extent of the dislocation transport of hydrogen and local hydrogen accumulation at the grain boundaries [33].

Evidence to prove hydrogen embrittlement in AA7xxx alloys is the observation of arrest markings from the SCC process. SCC in AA7xxx alloys was found to be a discontinuous process [52]. Observation of arrest markings supports the discontinuous mode of crack growth [45, 47, 53]. Once the crack has propagated into a region where the grain boundary strength has not been reduced by hydrogen embrittlement to a level below that of the yield stress of the surrounding alloy matrix, an arrest stage of the process occurs [54]. This assumption is based on the transport of hydrogen in front of the crack tip to cause embrittlement. Gest and Troiano suggested an incubation time for hydrogen transport ahead of the crack for further crack advance [46]. Therefore, the discontinuous propagation and arrest markings are the characteristic features of hydrogen embrittlement.
Magnesium segregation was reported to promote hydrogen entry into grain boundaries in aluminum, although it does not induce SCC by itself [55]. Hydrogen permeation through grain boundaries was found much greater in Mg-containing alloys than in Mg-free alloys [55]. Pickens and Langan studied Al-Zn-Mg alloys and observed the presence of segregated Mg at the grain boundaries (Mg unbound in MgZn$_2$ precipitates that was present in the grain boundaries) [44]. Pickens and his co-workers proposed that the segregated Mg might facilitate hydrogen concentration on the grain boundaries in sufficient quantities to cause embrittlement [56]. Magnesium hydride formation may also take place selectively on the incoherent interfaces of grain boundary precipitates and promote crack nucleation at such sites [55]. Further aging is able to discharge hydrogen to form molecular hydrogen bubbles and prevent hydride formation [55]. However, hydrogen bubbles may become another source of hydrogen damage.

The hydrogen effect on SCC in aluminum alloys was observed, but the actual mechanism is still being investigated. Hydrogen can be transported by dislocations and accumulate at the grain boundaries to cause embrittlement in aluminum alloys. While investigating the mechanisms of IGC and SCC in AA7xxx, hydrogen embrittlement cannot be excluded.

2.6 Temper Effects

Strength and corrosion susceptibility of AA7xxx alloys are strongly dependent upon temper, which is varied by heat treatment. T6 is the highest strength temper for AA7xxx, but it is susceptible to localized corrosion [1]. It is well documented that
AA7xxx in overaged tempers, such as T7, exhibits improved SCC resistance, although the strength is decreased [19, 44, 57-62].

Najjar et al. performed slow strain rate experiments in 3% chloride solution in AA7050 alloys with T6 and T7 tempers [47]. Their results showed that AA7050-T6 was highly sensitive to SCC. Overaged AA7050-T7 alloys have a lower occurrence of intergranular fracture and improved SCC resistance. It is possible that overaging induces a reduction of 1) the localized anodic dissolution at the grain boundary regions, 2) hydrogen diffusion into the grain boundaries, and 3) local stress concentrations through the homogeneity of deformation at the grain boundaries [47]. Therefore, overaged grain boundary regions are less sensitive to SCC and the fracture has to propagate by a discontinuous cleavage-like crack [47].

Coarsening of grain boundary precipitates is reported to be responsible for the improvement in the resistance to SCC [19, 39, 62]. Rajan et al. examined the grain boundary precipitates of AA7075 alloy in T6, T73 and RRA tempers and performed SCC testing [62]. The results showed that the heat treatments that produced better SCC resistance have a significantly larger grain boundary precipitate size than the T6 condition, which has poor SCC resistance. Tsai et al. reported a similar observation in AA7475 alloys between T6 and RRA tempers [59, 63]. It is suggested that RRA temper can produce larger and more spaced grain boundary precipitates than T6 temper condition [59, 62, 63]. The more spaced incoherent grain boundary precipitates can delay the localized anodic dissolution and can act as trapping sites for hydrogen, where bubbles of gaseous hydrogen can form. Therefore, the hydrogen concentration at grain boundaries can be reduced to below a critical value to inhibit hydrogen embrittlement and improve
SCC resistance.

Another hypothesis of SCC susceptibility provided by Jacobs is the presence of dislocations developed during quenching from solution treatment [64]. From the earlier discussion of hydrogen embrittlement, dislocations provide faster transport of hydrogen. Talianker and Cina observed an intense density of dislocations adjacent to grain boundaries and in the bulk of the grains of several AA7xxx alloys in the T6 temper [16]. But those dislocations disappeared after RRA treatment [16]. They suggested that the short stage and high temperature of retrogression could annihilate dislocations without causing overaging. The disappearance of dislocations results in retarding transport of hydrogen into the alloy and decreasing the susceptibility to SCC. They believed that the increased resistance to SCC of the RRA in AA7075 alloys is due to the major change in dislocation density rather than by the minor change in precipitate structure.

Potential measurements are useful for evaluating the effects of solution heat treatment and the subsequent aging process. Anodic polarization curves for AA7xxx-T6 in chloride solution typically exhibit two breakdown potentials, whereas the T7 exhibits only one [29, 65, 66]. In Maitra et al.’s research, only IGC was observed between the two breakdown potentials and both pitting and IGC were seen above the more noble breakdown potential in AA7075-T6 [65]. This result is consistent with Galvele and Micheli’s observation in Al-Cu alloys: the T7 specimens were immune to IGC and pitting only occurred above the breakdown potential [67]. Therefore, Maitra and English suggested that the disappearance of the second breakdown potential in T7 resulted in an improvement of IGC resistance.

However, Ramgopal et al. observed different results from Maitra and English.
Only pitting, instead of IGC, occurred in AA7075-T6 at a potential between the two breakdown potentials [29]. They further investigated AA7150 alloys in T6 and T7 tempers. Similar to AA7075 alloys, two breakdown potentials were shown in the T6 temper and only one breakdown potential in the T7 temper [20]. This time, they performed both short and long (1 hour and 24 hours) potentiostatic tests on their samples. In the short potentiostatic tests, the results were the same as those in the AA7075 alloys: no intergranular corrosion in T7 samples and only pitting in T6 samples between the two breakdown potentials while both pitting and IGC appeared above the more noble breakdown potential. However, when they potentiostatically tested their samples for 24 hours, both pitting and IGC were shown on all their specimens. As a result, they presumed that IGC of AA7150 alloys is a time-dependent phenomenon and that there is an incubation time associated with the onset of IGC [20].

Meng et al. proposed another scenario for the corrosion mechanism according to the two breakdown potentials in AA7xxx-T6 [66]. When applying a potential between two breakdown potentials, dark uniform corroded regions were observed on the sample surface. The dark regions were recognized as corrosion products by SEM, and no large and deep pits were observed on the surface. When the applied potential was above the second breakdown potential, selective grain attack and IGC were evident. They concluded that the first breakdown potential corresponds to transient dissolution, while stable dissolution occurs above the second breakdown potential.

Recently, in situ image techniques were used to investigate corrosion mechanism associating with two breakdown potentials in AA7xxx-T6. Issacs ground AA7075-T6 to 600 grit and exposed the sample at OCP for 1 h before polarization [68]. He used image
subtraction and found streaking attack along the scratched lines on the surface. The streaking attack was not observed in T7 temper. He suggested that the streaking attack was caused by mechanical polishing and resulted in two breakdown potentials [68]. However, he failed to explain why AA7xxx-T7 is immune to the streaking attack, since the sample preparation by polishing was same as AA7xxx-T6.

Ramgopal et al. examined the grain boundary precipitates of AA7150 alloys in T6 and T7 tempers and found that the Cu concentration in the grain boundary precipitates was a lot higher in T7 temper than in T6 temper [20]. This is consistent with Peel and Poole’s observation that Cu entered grain boundary precipitates (MgZn₂) during overaging, leading to more positive electrochemical potentials in saline environments [69]. In addition to the increase in electrochemical potentials, the high Cu concentration will change the pit environment of the grain boundary region after the dissolution of the precipitates [20]. Ramgopal et al. presumed that the presence of high Cu ions in solution due to dissolution of the T7 grain boundary precipitates may be responsible for preventing dissolution of the PFZs near the grain boundary region and making T7 temper less susceptible to IGC [20]. As a result, they suggested that the breakdown potential in T7 temper is due to pitting in the matrix. However, creating a high Cu environment in the PFZs is needed to dissolve the grain boundary precipitates first. If no dissolution of grain boundary precipitates occurs, the PFZs are still more vulnerable than the matrix. Since higher IGC resistance was observed in T7 temper, it could be suggested that the only breakdown potential in this temper is due to the dissolution of the precipitates.

In summary, it was proved that corrosion resistance in over-aged AA7xxx was better than peak-aged AA7xxx. AA7xxx-T6 exhibits two breakdown potentials while
only one in AA7xxx-T7. The first breakdown potential has been attributed to pitting in the matrix, pitting of the solute-enriched grain boundary region, or streaking attack created by mechanical processing or polishing. Some people believe that the improvement of corrosion resistance is a result of the coarsening of precipitates and more space between the precipitates at the grain boundary although others proposed that it is because of annihilation of dislocations as well as a retarding of the transport of hydrogen into the alloys. While the real mechanism is still under debate, it is no doubt that heat treatment can greatly decrease the susceptibility to SCC in AA7xxx alloys.

2.7 Foil Penetration Technique

Electrochemical techniques are commonly used for the study of localized corrosion growth [70-72]. The kinetics of electrochemical processes such as corrosion are often described by a relationship between current density and applied potential. However, there are several problems associated with the use of electrochemical techniques. First, the active area during localized corrosion is typically unknown and difficult to measure. Many assumptions regarding the number and morphology of localized corrosion sites are needed in order to translate measured current transients into localized corrosion growth rate. This is complicated by the fact that localized corrosion often takes more than one form, such as pits, crevices, and intergranular attack. Microscopic observation of corrosion from above the sample is limited by the line-of-sight nature of microscopy and does not adequately describe convoluted morphologies.

The foil penetration technique is a simple and direct non-electrochemical method that was developed for the study of pit growth kinetics in aluminum foils [73, 74]. It
overcomes many of the limitations of electrochemical methods as there is no need to make assumptions regarding pit shape or hydrogen evolution current. The penetration time is measured by detecting a resistance change of filter paper, which is sandwiched between the sample and a backing of Cu foil. Once the sample is penetrated, solution will wet the filter paper, reduce the resistance of the filter paper and trip the circuit. In the case of the foil penetration technique, the kinetics of the corrosion growth is determined by measuring the time for the fastest-growing localized corrosion site to perforate foils of varying thickness.

\[ t = f(d) \]

The corrosion rate can be obtained by converting the thickness as a function of time:[75]

\[ d = a \times t^n \]

where:

\[ d = \text{depth of attack or sample thickness} \]
\[ a, n = \text{constants depend on the metal and environment} \]
\[ t = \text{time} \]

Sehgal et al. studied the pit growth on AA2200-O and AA2024-T3 in different solutions by the foil penetration technique[74]. Zhang et al. also used this technique to measure the localized corrosion kinetics on AA2024 in NaCl solutions with applying a range of applied anodic potentials [75, 76].

A limitation of this technique is that samples need to be tested during immersion in an aqueous environment. The corrosion morphology that develops in an aqueous environment is different than the sharp IGC fissures found during environmental
exposure. Moreover, the corrosion environment for aircraft components is typically not immersion in an aqueous solution. Therefore, an approach which duplicates the sharp IGC fissures and provides the kinetics of their growth is needed.

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CHAPTER 3

THE INFLUENCE OF THE GRAIN STRUCTURE ON ANISOTROPIC LOCALIZED CORROSION KINETICS OF AA7XXX-T6 ALLOYS

3.1 Introduction

AA7xxx alloys are widely used in aircraft applications, especially for wing structures, because of their high strength and low weight. However, they are very susceptible to localized corrosion. Corrosion is one of the main issues for aging aircraft. Crevice corrosion has been found in lap joints areas, intergranular corrosion (IGC) in the steel fastener holes, and pitting and exfoliation corrosion in the flat areas [1]. These localized corrosion sites are usually hidden and can result in structural failure if they are allowed to grow to critical dimensions. Any model that incorporates corrosion into a prediction of structural integrity must accurately consider the propagation kinetics of localized corrosion.

High strength Al alloys are often used in the rolled or extruded condition, so that the microstructure is elongated and anisotropic. The corrosion kinetics will also be anisotropic in such a structure if the form of the attack is intergranular in nature. It was reported that the localized corrosion kinetics for a rolled AA2024-T3 plate are different in different orientations relative to the rolling direction, with the fastest nominal localized
corrosion growth rate in the longitudinal (L) or rolling direction and the slowest in the short transverse (S) or through-thickness direction [2, 3]. This is due to the straight IGC path along the L direction and the circuitous path in the S direction. Exfoliation corrosion is a special case of IGC, which occurs on the surface of a component with an elongated microstructure. Robinson and Jackson have reported that grain structure affects the exfoliation corrosion of high strength Al-Cu-Mg alloys and the severity of exfoliation corrosion was shown to be related to the grain aspect ratio of the material [4, 5].

The foil penetration technique is a simple method that has been used to determine the kinetics of localized corrosion [6]. In this technique, the penetration time for the fastest-growing localized corrosion site is measured. It is a non-electrochemical technique which overcomes many of the limitations for electrochemical methods. There is no need to make assumptions regarding pit shape or hydrogen evolution current. By varying the sample thickness, sample orientation, solution environment and applied potential, the corrosion growth kinetics of the fastest-growing localized corrosion can be determined regardless of the corrosion growth path. In recent years, Sehgal et al. studied pit growth on AA1100-O and AA2024-T3 in different solutions by the foil penetration technique [7]. Zhang et al. also used this technique to measure the localized corrosion kinetics on AA2024 in NaCl solutions during application of a range of anodic potentials [3].

The purpose of this work was to study the localized corrosion morphology and growth kinetics in high strength AA7xxx, and the relationship between the grain structure and the localized corrosion kinetics.
3.2 Experimental

Plates of AA7178 and AA7075 were used in this study. One AA7178 plate was taken from the wing of a retired KC-135 airplane and had an elongated grain structure, and one AA7178 plate had an equiaxed microstructure. The AA7075 plate was rolled with an elongated microstructure. These plates are referred to as wingskin AA7178, equiaxed AA7178, and rolled AA7075. The thickness of these plates were 8.5, 20.4, 19.1 mm, respectively, and their compositions, determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis, are shown in Table 3.1. Equiaxed AA7178 and rolled AA7075 were solution heat treated and artificially aged to the T6 temper. The solution heat treatment was conducted in an air furnace at 465°C for 3h for equiaxed 7178 and 480°C for 1h for rolled AA7075, followed by water quenching [8]. The T6 temper was achieved for both materials by artificially aging at 120°C in an air furnace for 24 h, followed by air cooling [8]. There was no evidence of recrystallization. The wingskin AA7178 was tested in the as-received condition. Although the temper of the wingskin AA7178 is unknown, it is believed that it was originally in the T6 temper and was naturally aged during an unknown period of service that was likely decades. Nonetheless, the wingskin AA7178 is designated as being in the T6 temper in this paper.

The nomenclature used for the plate orientations relative to the rolling direction [9] and the preparation of foil samples in different orientations are indicated in Figure 3.1. The microstructures were characterized by optical metallography after polishing and etching in Keller’s reagent for about 50 seconds. The grain size was measured using L and T sections. At least 20 grain size measurements were randomly made on each plate both in the L (or T) and S directions. The grain sizes in L and S directions were measured
in the T-section sample and the grain sizes in T and S directions were measured in the L-section sample.

Polarization curves were measured in deaerated 1 M NaCl at a potential scan rate of 0.1 mV/s to determine the breakdown potentials. The solution was Ar-deaerated for several days before the polarization experiment, and was continuously purged with Ar during the measurement. The breakdown potentials were taken as the points in the anodic polarization curve at which the current increased sharply. Different samples of equiaxed AA7178-T6 and rolled AA7075-T6 were prepared with surfaces in the three perpendicular orientations relative to the rolling direction. It should be noted that the perpendicular sections from the equiaxed AA7178-T6 plate were still labeled as L, T and S according to the nominal dimensions of the plate even though there was no obvious working direction. Samples of wingskin AA7178-T6 were prepared only in the S direction for polarization measurements due to the limitation of the plate thickness. All samples were ground to 800 grit in alcohol prior to testing.

Foil penetration experiments were performed on foil samples sliced using a band saw or a diamond saw in three perpendicular orientations with thickness from 0.1 to 1 mm. All samples were ground mechanically and polished through a series of silicon carbide (SiC) papers (up to 800 grit) on both sides. The last polishing step in 800 grit paper was performed in alcohol to minimize corrosion. A Teflon knife-edge O-ring was used to define the exposed specimen area. Except for wingskin AA7178-T6 in the L and T directions for which a smaller area of 41 mm² was used due to the thickness limitation of the wingskin plates, all samples were tested with an exposed area of 70 mm². The test solution was 1 M NaCl bubbled with O₂. All samples were first anodically polarized to –
290 mV SCE for 1 s to initiate corrosion, followed by an immediate change to the desired applied potential. Details regarding the foil penetration experiment and the detection circuit have been published previously [6, 7]. After the penetration experiments, the samples were cross-sectioned and examined by optical microscopy.

3.3 Results and Discussion

3.3.1 Grain Size and Aspect Ratio

Orthogonal metallographic sections of the three plates used in this study are shown in Figure 3.2. The grain sizes of wingskin AA7178-T6, equiaxed AA7178-T6 and rolled AA7075-T6 are given in Table 3.2. It is clear that the grain size of the equiaxed AA7178-T6 is independent of orientation and that the wingskin AA7178-T6 and rolled AA7075-T6 have elongated grains along the L and T directions. Moreover, the microstructure in the wingskin AA7178-T6 is more elongated than that of rolled AA7075-T6. The large values of standard deviation indicate considerable variation in the grain sizes. Wingskin AA7178-T6 and rolled AA7075-T6 microstructures were more elongated in the center of the plates. The less elongated microstructure near the surface could be due to recrystallization during hot-rolling or to non-uniformity in the deformation process.

One method to quantify the degree of anisotropy of a microstructure is the grain aspect ratio (GAR), defined as the ratio of average grain size in the longitudinal or transverse direction to that in the short transverse direction, \( d_L/d_S \) or \( d_T/d_S \), respectively. Table 3.3 shows the GAR values of these materials. The equiaxed AA7178-T6 has GAR
values close to 1, whereas the wingskin AA7178-T6 and rolled AA7075-T6 have large GAR values. The wingskin alloy is more elongated than the rolled alloy.

It is also shown in Table 3.2 that the wingskin AA7178-T6 has overall larger grain size than the rolled AA7075-T6. Assuming that the anisotropic structure is the result of a rolling process of an originally equiaxed material, the grain dimension in the S direction would be reduced and that in the L direction would be increased, with little change in the T direction. Therefore, the original equiaxed grain dimension of the rolled AA7075-T6 likely had a finer microstructure than the equiaxed AA7178 even before the rolling deformation.

3.3.2 Polarization Curves

To test the influence of sample orientation on the corrosion properties, potentiodynamic polarization experiments were performed on L, T and S samples of equiaxed AA7178-T6 and rolled AA7075-T6 in Ar-deaerated 1 M NaCl solution. Figures 3.3 and 3.4 show the polarization curves of equiaxed AA7178-T6 and rolled AA7075-T6 in the three perpendicular orientations. Breakdown potentials were taken as the points when the current increased sharply. Tables 3.3 and 3.4 show the breakdown potentials of equiaxed AA7178-T6 and rolled AA7075-T6 in different orientations while Table 3.5 shows the breakdown potentials of wingskin AA7178-T6 in the S direction. The reported values are the average of at least three separate experiments. As can be seen from the tables, the breakdown potentials were almost independent of the sample orientation. Wingskin AA7178-T6 and rolled AA7075-T6 both exhibited two breakdown potentials, which were nominally similar. In contrast, equiaxed AA7178-T6 exhibited three clear
breakdown potentials. The 1st and 2nd breakdown potentials for equiaxed AA7178-T6 were lower than those for the other alloys. The polarization curves for equiaxed AA7178-T6 exhibited a feature at high potentials that is being interpreted as a 3rd breakdown potential. A third breakdown potential was never before reported in the literature.

Two breakdown potentials have been reported in aged Al-4%Cu [10], AA7075-T6 [11-14] and AA2024-T3 [3]. The exact cause of the two breakdown potentials is still under debate. The 1st breakdown potential has been reported to be due to transient dissolution, which could be attributed to pitting in the matrix [11, 13], pitting of the solute-enriched grain boundary region [11, 13], or dissolution of a thin susceptible surface layer created by mechanical processing or polishing [15]. Above the noble breakdown potential, corrosion is stabilized and is associated with IGC or selective grain attack [13, 14, 16]. The third breakdown in equiaxed AA7178-T6 was reproducible and independent of orientation. The elbows in the polarization curves of the multiple breakdown potentials indicate a decrease in reaction rate with increasing potential. Localized corrosion is usually autocatalytic in that it tends to continue to propagate once initiated. The decrease in current indicates a transient phenomenon associated with a limited supply of corroding material, such as active particles [13] or a thin surface layer [15]. Figure 3.5a is the schematic plot of this scenario for a two-breakdown-potential case. A third breakdown potential, such as observed for equiaxed AA7178-T6, suggests that there were two transient phenomena associated with transient dissolution of two different types of active sites having slightly different susceptibilities, but limited in extent, Figure 3.5b. The phenomena responsible for these multiple breakdowns were not clarified, but it is
apparent that there were two transient dissolution phenomena that did not transition to stable localized corrosion for equiaxed AA7178-T6.

### 3.3.3 Foil Penetration Experiments

A potential of $-725$ mV SCE was selected for the foil penetration experiments. This value is above the 3<sup>rd</sup> breakdown potential for equiaxed AA7178-T6 and above the 2<sup>nd</sup> breakdown potential for wingskin AA7178-T6 and rolled AA7075-T6. Figures 3.6-3.8 show the results of foil penetration experiments on wingskin AA7178-T6, equiaxed AA7178-T6 and rolled AA7075-T6 in three orientations in aerated 1.0 M NaCl solution at $-725$ mV SCE. The experiment determines penetration time as a function of sample thickness, but the data are plotted as thickness (depth of the fastest growing localized corrosion site) as a function of time. The lines in Figures 3.6-3.8 show that the localized corrosion growth can be fitted to a power law of the form:

$$d = A \times t^n$$  \hspace{1cm} (1)

where $d$ is the depth of the fastest localized corrosion site, $t$ is time and $A$ and $n$ are constants. The exponent $n$ was found to be close to 0.5 for pits in pure Al [6] and is shown to be in a range between 0.18 and 0.47 here for localized corrosion in AA7xxx-T6. The meaning of this value is unknown at this time. For a hemispherical pit, an exponent of 0.5 is expected for either mass transport or ohmic control [17]. The complex geometry of these localized corrosion features complicates the time dependence of the growth laws.

Figures 3.9-3.11 show metallographic cross-sections of the three materials in the three orientations after the foils were penetrated. The localized corrosion in the foil penetration experiments was a combination of IGC and selective grain attack, which has
been seen previously for AA7xxx alloys [13, 18]. Figure 3.12 is the etched cross-section of Figure 3.10a. It is clear that the localized corrosion attack on equiaxed AA7178-T6 was basically along the grain boundaries, but parts of the grains were also attacked. The form of corrosion for wingskin AA7178-T6 and rolled AA7075-T6 was similar to that of equiaxed AA7178-T6. The pit-like cavities shown on wingskin AA7178-T6 (Figure 3.9) indicate that some selected grains have dissolved but then the attack stopped at the next grain boundary for some reason. This kind of selective grain attack was also seen on rolled AA7075-T6 samples (Figure 3.11). It is not clear why this form of localized attack in AA7xxx stops at grain boundaries rather than developing into a hemispherical pit. But it is clear that the attack is preferentially along the grain boundaries with simultaneous attack of selected grain bodies.

The localized corrosion growth rates in equiaxed AA7178-T6 shown in Figure 3.7 are independent of the orientation, which is to be expected for IGC in an equiaxed microstructure. Figure 3.8 shows that the localized corrosion growth rate of rolled AA7075-T6 in the T direction was faster than that in the S direction and slightly slower than that in the L direction. This anisotropic growth of localized corrosion has been observed in AA2024-T3 and was attributed to the intergranular nature of attack and the elongated microstructure in the rolling direction [2]. The corrosion rates of rolled AA7075-T6 in the S (through thickness) direction were very slow because the IGC path was meandering, which is confirmed by the cross-section (Figure 3.11c). The corrosion rates in the L (longitudinal or rolling) direction were similar to those in the T (transverse) direction when samples were very thin. However, the corrosion rates in the T direction became slower when the sample thickness was larger. It is expected that the local rates of
IGC propagation are independent of orientation and that the nominal growth rate is controlled by the path length. The difference in kinetics for thicker samples is possibly caused by a longer intergranular corrosion path in the T direction for thick samples, due to jogs at grain intersections. The similar corrosion rates in the L and T directions for thin samples are likely because the IGC path is of length close to the dimension of one grain. Therefore, the critical thickness, $d_c$, that differentiates the localized corrosion growth rates of rolled AA7075-T6 in the T direction from the L direction can be assumed to be the largest grain dimension in the T direction. The data in table 3.2 indicate that one standard deviation above the average is a grain size of about 155 $\mu$m for the T orientation in this material. In Figure 3.8, the kinetics lines in L and T directions diverge at a thickness of around 0.17 mm = 170 $\mu$m, which supports the explanation given above. Figures 3.11a and 3.11b indicate that the localized corrosion path in the T direction involves more grains than in the L direction.

Figure 3.6 shows the localized corrosion kinetics of wingskin AA7178-T6 in O$_2$ bubbled 1 M NaCl at a potential of $-725$ mV SCE. The slow corrosion rate in the S direction results in strong anisotropic localized corrosion kinetics. However, the corrosion growth rates in L and T directions here are similar. It should be noted that the wingskin AA7178-T6 has a very elongated microstructure. The more elongated the plate is, the closer are the IGC rates for the L and T directions and the more separated are these from the S direction. Furthermore, for wingskin AA7178-T6, the one standard deviation above the average grain dimension in the T orientation is shown in Table 3.2 to be 772 $\mu$m, whereas the thickest T foil tested was only 830 $\mu$m. Therefore, the samples were about the same size as the critical thickness in the T direction. If the localized corrosion
growth rates of AA7178-T6 in T direction are slower than those in L direction, it is not likely to be distinguishable for samples thinner than the critical thickness.

The exponents of n for wingskin AA7178-T6 were smaller than those for rolled AA7075-T6 in L and S directions, and were similar in the T direction. However, the line for rolled AA7075-T6 in the T direction represents the localized corrosion growth rates above the critical thickness whereas the line for wingskin AA7178-T6 in the T direction is the localized corrosion growth rate for thicknesses less than the critical thickness. It is possible that localized corrosion of wingskin AA7178-T6 will grow slower in T direction than as shown in Figure 3.6 for samples thicker than the critical thickness and the exponent of n will decrease. Therefore, the exponents of n are smaller for wingskin AA7178-T6 than for rolled AA7075-T6 in each orientation. Although the meaning of n is still unknown, the above observations indicate that it could depend on the material microstructure.

It has been shown that the GAR of equiaxed AA7178-T6 is 1.0. The GAR of wingskin AA7178-T6 and rolled AA7075-T6 are 7.4 and 4.6 respectively, which indicate the anisotropy of the microstructure. The study shows that the localized corrosion kinetics were anisotropic for wingskin AA7178-T6 and rolled AA7075-T6, which have elongated microstructure, and were independent of orientation for the equiaxed AA7178-T6. The cross-sections show that localized corrosion paths in wingskin AA7178-T6 and rolled AA7075-T6 were very directional. In summary, localized corrosion in AA7xxx-T6 is strongly affected by the microstructure.
3.4 Summary

Different plates of AA7xxx-T6 were studied for their localized corrosion kinetics and were related to their GAR. The following observations were made:

1. AA7xxx-T6 samples exhibited elbows in the polarization curves, indicating the presence of transient dissolution processes before localized corrosion stabilized.

2. The breakdown potentials were independent of sample orientations.

3. Anisotropic localized corrosion kinetics were found for rolled AA7xxx-T6 plates (with grain aspect ratio > 1) while the localized corrosion kinetics for an equiaxed AA7178-T6 (with grain aspect ratio = 1) were independent of the orientation.

4. The localized corrosion growth rate in the S direction was much slower than that in either the L or T direction for rolled plates due to the microstructural anisotropy and intergranular attack in nature.

5. A critical thickness differentiated the localized corrosion growth rate in T direction from that in L direction. For samples thinner than the critical thickness, the localized corrosion growth rates in T and L directions were similar.

6. The localized corrosion morphology on AA7xxx-T6 was a combination of IGC and selective grain attack.
REFERENCES


### TABLES

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Mn</th>
<th>Mg</th>
<th>Cr</th>
<th>Zn</th>
<th>Ti</th>
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<tr>
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<td>0.04</td>
<td>0.28</td>
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<td>0.053</td>
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<td>5.68</td>
<td>0.024</td>
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Table 3.1 Composition in wt% of wingskin AA7178, equiaxed AA7178 and rolled AA7075 quantified by ICP-OES.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>wingskin AA7178-T6</th>
<th>equiaxed AA7178-T6</th>
<th>rolled AA7075-T6</th>
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</thead>
<tbody>
<tr>
<td>L</td>
<td>1040 ± 692</td>
<td>183.9 ± 68.9</td>
<td>236.1 ± 120.5</td>
</tr>
<tr>
<td>T</td>
<td>511 ± 261</td>
<td>189.2 ± 64.2</td>
<td>108.7 ± 46.4</td>
</tr>
<tr>
<td>S</td>
<td>39 ± 17</td>
<td>174.6 ± 56.0</td>
<td>24.6 ± 11.2</td>
</tr>
</tbody>
</table>

Table 3.2 Grain dimensions in µm of wingskin AA7178-T6, equiaxed AA7178-T6 and rolled AA7075-T6.

<table>
<thead>
<tr>
<th>Aspect Ratio</th>
<th>wingskin AA7178-T6</th>
<th>equiaxed AA7178-T6</th>
<th>rolled AA7075-T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_L/d_S</td>
<td>26.7</td>
<td>1.1</td>
<td>9.6</td>
</tr>
<tr>
<td>d_T/d_S</td>
<td>13.1</td>
<td>1.1</td>
<td>4.4</td>
</tr>
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Table 3.3 Grain aspect ratios of wingskin AA7178-T6, equiaxed AA7178-T6 and rolled AA7075-T6. \( d_L, d_T \) and \( d_S \) are the average grain sizes in L, T and S directions, respectively.
### Table 3.4 Breakdown potentials in mV SCE of equiaxed AA7178-T6 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample orientation</th>
<th>1st Breakdown Potential</th>
<th>2nd Breakdown Potential</th>
<th>3rd Breakdown Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-814.1 ± 4.1</td>
<td>-772.4 ± 4.7</td>
<td>-731.7 ± 2.6</td>
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<tr>
<td>T</td>
<td>-823.4 ± 1.4</td>
<td>-775.9 ± 4.9</td>
<td>-738.3 ± 3.6</td>
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<tr>
<td>S</td>
<td>-828.0 ± 0.9</td>
<td>-780.7 ± 5.0</td>
<td>-737.1 ± 1.9</td>
</tr>
</tbody>
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### Table 3.5 Breakdown potentials in mV SCE of rolled AA7075-T6 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample orientation</th>
<th>1st Breakdown Potential</th>
<th>2nd Breakdown Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-798.0 ± 6.4</td>
<td>-761.0 ± 6.4</td>
</tr>
<tr>
<td>T</td>
<td>-794.7 ± 4.5</td>
<td>-756.5 ± 2.9</td>
</tr>
<tr>
<td>S</td>
<td>-794.2 ± 6.5</td>
<td>-755.6 ± 8.6</td>
</tr>
</tbody>
</table>

### Table 3.6 Breakdown potentials in mV SCE of wingskin AA7178-T6 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s\(^{-1}\).

<table>
<thead>
<tr>
<th>Sample orientation</th>
<th>1st Breakdown Potential</th>
<th>2nd Breakdown Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>-804.0 ± 14.7</td>
<td>-745.3 ± 11.4</td>
</tr>
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</table>
Figure 3.1 Schematic diagram of foil sample orientations relative to the rolling direction.
Figure 3.2 Metallographic sections of (a) wingskin AA7178-T6, (b) equiaxed AA7178-T6 and (c) rolled AA7075-T6 plates, and the terminology used for the three orientations: L (longitudinal), T (long transverse) and S (short transverse).
Figure 3.3 Anodic polarization curves for equiaxed AA7178-T6 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s$^{-1}$. 
Figure 3.4 Anodic polarization curves for rolled AA7075-T6 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s$^{-1}$. 
Figure 3.5 Scenario of the multiple breakdown potential process. Dash lines indicate transient dissolutions. Thin solid lines represent possible polarization curves of the alloy without transient dissolution. Thick solid lines are the measured polarization curves with multiple breakdown potentials. (a) Two breakdown potentials. (b) Three breakdown potentials.

Figure 3.6 Localized corrosion kinetics of wingskin AA7178-T6 in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure 3.7 Localized corrosion kinetics of equiaxed AA7178-T6 in O\textsubscript{2} bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.

Figure 3.8 Localized corrosion kinetics of rolled AA7075-T6 in O\textsubscript{2} bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure 3.9 Unetched cross-sections of wingskin AA7178-T6 foil penetration samples having corrosion growth direction in various orientations (a) L, (b) T and (c) S.

Figure 3.10 Unetched cross-sections of equiaxed AA7178-T6 foil penetration samples having corrosion growth direction in various orientations (a) L, (b) T and (c) S.

Figure 3.11. Unetched cross-sections of rolled AA7075-T6 foil penetration samples having corrosion growth direction in various orientations (a) L, (b) T and (c) S.
Figure 3.12 Etched cross-section of Figure 10(a).
CHAPTER 4

A STATISTICAL MODEL FOR LOCALIZED CORROSION IN AA7XXX

4.1 Introduction

High strength aluminum alloys are susceptible to localized corrosion. For AA7xxx (Al-Zn-Mg-Cu) alloys in NaCl solutions, the corrosion morphology is a combination of intergranular corrosion (IGC) and pitting corrosion [1, 2]. This kind of localized corrosion has been called selective grain attack (SGA) [3]. A discussion of the possible routes to an SGA type of corrosion morphology is given below but the end result is the selective dissolution of a limited number of grains in the material. The attack is limited to the matrix of the attacked grains; unlike pitting corrosion, the attack does not spread to neighboring grains.

The localized corrosion kinetics have been successfully measured on materials of AA2024, AA7075 and AA7178 by the foil penetration technique [1-6]. It has been shown that the corrosion kinetics are strongly related to the microstructure [4, 7-9]. For a plate formed by a rolling process, the microstructure is elongated and anisotropic. The corrosion rates have been shown to be the fastest along the longitudinal (L) or rolling direction and the slowest along the short transverse (S) or through-thickness direction. This is due to the structural anisotropy of the material and its effect on IGC.
Robinson and Jackson [7] proposed an equation describing the mean IGC velocity for AA2xxx alloys, which involves the total length of grain boundary corrosion divided by the total exposure time. Their calculation of the length of grain boundary was based on the average grain dimensions in each orientation. According to this equation, the severity of exfoliation corrosion (a special case of IGC) on AA2024-T3 was shown to be related to the grain structure of the material. However, this equation is extremely simplified.

Ruan et al. proposed a more detailed model predicting the anisotropy of IGC kinetics in AA2024-T3 [9, 10]. The material was a rolled plate with an elongated microstructure. The kinetics of IGC growth in the S direction was calculated from the measured kinetics in the L direction and the corrosion path length determined from a model of the microstructure. The calculated kinetics of IGC growth in the S direction were then compared to measured values. In the first version of the model, several simplifying assumptions were made: 1) each corrosion path would make a turn when it reaches an intersection, 2) the corrosion path always goes deeper, and 3) the corrosion path does not split into two at an intersection. The thickness of grains in the S direction was assumed to be constant and the grain lengths were described by different types of distributions. They first assumed the length of each grain to be constant. The horizontal distance that the $i$th IGC site will travel on the $j$th layer, $X_i(j)$, was simulated by a uniform distribution and a normal distribution separately. Simulation results with both distributions indicated some discrepancies from the experimental result. The uniform distribution predicted a faster corrosion rate while the normal distribution had unreasonable results according to the material microstructure. It was pointed out that grain size distribution should not be ignored. A gamma distribution was then used for the
length of the grains and $X_i(j)$ was assumed to be uniformly distributed. This did not provide an improved data fit because the assumption of constant grain thickness. When a gamma distribution was also used for the thickness of the grains, the simulation results were greatly improved, but still had some discrepancies from the experimental data.

Ruan et al. revised their model by modifying their assumptions about IGC path [11]. The IGC was allowed various options at grain intersections, and probabilities were assigned for the IGC path to move past or skip the intersection, split or turn upward. By varying the probabilities, a good fit of the experimental data was achieved using a combination of probabilities with reasonable physical meaning according to the material microstructure and corrosion phenomena. This version of the model well predicts the localized corrosion rate of AA2024-T3 in S direction based on measured rates in the L direction.

In this work, the statistical model by Ruan et al. was modified and applied to the corrosion of AA7xxx in different orientations of different plates, including equiaxed and anisotropic microstructure. The statistical model provides an approach to quantify the relationship between the microstructure of the material and its corrosion kinetics. Furthermore, it helps to understand corrosion mechanism.

4.2 Statistical Model and Simulations

IGC kinetics are strongly related to the total length of the IGC path. It is assumed in this work that other factors, such as orientation relative to gravity or grain boundary misorientation are relatively unimportant. Therefore, the fastest nominal IGC growth rate, which is measured in foil penetration experiments [6, 12], will correspond to the shortest
IGC path length. The fastest nominal IGC growth kinetics can be predicted by modeling and simulating the shortest IGC path length.

The brick-wall model used by Ruan et al. was modified by using a more realistic three-way junction to describe grain boundary intersections instead of a four-way junction. Grain sizes of different materials were measured and are listed in Table 4.1, showing the mean values, M, and standard deviations, S. Gamma distributions were used to model the grain size distributions. The method of moments was used to estimate the parameters of these gamma distributions from the following equations [10, 13]:

\[
\alpha \beta = M \quad (1)
\]

\[
\alpha \beta^2 = S^2 \quad (2)
\]

The gamma distribution parameters \( \alpha \) and \( \beta \) obtained using equations (1) and (2) for the materials used in this study are given in Table 4.2.

Consider foil samples composed of grains in certain orientations as shown in Figure 4.1. If a sample has thickness \( D \), the total layers \( N \) across the thickness can be estimated as:

\[
N = \frac{D}{b} \quad (3)
\]

where \( b \) is the median of the estimated gamma distribution model for the grain size in the through-thickness direction. Suppose that there is a fixed number of IGC corrosion sites, \( m \), which are initiated on the surface and grow into the microstructure along different IGC paths \( i \), where \( i = 1, 2, \ldots, m + u - v \) (\( u \) and \( v \) will be defined later). Denote \( W_{i,D} \) to be the total length of the \( i \)th IGC path to get through the sample thickness of \( D \).

\[
W_{i,D} = \sum_{j=1}^{k} b_j + \sum_{j=1}^{k} H_i(j) = W_{i,D,V} + W_{i,D,H} \quad (4)
\]
where \( k \) is the total layers that the \( ith \) IGC travels. (\( k \geq N \). When \( k = N \), the IGC path always goes down, not turns up.) \( H_i(j) \) is the horizontal distance that the \( ith \) IGC site will travel on the \( jth \) layer, where \( j = 1, 2, \ldots, k \). \( W_i,D,V \) and \( W_i,D,H \) are the total vertical and horizontal distances that the \( ith \) IGC path travels.

To determine \( k \), \( W_i,D,V \) and \( W_i,D,H \), the types of grain junctions need to be considered. Different from a four-way junction used in Ruan et al.’s model [9-11], a more realistic three-way junction was used in this work. Two types of three-way junctions, "T" and "⊥", were considered. When a horizontal IGC path meets a "T", it can skip this junction and continue on or turn downward. Similarly, when a horizontal IGC path meets a "⊥", it can skip this junction or turn upward. Splitting of the IGC to follow both paths at this type of intersection was not considered at this stage. Therefore, the probabilities for both situations are:

\[
P_{down} + P_{sdown} = 1 \tag{5}
\]
\[
P_{up} + P_{sup} = 1 \tag{6}
\]

where \( P_{down} \) is the probability that a horizontal IGC path turns downward at a "T", \( P_{sdown} \) is the probability that a horizontal IGC path skips at a "T", \( P_{up} \) is the probability that a horizontal IGC path turns upward at a "⊥", and \( P_{sup} \) is the probability that a horizontal IGC path skips at a "⊥".

When a growing IGC site turns upward or downward, it will meet another "⊥" or "T" junction in the next layer. When such a vertical IGC site meets a junction, it will always turn to a horizontal direction. Such vertical IGC sites are also allowed to split into two, following both directions. If it does split into two, each resulting IGC site is considered from that point to be independent. \( P_{split} \), the probability that a vertical IGC
path splits into two at a junction, and $P_{\text{nsplit}}$, the probability that a vertical IGC path will follow one side at a junction, sum to unity:

$$P_{\text{split}} + P_{\text{nsplit}} = 1$$  \hspace{1cm} (7)$$

All IGC sites start from top surface. A tracking parameter $X$ is defined such that $X = 0$ when an IGC site starts from top surface. When an IGC site travels one layer away from top surface, $X$ is increased by one. When an IGC site turns upward and is one layer closer to top surface, $X$ is reduced by one. If the IGC path goes back to top surface during the simulation such that $X = 0$, the simulation of that path will stop. When $X = N$, the IGC site has traveled to the bottom surface and the foil sample is penetrated. Simulation will also stop when the sample is penetrated, and this is the only situation counted. Figure 4.2 is a schematic plot of an IGC path in S direction with definitions of the possible situations at the junctions.

When a vertical IGC path turns to horizontal direction at a junction, it then needs to be decided whether the next junction is a "T" or "⊥". Figure 4.3 shows the possible situations. In Figure 4.3, $a$, $b$, $c$, $d$ and $e$ represent five different grains. An IGC path first travels vertically downward between grains $b$ and $e$. Assume that it does not split and turns right when it meets the junction between grains $a$, $b$ and $e$. Let $R_b$, the length of grain $b$, be $rG$, a random value generated from the estimated gamma. The vertical IGC path could meet grain $a$ at any point along its length. Therefore, let $R_a$, the portion of grain $a$ to be traveled, be $rU(1) \times rG$, where $rU(1)$ is a random number generated from the uniform(0,1) and $rG$ are taken to be independent.

Define $L_{\text{up}}$ and $L_d$ to be the distance in the horizontal direction until reaching a junction going up and down, respectively. At this moment, $L_{\text{up}} = R_b$ and $L_d = R_a$. If $L_{\text{up}} <$
the next junction would be a “⊥”. If it turns upward at this junction, the total horizontal distance that it travels in this layer, \( H \), is \( L_{up} \). If \( L_{up} > L_d \), the next junction is a "T" (which is the case in Figure 4.3). When it turns downward at this junction, the total horizontal distance that it travels in this layer, \( H \), is \( L_d \).

However, if the next junction is a “⊥” and the IGC skips this junction, the length \( R_d \), which is associated with grain \( d \), will be generated by \( rG \) and the new \( L_{up} = L_{up} + rG = R_b + R_d \). Similarly, if the next junction is a "T" and the IGC skips this junction, grain \( c \) needs to be considered and the new \( L_d = L_d + rG = R_a + R_c \). This process repeats until the IGC path turns upward or downward. By comparing the new \( L_{up} \) and \( L_d \), the junction type can be decided. Figure 4.4 shows the flow chart of this simulation. Through this process, \( H_i(j) \), the horizontal distance that the \( i \)th IGC path travels in the \( j \)th layer, can be determined.

The number of additional paths resulting from splitting is defined as \( u \), which is \( \geq 0 \). The number of IGC paths terminated at the top surface is defined as \( v \), which is also \( \geq 0 \). With the number of initial IGC sites being \( m \), the total number of effective IGC paths traveling through the foil sample from top surface to the bottom is \( m+u-v \). Among the \( m+u-v \) IGC paths, the shortest IGC path is \( W_{\text{min},D} \).

\[
W_{\text{min},D} = \min \ W_{i,D}, \ i = 1, 2, \ldots, m+u-v
\]

This path generates the fastest penetration time and represents the fastest nominal localized corrosion rate to be compared with foil penetration data.

The localized corrosion kinetics in AA7xxx and AA2xxx have been found to follow the equation [1, 2, 4, 5]:

\[
d = A \times t^a
\]
where \( d \) is the depth of the fastest localized corrosion site, \( t \) is time and \( A \) and \( n \) are constants. Figures 4.5-4.7 are the fastest localized corrosion rates of equiaxed AA7178-T6, wingskin AA7178-T6 and rolled AA7075-T6 in different orientations, measured by the foil penetration technique. Each material has a unique \( n \) and the localized corrosion rates in different orientations can be compared by the \( A \) values. The larger the \( A \), the faster the localized corrosion rate. Rates are also in reverse relationship with the total lengths of IGC path; in other words, the faster the rate (larger \( A \)), the shorter the total length of IGC path. Therefore, ratios of \( A^{-1} \) in different orientations for each material were calculated to compare with the ratios of \( W_{\text{min,D}} \) in different orientations by statistical simulations. Table 4.3 lists \( A^{-1} \) ratios of the three orientations for the three materials separately.

Different combinations of the three independent parameters in this model, \( P_{\text{up}}, P_{\text{down}} \) and \( P_{\text{split}} \), were examined. It was first considered that the parameters are independent of orientation since the local corrosion condition should also be independent of orientation. Several combinations of probabilities are consistent with the experimental results for equiaxed AA7178-T6 and wingskin AA7178-T6. One of the reasonable combinations is shown in Table 4.4, with \( P_{\text{up}} = 0.1, P_{\text{down}} = 0.83 \) and \( P_{\text{split}} = 0.05 \) for all three orientations. The resulting ratios of \( W_{\text{min,D}} \) are also shown in the Table, and are seen to match closely the ratios of \( A^{-1} \) given in Table 4.3 for these materials. Small values of \( P_{\text{up}} \) and \( P_{\text{split}} \) indicate that the IGC path rarely goes upward or splits, and high \( P_{\text{down}} \) indicates that the IGC path tends to go downward most of the time. These observations are consistent with the localized corrosion paths from the experiments. Therefore, this
model addresses the localized corrosion kinetics of equiaxed AA7178-T6 and wingskin AA7178-T6 very well.

For rolled AA7075-T6, there is no combination of the parameters that fits the experimental results if the same probabilities are used for the different orientations. Therefore, probabilities were taken independently for each orientation for rolled AA7075-T6. Table 4.5 lists the only combination of probabilities that reach good agreement with the experimental results. It is interesting that the probabilities need to be taken differently for different orientations in the model for rolled AA7075-T6 to fit to the experimental results. Moreover, a probability of $P_{down} = 0.3$ in the T direction seems to be too small based on the corrosion morphology of the samples. The corrosion path in the T direction looks similar to that in L direction and $P_{down}$ should be close to 1. Therefore, this statistical model might not work for the localized corrosion kinetics of rolled AA7075-T6.

Overall, this model provides a quantitative approach to relate the microstructure of the material to its localized corrosion kinetics for AA7178.

4.3 Discussion

Figure 4.8 shows the localized corrosion morphology in equiaxed AA7178-T6, wingskin AA7178-T6 and rolled AA7075-T6 respectively. The localized corrosion morphology looks similar, especially for wingskin AA7178-T6 and rolled AA7075-T6. Corrosion attacks the grain matrix partially or fully along the grain boundaries. The images of the cross-sections reflect only the corrosion morphology after experiments, not providing the detail of the in-situ corrosion process. As described above, the SGA
morphology includes some clear IGC and also missing grains, where the material dissolved, but the attack did not spread to neighboring grains. Figure 4.9 shows two possible scenarios for the development of SGA: pitting corrosion and IGC/wake attack.

The first scenario for SGA is pitting corrosion of selected grains, Figure 4.9a. Attack is initiated at certain grains on the surface, perhaps because of orientation, but more likely because they contain initiation sites such as susceptible intermetallic particles. The attack, once initiated, consumes the grain but does not bridge to neighboring grains. The grain boundary is for some reason less susceptible to attack and acts as a barrier to further growth. This might be associated with a Zn-depleted region near the grain boundary. However, the attack seems to continue downwards to a neighboring grain below the attacked grain since the attack eventually penetrates the sample under the experimental conditions. This transition of SGA from one grain to a neighboring grain below it is not understood.

The second scenario for the development of SGA is IGC/wake attack, as shown in Figure 4.9b. In this view, the sample is penetrated primarily by an IGC mechanism and the neighboring grain body is consumed behind, or in the wake of the advancing IGC. Again, the attack stops at the next neighboring grain boundary, which is hard to rationalize for a structure in which the grain boundary is the susceptible feature leading to IGC. However, the continued attack through the microstructure is justified by an IGC mechanism.

The model developed in this work is based on the total IGC path, which only considers pure IGC attack. Even though the final corrosion morphology involves more than just IGC as assumed in the model, the localized corrosion kinetics of equiaxed
AA7178-T6 and wingskin AA7178-T6 can be fit well by this model. This suggests that the mechanism is IGC/wake attack rather than selective grain pitting corrosion. The corrosion morphology for rolled AA7075-T6 is similar to wingskin AA7178-T6, Figure 4.8, but the IGC model does not work well for rolled AA7075-T6. It is possible the attack in this case involves selective grain pitting corrosion rather than wake attack. A high resolution in situ nondestructive inspection technique is needed to sort out these mechanisms definitively.

4.4 Summary

A modified and improved statistical model, based on the work of Ruan et al., was presented to describe the localized corrosion kinetics in high strength AA7xxx alloy plates in different orientations. The model explains well the influence of the microstructure on the localized corrosion kinetics in AA7178. This agreement was used to suggest that the mechanism for formation of the selective grain attack morphology is IGC/wake corrosion. This model does not work for rolled AA7075-T6, suggesting a different corrosion mechanism.
REFERENCES


### TABLES

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Equiaxed AA7178-T6</th>
<th>Wingskin AA7178-T6</th>
<th>Rolled AA7075-T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>183.9 ± 68.9 µm</td>
<td>1040 ± 692 µm</td>
<td>236.1 ± 120.5 µm</td>
</tr>
<tr>
<td>T</td>
<td>189.2 ± 64.2 µm</td>
<td>511 ± 261 µm</td>
<td>108.7 ± 46.4 µm</td>
</tr>
<tr>
<td>S</td>
<td>174.6 ± 56.0 µm</td>
<td>39 ± 17 µm</td>
<td>24.6 ± 11.2 µm</td>
</tr>
</tbody>
</table>

Table 4.1 Grain dimensions of equiaxed AA7178-T6, wingskin AA7178-T6 and rolled AA7075-T6. Average values and standard deviations are shown.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Equiaxed AA7178-T6</th>
<th>Wingskin AA7178-T6</th>
<th>Rolled AA7075-T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>Gamma (7.13, 25.81)</td>
<td>Gamma (2.26, 460.45)</td>
<td>Gamma (3.84, 61.50)</td>
</tr>
<tr>
<td>T</td>
<td>Gamma (8.69, 21.78)</td>
<td>Gamma (3.83, 133.3 )</td>
<td>Gamma (5.49, 19.81 )</td>
</tr>
<tr>
<td>S</td>
<td>Gamma (9.72, 17.96)</td>
<td>Gamma (5.26, 7.41)</td>
<td>Gamma (4.82, 5.10)</td>
</tr>
</tbody>
</table>

Table 4.2 Gamma distribution parameters ($\alpha$, $\beta$) for grain size along each direction of equiaxed AA7178-T6, wingskin AA7178-T6 and rolled AA7075-T6.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$A^{-1}$ ratio (L : T : S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiaxed AA7178-T6</td>
<td>1 : 0.91 : 1.05</td>
</tr>
<tr>
<td>Wingskin AA7178-T6</td>
<td>1 : 1.03 : 4.01</td>
</tr>
<tr>
<td>Rolled AA7075-T6</td>
<td>1 : 1.67 : 5.25</td>
</tr>
</tbody>
</table>

Table 4.3 $A^{-1}$ ratio of different orientations in equiaxed AA7178-T6, wingskin AA7178-T6 and rolled AA7075-T6.
Table 4.4 Simulation results for equiaxed AA7178-T6 and wingskin AA7178-T6 by a statistical model for IGC. Probabilities are same for different orientations. $P_{up}$, $P_{down}$ and $P_{nsplit}$ are not shown here because $P_{up} + P_{sup} = 1$, $P_{down} + P_{sdown} = 1$ and $P_{split} + P_{nsplit} = 1$.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>$P_{up}$</th>
<th>$P_{down}$</th>
<th>$P_{split}$</th>
<th>Ratio of $W_{min,D}$ (L : T : S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equiaxed AA7178-T6</td>
<td>0.1</td>
<td>0.83</td>
<td>0.05</td>
<td>1 : 1 : 1</td>
</tr>
<tr>
<td>Wingskin AA7178-T6</td>
<td>0.1</td>
<td>0.83</td>
<td>0.05</td>
<td>1 : 1 : 4.0</td>
</tr>
</tbody>
</table>

Table 4.5 Simulation results for rolled AA7075-T6. Probabilities are taken differently for different orientations. $P_{sup}$, $P_{sdown}$ and $P_{nsplit}$ are not shown here because $P_{up} + P_{sup} = 1$, $P_{down} + P_{sdown} = 1$ and $P_{split} + P_{nsplit} = 1$.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>$P_{up}$</th>
<th>$P_{down}$</th>
<th>$P_{split}$</th>
<th>Ratio of $W_{min,D}$ (L : T : S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>0.1</td>
<td>0.9</td>
<td>0.1</td>
<td>1 : 1.6 : 5.2</td>
</tr>
<tr>
<td>T</td>
<td>0.3</td>
<td>0.3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
<td>0.43</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.1 Schematic plot of IGC paths for a 2-D brick model in different orientations. (a) L, (b) T, and (c) S directions.
Figure 4.2  Explanation of junction types and parameters of turning upward, turning downward, skipping and splitting. The bold lines represent IGC paths.

Figure 4.3  A schematic plot to determine junction types.
Figure 4.4 A flow chart for the computer simulation of the statistical model.
Figure 4.5  Localized corrosion kinetics of equiaxed AA7178-T6.

Figure 4.6  Localized corrosion kinetics of wingskin AA7178-T6.
Figure 4.7 Localized corrosion kinetics of rolled AA7075-T6.

Figure 4.8 Corrosion morphology of (a) equiaxed AA7178-T6, (b) wingskin AA7178-T6 and (c) rolled AA7075-T6.
Figure 4.9 Proposed selective grain attack mechanisms. (a) pitting corrosion; (b) IGC/Wake attack.
CHAPTER 5

EFFECTS OF TEMPER AND POTENTIAL ON LOCALIZED CORROSION

KINETICS OF AA7075

5.1 Introduction

Strength and corrosion susceptibility of AA7xxx alloys are strongly dependent upon temper, which is varied by heat treatment. T6 is the highest strength temper for AA7xxx, but it is susceptible to localized corrosion [1]. It is well documented that AA7xxx in overaged tempers, such as T7, exhibits improved stress corrosion cracking (SCC) resistance, although the strength is decreased [2-9].

The corrosion properties of AA7xxx alloys primarily have been evaluated using stress corrosion cracking (SCC) tests [5-15]. Very few reports have been published regarding the effects of alloy temper on the unstressed localized corrosion in AA7xxx. This study focuses on the localized corrosion susceptibility in different tempers of AA7075 in the absence of applied stress.

Anodic polarization curves for AA7xxx-T6 in chloride solution typically exhibit two breakdown potentials, whereas the T7 and W (water quenched) tempers exhibit only one [16-19]. If an alloy exhibits only one breakdown potential, it is clear that localized corrosion becomes stable above that potential. However, it is still under debate why
localized corrosion is not stabilized below the second breakdown potential. The first breakdown has been attributed to pitting in the matrix [17], pitting of the solute-enriched grain boundary region [16], or dissolution of a thin susceptible surface layer created by mechanical processing or polishing [19, 20]. Polarization curves only provide the relationship between potential and current at the time of the measurement, and the phenomenon causing the first breakdown is likely transient in nature. Therefore, the localized corrosion susceptibility should be assessed after long time exposure.

The foil penetration technique is a simple and direct non-electrochemical method that provides localized corrosion growth kinetics [21, 22]. The penetration time for the fastest-growing localized corrosion site is determined for foil samples of varying thickness, which generates a relationship that can be inverted to provide an expression for the depth of the fastest growing site as a function of time. There is no need to make assumptions regarding the shape of the corrosion feature or the extent of hydrogen evolution current to determine the kinetics, as is required for most electrochemical methods. The net current density is also measured during potentiostatic foil penetration experiments. Although the net current density cannot be converted to corrosion kinetics directly, it more or less reflects the corrosion susceptibility of the material. Zhang and Frankel used this approach to show that the IGC of wrought AA2024-T3 was extremely anisotropic owing to the elongation of the microstructure along the working direction [23, 24].

This study focuses on evaluating the localized corrosion susceptibility in AA7075 by comparing the current density and measuring the corrosion kinetics in the absence of applied stress using the foil penetration technique. The localized corrosion kinetics in
different tempers of AA7075 at different potentials will be presented and discussed for the purpose of understanding the effects of temper.

5.2 Experimental

A plate of AA7075 with thickness of 19.1 mm was used in this study. Samples were heat treated to W, T6 and T7 tempers. The heat treatment cycles were performed in air furnaces and are shown in Figure 5.1 [25]. The nomenclature used for the plate orientations relative to the rolling direction [26] and the preparation of foil samples in different orientations are indicated in Figure 5.2. Before heat treatment, plates were sliced to strips by Electrical Discharge Machining (EDM) for the S samples and by water jet for the L and T samples. All specimens were stored in a freezer at –10 °C after heat treatment to minimize natural aging. Sections in different orientations and tempers were polished to 1 μm, etched by Keller’s reagent for 40 to 50 s, and observed under an optical microscope.

Polarization curves were measured to determine the breakdown potential of each material. The breakdown potential was taken as the point in the anodic polarization curve at which the current increased sharply. Measurements were made in both aerated and deaerated 1 M NaCl solution. The aerated solution was bubbled with O₂ during the measurement and the deaerated solution was pre-purged with argon. The measured potential scan rate was 0.1 mV/s. Samples were prepared in three perpendicular orientations relative to the rolling direction and were ground to 800 grit in alcohol prior to testing. Measurements were repeated at least three times for each condition.
Foil penetration experiments were performed on specimens in three perpendicular orientations with thicknesses from 0.1 to 1 mm. All samples were ground mechanically and polished through a series of silicon carbide (SiC) papers to 800 grit on both sides. The last polishing step in 800 grit paper was performed in alcohol to minimize corrosion. A Teflon knife-edge O-ring was used to define the exposed specimen area of 1 cm². The solution used in the foil penetration experiments was 1 M NaCl bubbled with O₂. Each experiment was conditioned for 1 second at –290 mV SCE to initiate localized corrosion, followed by an immediate change to the desired applied potential. After the penetration experiments, samples were cross-sectioned and examined by optical microscopy. Some of the cross-sections were etched by Keller’s reagent for 40 to 50 s to reveal the grain boundaries so as to compare the localized corrosion morphology to the microstructure.

5.3 Results and Discussion

5.3.1 Microstructure and Tempers

The AA7075 plate in this study was a rolled plate, with thin elongated grains as shown in Figure 5.2. Grain size and shape were not affected by artificial aging. Grain size was measured using L and T sections polished to 1 μm diamond paste and etched by Keller’s reagent. At least 20 grain size measurements were randomly made on each section both in the L (or T) and S directions. The grain sizes in L and S directions were measured in the T-section sample and the grain sizes in T and S directions were measured in the L-section sample. Average grain sizes of AA7075-T6 in different orientations are given in Table 5.1. Table 5.2 shows the hardness of AA7075 measured on S surfaces. The results confirm that T6 was peak-aged and T7 was overaged.
5.3.2 Polarization Curves

Typical anodic polarization curves of AA7075 in 1 M Ar-deaerated NaCl solution are shown in Figure 5.3. Deaeration of the solution results in separation of the breakdown potential from the OCP and allows clear observation of the passive region. Significant changes in the anodic polarization curves due to artificial aging are apparent. Two breakdown potentials were observed under the test conditions for the T6 temper, while the W and T7 tempers exhibited a single breakdown potential. Breakdown potentials were determined in three orientations for the different tempers. Figure 5.4 shows distributions of the results from all experiments and Table 5.3 shows average values. The breakdown potentials were almost independent of the sample orientation. The breakdown potential in W was lower than the first breakdown potential in T6, and the breakdown potential in T7 was very close to the second breakdown potential in T6.

Anodic polarization curves were also measured in aerated NaCl solution, which is the environment for the foil penetration experiments. Figure 5.5 shows the upward scanned polarization curves for different tempers of AA7075 in aerated 1 M NaCl solution. Samples were only tested on L surfaces since the breakdown potential was independent of orientation. For W and T7 tempers, the OCP in aerated solutions was pinned at the breakdown potential, and the value of OCP was similar to the breakdown potential in deaerated solution. The OCP of the T6 sample was pinned at the first breakdown potential, and a second breakdown was also observed during the upward scan. (Note that the OCP was measured for 10 minutes; it is possible that the transient phenomenon responsible for the first breakdown would die out with time and the OCP
would then rise to a higher value.) The values are very close to the two breakdown potentials observed in deaerated solution. The primary difference between aerated and deaerated polarization curves in AA7075 is the absence of the passive region in the aerated solutions.

### 5.3.3 Foil Penetration Experiments

A potential of −725 mV SCE was first selected for the foil penetration experiments on samples in different tempers and different orientations. This potential is above the breakdown potential of AA7075-W and AA7075-T7, and above the second breakdown potential of AA7075-T6, as shown in Figure 5.5. Figures 5.6-5.8 show the results of foil penetration experiments on different tempers of AA7075 in different orientations at −725 mV SCE in O₂ bubbled 1 M NaCl solution. The experiment determines penetration time for samples with different thickness, but the data are inverted to show the depth of the fastest growing localized corrosion site as a function of time. The localized corrosion kinetics in aluminum alloys follow a power law [23, 24, 27, 28]. To facilitate comparison of the data, an equation of the form $d = At^n$ was fitted to the data in each condition, where A and n are constants, $d$ is the sample thickness in mm and $t$ is the penetration time in h. The values of the constants are reported in each figure. For each temper, localized corrosion grew fastest in the L direction and slowest in the S direction. This anisotropy of localized corrosion growth has been previously reported for wrought AA2024-T3 [23].


5.3.4 Corrosion Morphology

The corrosion morphology of AA7075 was similar at all potentials tested in NaCl solutions. Figures 5.9-5.11 show the corrosion morphology for AA7075 in different tempers and different orientations in O₂ bubbled 1 M NaCl solution at –725 mV SCE. The attack in the S direction for all three tempers was very wide with considerable material loss near the penetration site. The attack along the elongated L and T directions was more focused and directional, especially for the T6 and T7 tempers, which exhibited long and narrow localized attack. The attack in the W temper was much wider, even in the L and T directions, as if it were still directional, but spread to neighboring grains. In general, the W temper exhibited more uniform attack and T6 and T7 tempers had more localized corrosion morphology.

Figure 5.12 shows etched cross sections of specimens tested at OCP. It is clearer from the etched cross sections that the corrosion attack was related to the microstructure. In the W temper, the corrosion attack was similar to pitting corrosion, but it was still directional, with preferential growth along the longitudinal direction. In T6 and T7 tempers, the corrosion attack was limited to the dissolution of certain grains. This type of corrosion has been termed selective grain attack [29]. The morphology of selective grain attack indicates that some selected grains have dissolved but then the attack stopped at the grain boundary for some reason. This kind of selective grain attack is also observed for other AA7xxx alloys [30, 31]. It is clear that the attack is localized in nature. However, it is not clear why this form of attack in AA7xxx stops at grain boundaries rather than developing into a hemispherical pit. It is possible that solute depleted zones surrounding the grain boundaries are less corrodible owing to a depletion of Zn [17, 32].
When the attack occurs at the grain boundary first, only one side of the solute depleted zones will be preferentially attacked continuously and the other side becomes immune.

**5.3.5 Critical Thickness to Separate Rates in L and T Directions**

The foil penetration experiments showed that the rate of localized corrosion was faster for the L direction than for the T direction in the AA7075 alloys. This is interesting because the attack in both these directions was along the same elongated L-T planes in the microstructure. Closer examination reveals that there is a critical thickness that differentiates the localized corrosion rate in the T direction from that in the L direction for AA7075. In Figures 5.6-5.8, localized corrosion kinetics were described by fitted power law curves. For each temper, the values of $n$ were different for the L and T directions and the curves crossed at low thickness values. In other words, the penetration rates in the L and T directions were the same for very thin samples. The corrosion kinetics diverged as the sample thickness increased, with L being faster than T. One explanation is that the fastest corrosion path in thin L or T samples was along a single grain; for thicker samples, the corrosion path encountered fewer grains in the L direction than in the T direction because the microstructure was more elongated in the L direction. The corrosion rate in the T direction slowed as the selective grain attack intersected different grains. Figures 5.10(a) and (b) show clearly that the corrosion path in AA7075-T6 involved more grains in the T direction than in the L direction. Recall that the average grain size for this plate is 236 $\mu$m in the L direction and 109 $\mu$m in the T direction. The foil penetration growth kinetics curves in L and T directions for each temper cross at a thickness of around 170 $\mu$m, which is between these values. This crossover point is
considered to be \( d_c \), the critical thickness to separate the localized corrosion rates in the L and T directions for this material, and is indicated in Figures 5.6-5.8.

### 5.3.6 Effects of Potential

Foil penetration experiments were performed on AA7075 at different potentials. Table 5.4 lists the current density range measured during the foil penetration experiments on AA7075. These values do not include the high currents in the first few minutes after the experiments started, which were due to the initiation of corrosion at -290 mV SCE for 1 second. All three tempers were studied and the response varied with temper, so the effects of potential will be discussed in turn for each temper.

Figure 5.13 shows the results of foil penetration experiments on L-oriented AA7075-W samples in O\(_2\) bubbled 1 M NaCl at different potentials. The localized corrosion rates were almost identical at applied potentials of -725, -740 and -750 mV SCE, whereas at OCP the corrosion rate was slower. The potential during an OCP foil penetration experiment on AA7075-W was stable at around -830 mV SCE (Figure 5.14), which is significantly lower than the values of the applied potentials. The net current density measured during potentiodynamic polarization of the material in the same solution, Figure 5.5(a), increased from about 3 to 5 mA/cm\(^2\) with increasing potential in the range of -750 to -725 mV SCE. Table 5.4 shows that the current densities measured during the foil penetration experiments were at somewhat higher levels, and increased slightly with increasing potential, from around 4 to 6.6 mA/cm\(^2\). A higher current density usually indicates a higher corrosion rate, but the rates of localized corrosion were almost identical. The reason for this discrepancy is that the measured current originated at
localized corrosion sites, and current density determined by normalizing the measured current to the total exposed area cannot be used as a measure of localized corrosion rate. The active area, which depends on the number and size of the localized corrosion sites, is required. As described above, the advantage of the foil penetration method is that the localized corrosion rate can be determined without consideration of these effects. At OCP, both the nominal current (equal to the corrosion current density) and the localized corrosion rate were lower because of the much lower potential.

Foil penetration experiments were performed on L-oriented AA7075-T6 samples at the same potentials, Figure 5.15. There was considerable scatter at the low potentials, but the localized corrosion rates decreased as the applied potential decreased. Figure 5.5(b) shows that the current density measured during potentiodynamic polarization was more dependent on potential than for the W temper, increasing from 0.15 to 0.98 mA/cm² as the potential increased from -750 to -725 mV SCE. This potential region is just above the second breakdown potential, where localized corrosion is just stabilizing. Even though the nominal current density cannot be directly related to the rate of localized corrosion growth, it seems that the dependence of localized corrosion rate on potential shown in Figure 5.15 is related to the dependence of measured current density on potential shown in Figure 5.5(b). The current densities recorded during the foil penetration experiments were lower than those measured during potentiodynamic polarization and varied over a wide range, especially at -740 and -750 mV SCE, Table 5.4. Figure 5.16 shows the nominal current density measured during a foil penetration experiment at -750 mV SCE on an AA7075-T6 sample. The current density stabilized at a few µA/cm², and then became negative after about 5 h. Localized corrosion apparently
continued to grow even while the measured current was negative, and the sample penetrated after 14.8 h.

The potential during a typical OCP foil penetration experiment on AA7075-T6 is shown in Figure 5.17. It started out at -800 mV, which is the same value measured at the start of the polarization curve in Figure 5.5(b), and is equal to the first breakdown potential in this solution. Over the first few days, it decreased to around -850 mV SCE and then slowly increased, with the baseline almost steady at just under -750 mV SCE. Large potential transients were measured during the last half of the experiment, with the potential dropping to -1 V SCE. (Note that the data acquisition rate was 1 point/10 min so it is likely that the potential transients went to even lower values.) Such transients are usually associated with metastable pitting events [33-37] It is interesting that even the baseline potential, or the highest OCP value, was more negative than -750 mV SCE, but the rate of localized corrosion was greater than for the potentiostatic experiments at -750 mV SCE. One difference between OCP and controlled potential experiments is the locations of the reactions. At OCP, the rate of the cathodic reaction always equals the rate of the anodic reaction and both reactions occur on one electrode. At a controlled potential, a net current flows from the electrode and charge-balancing reactions occur at the counter electrode. As shown in Figure 5.16, the net reaction at the working electrode was first anodic, then cathodic. This could have changed the surface in ways that affect the rate of localized corrosion. Another difference is the potential transients observed at OC. These activating events could play an important role in accelerating the attack.

Foil penetration experiments were also performed on L-oriented AA7075-T7 samples at the same potentials as the other tempers, Figure 5.18. The behavior of the T7
temper samples was intermediate to that of the W and T6 samples. The rate of localized corrosion increased with increasing potential, but the rates were similar for the potentiostatic experiments and much slower for the experiments at OCP. The current densities measured during potentiodynamic polarization were between 0.15 and 1.7 mA/cm² over the potential range from -750 to -725 mV SCE, Figure 5.5(c), and these values were in the range of stable localized corrosion; like the W temper, there was no region of transient attack associated with a first breakdown for AA7075-T7. However, owing to the higher OC/breakdown potential for T7, the tested potentials were in the region where the current density increased strongly with potential, whereas for the W temper these potentials were in the region where current density varied little with potential. The current densities measured during the potentiostatic foil penetration experiments were similar in magnitude, increased with increasing potential, and were always positive, Table 5.4.

The potential during a typical OCP foil penetration experiment on AA7075-T7 is shown in Figure 5.19. It started at about -770 mV SCE, similar to the OC/breakdown potential measured before the potentiodynamic polarization experiment on this AA7075-T7 material, Figure 5.5(c). It then oscillated slowly between this value and -850 mV SCE and exhibited some small rapid transients toward lower values. The average value was about -800 mV SCE, which is considerably lower than the lowest applied potential of -750 mV SCE, and the localized corrosion rate was much lower.

The effects of potential can be summarized as follows. The localized corrosion rate of AA7075 tended to decrease as the applied potential decreased from -725 mV SCE to OCP, but with slight differences depending on temper. The W temper exhibited very
little difference in rate for controlled potentials between -725 and -750 mV SCE, but the rate at OC, -820 mV SCE, was much lower. The T6 temper exhibited large differences in rate for potentiostatic conditions, but the rate at OC was faster than the rate for potentiostatic conditions at the highest value of OCP, -750 mV SCE. The T7 temper behavior was intermediate to that of the W and T6 tempers.

5.3.7 Effects of Temper

The effects of potential on the localized corrosion kinetics of AA7075 were discussed for each temper previously. To understand how artificial aging affects the localized corrosion kinetics in AA7075, data for different tempers were compared at each potential. Figure 5.20 shows the localized corrosion kinetics of L-oriented AA7075 samples in different tempers at a high potential of –725 mV SCE. Although the measured current densities during experiments in Table 5.4 show that W temper had the highest current density and T6 the least, the localized corrosion kinetics were almost identical for each temper at this potential. Similar comparisons on S-oriented samples at –700 mV SCE, T- and S-oriented samples at –725 mV SCE and L-oriented samples at –740 mV SCE also show that artificial aging has little effect on the localized corrosion kinetics in AA7075 at these potentials.

Effects of temper on localized corrosion kinetics of AA7075 become evident at potentials of –750 mV SCE and lower. Figure 5.21 shows localized corrosion kinetics of L-oriented AA7075 samples in different tempers in O₂ bubbled 1 M NaCl at -750 mV SCE. The W temper had the fastest localized corrosion rate and T6 the slowest. According to the polarization curves in Figure 5.5, the current density at this potential
was highest for the W temper and lowest for the T7. This potential is around the second breakdown potential for the T6 and the recorded current density of the T6 samples during the experiments varied widely between 40 µA and -18 µA. The unstable current density in T6 at this potential might be due to transient dissolution and results in a very slow localized corrosion rate.

It has been well documented that T7 has better SCC resistance than T6 for AA7xxx [2-9]. However, the foil penetration experiments show that T7 has faster localized corrosion rates than T6 at –750 mV SCE. It should be noted that most SCC tests reported in the literature were conducted at OCP, and real exposure environments are also at OCP. The localized corrosion kinetics at OCP for L-oriented samples of AA7075-W, T6 and T7 in O₂ bubbled 1 M NaCl are shown in Figure 5.22. W temper exhibited the fastest localized corrosion kinetics. However, unlike the potentiostatic condition at –750 mV SCE, the localized corrosion rate for T7 was slower than for T6 at OCP. The values of OCP for each temper were shown in Figures 5.14, 5.17 and 5.19. Ignoring the transients, the W temper exhibited the lowest OCP and T6 the highest, so there is no correlation between baseline OCP and localized corrosion rate. It is possible that the transients represent activating events that are critical in determining the overall localized corrosion rate.

In summary, at potentials above –740 mV SCE the effect of temper on localized corrosion kinetics of AA7075 is less than the effect of potential. However, the influence of temper became evident at –750 mV SCE and OCP. Under potentiostatic control at –750 mV SCE, T7 exhibited faster localized corrosion rate than T6, but the reverse was true at OCP.
5.4 Summary

Localized corrosion kinetics were studied on AA7075 in W, T6 and T7 tempers at different potentials. The following observations were made:

1. Two breakdown potentials were observed in T6 temper and only one breakdown potential in W and T7 tempers. The breakdown potentials were independent of sample orientation.

2. Anisotropic localized corrosion kinetics were found in AA7075 due to the microstructural anisotropy and the form of corrosion, which was selective grain attack.

3. A critical thickness associated with the microstructural anisotropy was found to separate the localized corrosion rate in L direction from that in T direction on AA7075.

4. Generally, the higher the applied potential, the higher the current density and the faster the localized corrosion rate. However, the difference was less at high potentials.

5. Temper did not affect the rate of localized corrosion at potentials above –740 mV SCE. At –750 mV SCE, the rate for T6 was slower than for T7, whereas the rate was slower for T7 during OCP exposures. W temper exhibited the fastest localized corrosion rate at both OCP and –750 mV SCE.
REFERENCES


20. Z. Zhao, Unpublished data, The Ohio State University.


Table 5.1 Grain dimensions of AA7075-T6.

<table>
<thead>
<tr>
<th>Orientation</th>
<th>AA7075-T6</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>236 ± 121 μm</td>
</tr>
<tr>
<td>T</td>
<td>109 ± 46 μm</td>
</tr>
<tr>
<td>S</td>
<td>25 ± 11 μm</td>
</tr>
</tbody>
</table>

Table 5.2 Hardness of AA7075 in different tempers. Test load is 300 gf and load time is 30 s.

<table>
<thead>
<tr>
<th>Tempers</th>
<th>Hardness Vickers (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA7075-W</td>
<td>141</td>
</tr>
<tr>
<td>AA7075-T6</td>
<td>205</td>
</tr>
<tr>
<td>AA7075-T7</td>
<td>185</td>
</tr>
</tbody>
</table>

Table 5.3 Breakdown potentials of AA7075 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s⁻¹.

<table>
<thead>
<tr>
<th>Temper</th>
<th>Breakdown Potential (mV SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>-812</td>
</tr>
<tr>
<td>T6</td>
<td>-796 (1ˢᵗ) -758 (2ⁿᵈ)</td>
</tr>
<tr>
<td>T7</td>
<td>-753</td>
</tr>
<tr>
<td></td>
<td>AA7075</td>
</tr>
<tr>
<td>-------</td>
<td>--------</td>
</tr>
<tr>
<td>W</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>5.7~6.6 mA</td>
</tr>
<tr>
<td>T</td>
<td>4.4~7.0 mA</td>
</tr>
<tr>
<td>S</td>
<td>5.5~7.0 mA</td>
</tr>
<tr>
<td>T6</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>250~880 µA</td>
</tr>
<tr>
<td>T</td>
<td>220~790 µA</td>
</tr>
<tr>
<td>S</td>
<td>420~850 µA</td>
</tr>
<tr>
<td>T7</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td>1.3~1.8 mA</td>
</tr>
<tr>
<td>T</td>
<td>1.5~1.8 mA</td>
</tr>
<tr>
<td>S</td>
<td>1.4~1.8 mA</td>
</tr>
</tbody>
</table>

Table 5.4 Range of currents measured during the foil penetration experiments on AA7075. Sample exposed area is 1 cm².
FIGURES

Figure 5.1  Heat treatment cycles for AA7075 [25].

![Heat treatment cycles diagram](image)

Figure 5.2 (a) Metallographic sections of AA7075-T6 and the nomenclature used for the plate orientations relative to the rolling direction: L (longitudinal), T (long transverse) and S (short transverse). (b) Schematic diagram of foil sample orientation.

![Metallographic sections and schematic diagram](image)
Figure 5.3 Polarization curves for different tempers of AA7075 in Ar-deaerated 1 M NaCl at 0.1 mV s\(^{-1}\). (a) AA7075-W; (b) AA7075-T6; (c) AA7075-T7.
Figure 5.3 continued

-1.6 -1.4 -1.2 -1 -0.8 -0.6 10^{-11} 10^{-9} 10^{-7} 10^{-5} 0.001

Potential (V SCE) Current density (A/cm²)

Breakdown Potential OCP (c)
Figure 5.4 Breakdown potential of AA7075 in Ar-deaerated 1 M NaCl at a scan rate of 0.1 mV s⁻¹.
Figure 5.5 Upward-scanned polarization curves of AA7075 in O\textsubscript{2} bubbled 1 M NaCl at a scan rate of 0.1 mV s\textsuperscript{-1}. Samples were measured in L direction. (a) AA7075-W; (b) AA7075-T6; (c) AA7075-T7. Three replicate curves are given for each temper.
Figure 5.5 continued

![Graph showing potential (V SCE) versus current density (A/cm²).](c)
Figure 5.6 Localized corrosion kinetics of AA7075-W in three orientations in O$_2$ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.

Figure 5.7 Localized corrosion kinetics of AA7075-T6 in three orientations in O$_2$ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure 5.8 Localized corrosion kinetics of AA7075-T7 in three orientations in O₂ bubbled 1 M NaCl at −725 mV SCE. Kinetics are shown by power curve fitting.

Figure 5.9 Corrosion morphology of AA7075-W in 1 M NaCl at -725 mV SCE. (a) L direction; (b) T direction; (c) S direction.
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Figure 5.12 Cross sections of etched specimens of AA7075 showing the corrosion attack in L direction in 1 M NaCl at OCP. (a) W; (b) T6; (c) T7.
Figure 5.12 continued

(c)
Figure 5.13 Localized corrosion kinetics of AA7075-W in L direction in O₂ bubbled 1 M NaCl at different potentials. Kinetics are shown by power curve fitting.

Figure 5.14 A typical curve of OCP vs. time of AA7075-W during foil penetration experiment. OCP is stable before sample penetration.
Figure 5.15 Localized corrosion kinetics of AA7075-T6 in L direction in O₂ bubbled 1 M NaCl at different potentials. Kinetics are shown by power curve fitting.

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Figure 5.20 Localized corrosion kinetics of L-oriented AA7075 samples in W, T6 and T7 tempers in O₂ bubbled 1 M NaCl at -725 mV SCE. Kinetics are shown by power curve fitting.
Figure 5.21 Localized corrosion kinetics of L-oriented AA7075 samples in W, T6 and T7 tempers in O₂ bubbled 1 M NaCl at –750 mV SCE. Kinetics are shown by power curve fitting.
Figure 5.22 Localized corrosion kinetics of L-oriented AA7075 samples in W, T6 and T7 tempers in O₂ bubbled 1 M NaCl at OCP. Kinetics are shown by power curve fitting.
CHAPTER 6

KINETICS OF SHARP INTERGRANULAR CORROSION FISSURES IN AA7178

6.1 Introduction

AA7xxx alloys have been widely used in aircraft applications, such as wing structures, because of their high strength and low weight. However, they are very susceptible to localized corrosion. Corrosion is one of the main issues for aging aircraft. Different forms of localized corrosion, such as crevice corrosion, intergranular corrosion (IGC), pitting corrosion and exfoliation corrosion, were found in different locations of wing structures made of AA7xxx [1]. These localized corrosion sites are usually hidden and could result in structural failure if allowed to grow to critical dimensions.

AA7178-T6 plates develop a special form of attack, sharp IGC fissures, upon static unstressed exposure to aggressive atmospheric conditions [1]. These fissures seemed to grow along grain boundaries, but their appearance is quite different than IGC that forms in AA7xxx during immersion in NaCl solutions [2-4]. They look similar to the sharp cracks caused by hydrogen embrittlement in AA7xxx. In particular, they have been found to initiate in plate through-holes and propagate long distances [1]. Because the microstructure of such structural components is typically elongated in the direction of the applied stress, such sharp intergranular fissures often propagate parallel to the applied
stress, which does not necessarily lead to a loss of strength. However, linking of different IGC sites can result in multi-site damage (MSD), which can lead to catastrophic failure. It is also possible that fatigue cracks can initiate at bends in IGC cracks, where the cracks can be perpendicular to the applied stress fluctuations.

The typical approach to aircraft maintenance requires replacement of any component that is found to contain corrosion. Maintenance costs could be reduced by allowing corrosion to exist as long as it did not critically degrade structural integrity. However, this requires an accurate prediction of corrosion kinetics. Therefore, measuring the kinetics of IGC is not only a way to evaluate corrosion susceptibility, but also very useful for a predictive model for corrosion.

The foil penetration technique is a simple and direct non-electrochemical method that has been used to measure localized corrosion growth kinetics [5, 6]. It overcomes many of the limitations of electrochemical methods as there is no need to make assumptions regarding shape of the attack or hydrogen evolution current. By varying the sample thickness, sample orientation, solution environment and applied potential, the corrosion growth kinetics of the fastest-growing localized corrosion can be determined regardless of the corrosion growth path. Sehgal et al. studied the pit growth in AA1100-O and AA2024-T3 in different solutions by the foil penetration technique [6]. Zhang et al. also used this technique to measure the localized corrosion kinetics in AA2024 in NaCl solutions under a range of applied anodic potentials [7, 8]. A limitation of this technique is that samples need to be tested during immersion in an aqueous environment. The corrosion morphology that develops in an aqueous environment is different than the sharp IGC fissures found during environmental exposure. Moreover, the corrosion environment
for aircraft components is typically not immersion in an aqueous solution. Therefore, an approach that duplicates the sharp IGC fissures and provides the kinetics of their growth is needed.

This paper describes a new approach to quantify the growth kinetics of the sharp IGC fissures, which includes electrochemical pre-treatment of the sample followed by exposure in a humid environment. The pre-treatment creates localized corrosion sites on the sample surface that contain corrosion products and aggressive environments that stimulate subsequent attack in humidity. Such initiating environments can be found in crevices and through-holes in aircraft. The kinetics were determined by the penetration time and the depth of corrosion. The effects of humidity and temper were studied. Different analytical methods were used to analyze the sharp IGC fissures. The mechanism of the sharp IGC fissures is discussed.

6.2 Experimental

An 8.5 mm thick AA7178 plate cut from a retired KC-135 wing structure was provided by S&K Technologies, Dayton, OH. The composition determined by Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) analysis is shown in Table 6.1. The nomenclature used for the plate orientations relative to the rolling direction are indicated in Figure 6.1 [9] along with metallographic sections of the as-received AA7178 wingskin plate.

Samples were tested in the as-received condition, which is expected to be in the T6 temper. However, natural aging during an unknown service time might have occurred so samples were also tested following heat treatment to the T6 and T7 conditions. The
heat treatment included solution heat treatment and artificial aging. The solution heat treatment was conducted in an air furnace at 465 °C for 1 hr, followed by water quenching [10]. T6 temper was then produced by artificial aging at 120 °C in an air furnace for 24 hr [10]. T7 temper was produced by artificial aging at 120 °C for 4 hr and then at 163 °C for 16 hr in an air furnace after solution heat treatment [10].

Foil samples were sliced from this plate by a diamond saw. Samples were prepared in L and T directions relative to the rolling direction, Figure 6.1. The pretreated side of each foil sample was ground to 800 grit and the back side was polished to 1 µm. Alcohol was used during polishing to minimize corrosion before testing. The thickness of the samples was in the range of 0.45 to 0.60 mm.

Electrochemical pretreatment was performed on an area of about 41 mm² on the ground side of the foil sample. The potential was controlled at –725 mV SCE in 1 M NaCl solution. Most samples were pretreated for two hours; a few samples were pretreated for one hour for comparison. Prior work indicated that these times are insufficient for localized corrosion to penetrate samples of the thickness used in this work [4]. After pretreatment, the corroded side was rinsed with water and wiped with dry cotton balls. The samples were then immediately placed in a humidity chamber with the polished side facing the transparent chamber wall to allow for observation. Care was taken through the entire process to keep the polished side dry and clean.

The relative humidity (RH) in the chambers was controlled by equilibration with a saturated solution of a chosen salt. The expected [11] and measured RH values for four different salts are shown in Table 6.2. The humidity chambers were 250-mL glass beakers containing about 100 mL of saturated solution and were sealed with polymeric
film. The humidity in a chamber was found to reach a stable value within 36 h. The measured RH values are higher than the expected values by a small amount.

The foil penetration in humidity test started when the pre-treated samples were placed in the humidity chambers. The condition of the polished back side of each sample was recorded daily using digital photography through the glass beaker. The appearance of corrosion on the polished side indicated that sample had been penetrated, and the test was stopped. The penetration time was recorded and the sample was removed to a freezer for storage until examination by serial sectioning. Details of the serial sectioning method are given below.

6.3 Results and Discussion

6.3.1 Selective Grain Attack and Sharp IGC Fissures

Figure 6.2(a) is a cross-sectional optical micrograph of the as-received AA7178 sample after an electrochemical treatment in 1 M NaCl at a potential of –725 mV SCE for 15 h. This potential is above the second breakdown potential in deaerated 1 M NaCl solution of around –745 mV SCE [4]. The top surface of this sample, an L surface, was exposed during the pretreatment, and the pit-like cavities that grew in the L direction represent a typical corrosion morphology generated by such an electrochemical treatment. Localized corrosion resulted in dissolution of selected grains, but then the attack stopped at the grain boundary. Similar attack was generated by a similar electrochemical treatment of AA7075-T6, Figure 6.2(b). This type of corrosion has been termed selective grain attack [12].
Figure 6.2(c) is a cross section of an as-received AA7178 sample following electrochemical pre-treatment and subsequent high humidity exposure. In addition to the selective grain attack formed during the pretreatment, a sharp IGC fissure pointed out by an arrow is also evident, and it looks very much like the attack formed during natural exposure of aircraft wingskins. Figure 6.2(d) shows an AA7075-T6 sample after pretreatment at a higher potential of -580 mV SCE, which generated more selective grain attack, and then exposure at high humidity. Sharp IGC fissures also formed in this material. Note that these images were not etched and special care was taken during polishing to prevent vertical scratches. These results indicate that the sharp IGC fissures grew in high humidity environment from the selective grain attack sites. In fact, the sharp IGC fissure in Figure 6.2(c) is seen to be connected to the selective grain attack near it.

The growth rates of the sharp IGC fissure were obtained in a fashion similar to the approach used by the foil penetration technique [5, 6], which measures the penetration time for samples with different thickness and then inverts the relation to get the corrosion depth as a function of time. Therefore, two important parameters need to be determined: penetration time and length of the sharp IGC fissure. The sensing mechanism used in the standard foil penetration setup, a drop in resistance between the sample and a Cu backing foil separated by a thin paper sheet, was attempted as a means of determining penetration time for the sharp IGC fissures growing during high humidity exposure. However, the solution present in the fissure was insufficient to wet even very thin paper to the extent required to result in a measurable decrease in resistance.
6.3.2 Determination of Penetration Time

The penetration time was determined by monitoring the backside of each sample using high resolution digital photographs. Such images were recorded daily without removing the sample from the chamber so that the humidity exposure was uninterrupted. It is very difficult to notice a sharp IGCC fissure when it first emerges on the backside because it is so small. However, after a few days, the penetrated site is easily observed because it grows and corrosion product exudes out of the site. Figures 6.3(a)-(d) are backside images of an as-received AA7178 sample, taken right after pre-treatment, and after 15, 16 and 17 days respectively. A penetration site shown in Figure 6.3(d) indicates that the sample was penetrated after 17 days. By examining prior photos carefully at the location of the penetration, it was possible to determine accurately the penetration time, within the resolution of the sampling period. Figure 6.3(c) shows a smaller penetration site at the same location as in Figure 6.3(d), but Figure 6.3(b) shows none. Therefore, the penetration of the sharp IGCC fissure occurred between the times that the images in Figure 6.3(b) and 6.3(c) were taken. The midpoint of the sampling period was used as the penetration time. When penetration of a sample was positively identified, it was removed from the humidity chamber and stored in a freezer to reduce the extent of further corrosion.

This experiment was not performed in a clean room, so dust particles occasionally appeared on the samples or cell walls. Such dust may look like a penetration site in a photograph. However, a penetration site grew larger with time whereas dust remained the same size.
6.3.3 Determination of Sharp IGC Length

The electrochemical pretreatment created localized corrosion attack inside the samples in the form of selective grain attack. Although the pretreated surface was rinsed with water and wiped with dry cotton balls after pretreatment, a certain amount of corrosion products or concentrated solution was believed to be trapped in those sites and they were the initiation sites for sharp IGC fissures. Figures 6.2(c) and 6.2(d) clearly show that the corrosion morphology included both selective grain attack and sharp IGC fissures. To determine the growth kinetics of the sharp IGC fissures, it was necessary to differentiate the sharp IGC fissure length from the depth of the pretreatment selective grain attack. Serial sectioning was used to accomplish this.

Figure 6.4 is a section of an L sample exactly at the penetration site. It appears as if this fissure initiated at a site on the top pretreated surface and grew straight through the sample. However, the sharp IGC fissures were always associated with a selective grain attack site, and it is likely that selective grain attack initiating site for this fissure was somewhere else in the sample and not seen in this particular section. The sharp IGC fissures could grow in two or three dimensions, so one section is not enough to determine where the sharp IGC fissure began and how far it traveled. Therefore, careful serial sectioning is needed for the determination of the length of the sharp IGC fissures that grew during the humidity exposure period.

To facilitate tracking of the location of the sharp IGC fissures while polishing, small plastic balls were mounted as a reference along with the samples. Following penetration, every sample was mounted in epoxy and cross sectioned to a depth near to the penetration location. Optical microscopy was used to record the un-etched section.
The sample was then repolished to view the sample at a deeper plane. The amount of material removed at each step was determined using a micrometer to measure the thickness of the sample after each step. Table 6.3 shows the average grain dimensions of the AA7178 wingskin plate in different orientations. Sectioning proceeded in the T direction when determining the depth of sharp IGC fissures in the L direction. Since the grain dimension in the T direction was 511 µm on average, about 20-30 µm was removed during each step so as not to miss important sections.

The sharp IGC fissure length used for assessment of the growth kinetics was determined by careful examination of the serial sections. This determination was not straightforward because the sharp IGC fissures grew in 2 and sometimes 3 dimensions. Figure 6.5 shows some important images from serial sections of a sample that penetrated after 706 h. Figures 6.5(c)-(f) show a sharp IGC fissure intersecting the backside at the bottom of the image. The sharp IGC fissure origin was taken as the point furthest away from the pretreated surface where it was connected to the pretreatment selective grain attack site. Figure 6.5(c) shows the deepest intersection of the sharp IGC fissure and the selective grain attack. Therefore, the depth of the sharp IGC fissure was determined from this image, from this intersection point to the bottom of the sample.

Figure 6.6 shows some important images from another sample that penetrated after 474 h. The sharp IGC fissure that penetrated to the back side of the sample can be seen in Figures 6.6(b)-(d). The deepest location of the selective grain attack associated with the sharp IGC fissure is marked P in Figure 6.6(c). However, from these images, it is suggested that the origin of the sharp IGC fissure associated with the selective grain attack is at point O, not point P in Figure 6.6(c). The sharp IGC fissure began from the
center, not the end, of the selective grain attack. Therefore, the depth of the sharp IGC fissure was measured from point O to the bottom of the sample in Figure 6.6(c).

### 6.3.4 3-D Image Reconstruction

To reveal the nature of sharp IGC fissure propagation inside the material, a 3-D image of a corrosion attack was reconstructed from the serial sections using the software package IMOD [13, 14]. Figure 6.7 shows a 3-D image of a sharp IGC fissure at different angles. This image was built from 29 serial sections of a sample. Each section was aligned vertically using the top surface and horizontally using the center of a plastic sphere that was mounted near the sharp IGC fissure site as a reference. The interval between each section ranged from 5 - 25 µm; however, they were evenly separated in the 3-D image with the total distance from the first section to the last equal to the sum of the intervals.

In Figure 6.7(a), the 3-D image is oriented so as to view the corrosion attack in three dimensions. The selective grain attack was highlighted to be dark and is found in the upper right corner. The top edge was exposed during the pretreatment. In this orientation, the selective grain attack is viewed primarily from the S direction, so the grain appears large. The sharp IGC fissure propagated from the edge and bottom of the selective grain attack site in both the vertical (L) and horizontal (T) directions along grain boundaries. The sharp IGC fissure propagation traced out the grain boundary surface. The circled area in Figure 6.7(a) shows where the L-T grain boundary surface that the sharp IGC fissure followed was offset by intersections with different grains in the S direction. Figure 6.7(b) is the same 3-D image viewed from an orientation down the T
direction. The sharp IGC fissure grew from only one side of selective grain attack. The grain offsets in the intergranular plane make the overlapped sections appear to have width in the S direction.

### 6.3.5 Sharp IGC Fissure Kinetics

Figure 6.8 shows the sharp IGC fissure length as a function of fissure penetration time of the as-received AA7178 in high humidity (96% RH). The data is scattered, especially for the time at around 500-600 h, where the sharp IGC fissure lengths in the L direction were found to vary from 100 to 400 µm. Some of the samples had more than one penetration site when the humidity test was stopped. Serial sectioning was performed on as many of those sites as possible. On one L sample, a first penetration site was evident after 464 h and a second site after 512.5 h. Examination by serial sectioning found that the sharp IGC fissure depths were 103.7 and 360.5 µm respectively. Apparently the first fissure that emerged from the sample grew slower than the second fissure that emerged. Therefore, this approach determines a range of sharp IGC fissure growth rates, not only the fastest sharp IGC fissure growth rates, and it provides the rates of long sharp IGC fissures, i.e. the ones that penetrated to the backside.

Anisotropic localized corrosion kinetics due to microstructural anisotropy of the materials have been reported for AA2024-T3 and AA7xxx alloys [2, 3, 7, 8]. The grain dimensions of this material indicate that the IGC path in the T direction should longer than in the L direction because of jogs at grain intersections. Therefore, the sharp IGC fissure rates should be slower in T direction than in L direction. However, no difference is seen in Figure 6.8. It should be noted that only thin foil samples were used in this
work. For thin foils, the sharp IGC fissure path could be only along one grain so that the rate in T direction should not be different than that in L direction. The results for different humidity and samples in different tempers presented below were all from L-oriented samples.

6.3.6 Effect of Pretreatment Time

Most samples were electrochemically pretreated in 1 M NaCl at −725 mV SCE for two hours. Figure 6.8 includes two data points for samples pretreated for only one hour. The sharp IGC fissure kinetics were the same as for the samples pretreated for the longer time. From the kinetics of selective grain attack measured by the foil penetration technique, one hour and two hours pretreatment were expected to produce selective grain attacks with longest depths of 240 and 300 µm, respectively [4]. However, the foil penetration technique determines the fastest localized corrosion rates, and selective grain attack sites with a range of shorter depths could be generated by a given pretreatment time. Furthermore, as shown in Figure 6.6, the sharp IGC fissures did not always initiate from the bottom of a selective grain attack. Pretreatment for either one or two hours generated selective grain attack of sufficient depth to trap an aggressive environment. As a result, the sharp IGC fissure growth rates were essentially independent of the size of the selective grain attack.
6.3.7 Humidity Effects

In this study the corrosion kinetics were measured during atmospheric exposure, not in aqueous environments. It is therefore of interest to know the effect of RH on the sharp IGC fissure growth kinetics.

Figure 6.9 shows the sharp IGC fissure growth kinetics of the as-received AA7178 in atmospheres with different humidity from 58-96% RH. The electrochemical pretreatment on each sample was same: 2 h in 1 M NaCl at –725 mV SCE. The sharp IGC fissure kinetics are seen to be independent of the RH in the range studied. Figure 6.10 shows an unetched cross section of a sample that was electrochemically pretreated and then stored in a dessicator for 5 months prior to sectioning. Sharp IGC fissures are seen in this figure (pointed out by arrows), indicating that they can grow even in extremely dry environments.

The lack of dependence of fissure growth rate on RH is interesting, especially in light of recent findings showing that the rate of exfoliation of the same material in humid environments depends strongly on RH, and that exfoliation ceases at an RH of 56% [15]. In that work, slices of AA7178 plate were given similar electrochemical pretreatments prior to humidity exposure, so selective grain attack sites were created in both types of samples. The difference is that the whole slice was treated and exposed to humidity, allowing exfoliation attack from the edges. In this work, only a limited region of the sample surface was exposed and the surrounding unexposed region provided a constraint on the material in the exposed area so the corrosion took the form of sharp IGC fissures.

It is clear that the external environment has a very different influence on sharp IGC fissures and exfoliation corrosion. The pretreatment selective grain attack sites in
both types of samples contained aggressive environment that resulted in further corrosion upon removal to a humid atmosphere. Drying of the environment in a selective grain attack pit would result in the precipitation of an aluminum hydroxy-chloride product. It has been reported that the critical humidity for a partially hydrolyzed aluminum chloride, Al(OH)\(_{3-x}\)Cl\(_x\), is in the range of 40-95% depending on the degree of hydrolysis [16]. Therefore, it would be expected that RH should affect the state of the corrosion product and that at low enough RH the product would dry up and corrosion would cease. This is exactly what is observed for the case of exfoliation corrosion, where the exfoliation process opens up the corrosion site and provides access of the localized corrosion environment to the external atmospheric environment. However in the case of a sample constrained to prevent exfoliation, the external atmosphere apparently does not have ready access to the internal localized corrosion environment. Corrosion proceeds at the selective grain attack regions in the form of sharp intergranular fissures and these fissures are apparently rather isolated from the external environment. It is expected that in a very dry environment the water in the localized corrosion site eventually would be consumed by the creation of corrosion product and sharp IGC fissure growth would cease. However, this was not observed during the time periods used in this work.

The isolation of the local environment in a sharp IGC fissure from the external environment has implications for predictive models of aircraft corrosion. Because the land locations of aircraft are limited to air bases or airports, their exposure environments are more tractable. However, it cannot be assumed that the growth kinetics of these sharp IGC fissures will quickly change if the land base location changes, and a memory effect should be expected. Such is not the case for exfoliation corrosion [17].
6.3.8 Temper Effects

It is well documented that AA7xxx in the over-aged temper exhibits better stress corrosion cracking (SCC) resistance than in the peak aged condition [18-24]. Most SCC testing is done in a solution environment, and it was just shown that humidity has little effect on the sharp IGC fissure kinetics. Therefore, it is also interesting to evaluate the temper effect on the sharp IGC fissure growth in humid environments. To determine the effects of temper on the sharp IGC fissure kinetics, samples of as-received AA7178 wingskin were re-heat treated to T6 and T7 tempers.

Electrochemical pretreatment of the T6 and T7 samples was the same as for the as-received wingskin samples: 2 h in 1 M NaCl at –725 mV SCE. The T6 and T7 samples exhibited a similar current density of about 1.4 mA/cm² during electrochemical pretreatment while it was only 0.73 mA/cm² for as-received samples. Vickers hardness testing was performed to verify the temper. The hardness values were HV 198, 199, and 184 for as-received, T6, and T7, respectively, suggesting that the re-heat-treated T6 and T7 samples were in the desired tempers and that the as-received plate was in the T6 temper. However, handbook hardness values for 7178-T6 and –T7 are only HV 189 and 177, respectively [25]. It is interesting that the hardness of the as-received AA-7178 was similar to the T6 sample, but the current density during pretreatment was lower than that measured on both the T6 and T7 samples. It has been reported that corrosion resistance is improved in the over-aged condition [18-24]. Given these conflicting data, the exact temper of the as-received samples is still in question.
Only one RH, 96%, was chosen to test the T6 and T7 samples, since the sharp IGC fissure rate was found to be independent of humidity. The results are shown in Figure 6.11 along with previous results on the as-received AA7178 wingskin in the same RH. Despite the scatter, it is clear that the sharp IGC fissure growth rate for T6 temper was higher than for T7, which is consistent with reports in the literature that the over-aged condition (T7) is more resistant to corrosion than peak-aged condition (T6). Furthermore, the sharp IGC fissure growth rate for the as-received samples was slower than for both re-heat-treated samples, which again calls into question the exact temper of this material.

To understand the effect of temper on sharp IGC fissure growth rate, the microstructures were examined by transmission electron microscopy (TEM). Several TEM samples were prepared from different locations of the as-received AA7178 plate. A variation of the microstructure was observed. It has also been found that localized corrosion varies across the plate as some locations are more susceptible than others [26]. As a result, it is difficult to analyze the microstructure of a whole plate and compare it to the other tempers. Therefore, in this work only the microstructure near sharp IGC fissures was examined and compared to understand the effect of temper on sharp IGC fissure growth rate.

The TEM samples were prepared using focused ion beam (FIB) sectioning to examine a location close to the sharp IGC fissures in each material. Figure 6.12 shows TEM images of the as-received, T6 and T7 samples near the locations of the sharp IGC fissures in each sample. The T7 matrix contains larger particles than the matrix of T6 and the as-received samples. At the grain boundary, the as-received and T7 have large and
spaced particles while T6 shows a high density of fine particles. Quantitative TEM analysis using electron dispersive spectroscopy (EDS) showed that these particles have high contents of Zn and Mg, suggesting that they are $\eta$ or $\eta'$. It was reported that $\eta$ or $\eta'$ is more active than the matrix in AA7xxx [27, 28]. It is possible that the fine particles in T6 grain boundaries resulted in a fast sharp IGC fissure growth rate and the absence of the small grain boundary particles in the as-received and T7 resulted in a slower sharp IGC fissure growth rate. The microstructure of the as-received material is similar to that of T7, consistent with the rate of sharp IGC fissure growth.

6.3.9 Sharp IGC Fissure Examination

Figure 6.13 is a secondary electron image of a sectioned IGC fissure prepared by FIB sectioning. The width of the sharp IGC fissure is about 200 nm. A thin TEM sample containing a sharp IGC fissure was prepared by FIB. Analysis of the fissure by Electron Dispersive Spectroscopy detected O and Cl, indicating that corrosion product filled the fissure crack.

The surface of a sharp IGC fissure was revealed by pulling apart a penetrated sample under tension and examining it by Scanning Electron Microscopy (SEM). Figure 6.14 shows the surface of a fractured sample. The morphology of the fracture surface has three distinct regions. At low magnification it is easy to discern a dimple fracture area associated with the tensile overload (area C). The non-dimpled area is relatively planar, and at higher magnification it is possible to distinguish the selective grain attack region associated with the pretreatment (area A) and the sharp IGC fissure area (area B). The
selective grain attack region contains rough shallow pits on the fracture surface, whereas the sharp IGC fissure area is much flatter.

Sharp IGC fissure surfaces were analyzed by x-ray photoelectron spectroscopy (XPS). A dual Mg X-ray source was used and an area of 100 µm diameter on matching sides of the sharp IGC fissure region of a fracture sample was analyzed. The spectra of O, C, Cl and Al lines were recorded as well as C for calibration. Figure 6.15 shows the spectra of Al, O and Cl. The Al 2p line can be fitted with two peaks at binding energies of 74.2 and 75.5 eV, which can be identified as aluminum oxide and aluminum hydroxychloride, respectively [29, 30]. The O 1s peak is primarily oxide, and a Cl 2p peak was also detected, which supports the designation of the Al 2p hydroxychloride peak. These observations support the notion that the sharp IGC fissure were filled with aluminum oxide and hydroxychloride corrosion products that cracked upon drying.

6.3.10 Sharp IGC Fissure Mechanism

AA7xxx alloys are known to be susceptible to intergranular stress corrosion cracking (IGSCC) when subjected to a tensile stress in an aggressive environment [20, 21, 31-35]. However, in this study the sharp IGC fissures grew in samples that were unstressed. Furthermore, the pretreated area from where the sharp IGC fissures grew was surrounded by material that was not exposed during pretreatment, and this region acted to constrain the material from opening up as in the case of exfoliation corrosion. Nonetheless, it is likely that the sharp IGC fissure phenomenon is very similar to SCC. Like exfoliation corrosion, the fissures could grow as a result of self-stressing by voluminous corrosion product formed at the grain boundary region. It has recently been
shown that very low stresses (as low as 10% of the yield stress) normal to the elongated microstructure in wrought aluminum alloys can increase localized corrosion penetration rates significantly [36]. For the sharp fissures in this study, the wedging stress from the corrosion product is apparently sufficient to drive cracking despite the constraining effect of the unexposed surrounding material. There is considerable evidence for the creation of corrosion product in the sharp IGC fissures. As mentioned, corrosion product was observed to creep out of the sharp IGC fissure onto the backside of the sample upon penetration, and the sharp IGC fissure surfaces were found to be covered with aluminum hydroxychloride.

Figure 6.9 shows that the rate of the sharp IGC fissure growth in the as-received AA7178 is approximately linear. A constant rate of crack growth is observed over a broad range of $K_I$ level in the stage II region of SCC. [19, 20, 31, 33, 35, 37] It was mentioned earlier that the temper condition of the as-received AA7178 is unknown, although seems to close to T7 temper (Figure 6.11). The sharp IGC fissure growth rate is around $4.5 \times 10^{-4}$ mm/hr for the as-received AA7178 in Figure 6.9 and it is about $7.3 \times 10^{-3}$ mm/hr for T6 in Figure 6.11. The reported crack growth rates of AA7075-T6 and –T7 in 0.6 M NaCl are around $2 \times 10^{-2}$ and $4 \times 10^{-4}$ mm/hr, respectively. [19] So the sharp fissure growth rates in AA7178 are similar in magnitude to the stage II SCC growth rates for AA7075 in seawater. This supports the notion that the fissure growth mechanism is related to SCC.
6.4 Summary

Corrosion morphology in AA7xxx is different in different environments. It is selective grain attack in a NaCl solution and is sharp IGC fissure in a humid environment. A new approach was developed to quantify the sharp IGC fissure kinetics in AA7178 wingskins in different humid environments. Samples were also heat treated to examine the temper effect. The following observations were made.

1. This new approach determines a range of sharp IGC fissure rates in high humidity, not only the fastest rates, and it provides the rates of long sharp IGC fissures.
2. Each sharp IGC fissure is associated with a selective grain attack, which provides an aggressive environment for sharp IGC fissures to grow in humid environments.
3. The sharp IGC fissure rates in T direction are similar as in L direction for thin foils; the sharp IGC path is very straight either in T direction or in L direction.
4. There seems to be no effect of varying electrochemical pretreatment time, but the pretreatment attacks are required for sharp IGC fissures to grow.
5. Humidity from 96% to 58% RH has little effect on the sharp IGC fissure growth rates due to little connection of the local sites to the external environment. Sharp IGC fissures can even grow in a dessicator.
6. The re-heat-treated AA7178 has higher corrosion rates and T7 is more resistant to sharp IGC fissure than T6. The faster sharp IGC fissure rate in T6 could be due to fine and continuous η phase particles at the grain boundary.
7. The sharp IGC fissure growth is caused by stress corrosion cracking associated with stresses generated by the intergranular corrosion product.
REFERENCES


### TABLES

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Table 6.1 Composition of AA7178 wingskin plate determined by ICP-OES.

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Table 6.2 The RH expected by equilibrium with the saturated solution of different salts at a given temperature [11] and measured RH at room temperature.

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<tr>
<td>S</td>
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Table 6.3 Grain dimension of AA7178-T6 wingskin plate
Figure 6.1 (a) Metallographic sections of as-received AA7178 wingskin plate and the terminology used for the three orientations: L (longitudinal), T (long transverse) and S (short transverse). (b) Schematic diagram of foil sample orientation.
Figure 6.2 Selective grain attacks and sharp IGC fissures. Sharp IGC fissures are pointed out by arrows. (a) AA7178-T6: polarization in 1 M NaCl at a potential of −725 mV SCE. (b) AA7075-T6: polarization in 1 M NaCl at a potential of −725 mV SCE. (c) AA7178-T6: polarization in 1 M NaCl at a potential of −725 mV SCE followed by high humidity exposure. (d) AA7075-T6: polarization in 1 M NaCl at a potential of −580 mV SCE followed by high humidity exposure.
Figure 6.3 Determination of the sharp IGC penetration time. (a) 1 day; (b) 15 days: no pit shown; (c) 16 days: first sign of penetration; (d) 17 days: corrosion products oozed out.

Figure 6.4 Cross-section of a penetrated sample showing only a sharp IGC fissure (pointed out by arrow). A related selective grain attack is not seen on this section.
Figure 6.5 Serial sections of a penetrated sample. A sharp IGC fissure (pointed out by arrow) grew from the end of a selective grain attack. 266.9 µm was determined as the depth of this sharp IGC fissure.

Figure 6.6 Serial sections from a penetrated sample. The sharp IGC fissure (pointed out by arrow) did not begin from the end of the selective grain attack. 377.5 µm was determined as the depth of this fissure.
Figure 6.7 3-D reconstruction of a sharp IGC fissure from serial 2-D cross-sections, shown at different angles. (a) The selective grain attack site is indicated as a dark region in the top right. The sharp IGC fissure grew from the side and bottom. (b) From this angle it is clear that the sharp IGC fissure only grew along one side of the selective grain attack.
Figure 6.8 Sharp IGC fissure rates of the as received wingskin AA7178 at high humidity (96% RH) with different electrochemical pretreated time and sample orientations.

Figure 6.9 Sharp IGC rates of the as received wingskin AA7178 in different humidity. The kinetics seem to be independent of humidity. A dash line is a fit of all of the data to a straight line.
Figure 6.10 Unetched cross section of AA7075-T6 sample following electrochemical treatment in 1 M NaCl at –725 mV for 5 h and storage in a dessicator for 5 months. Sharp IGC fissures were pointed out by arrows.

![Image](image_url)

Figure 6.11 Samples in different tempers were tested in 96% RH. The re-heat treated AA7178 shows higher corrosion rates and T7 is more resistant to sharp IGC fissures than T6.
Figure 6.12 TEM images of the as-received, T6 and T7 samples showing the grain boundary microstructure. T6 has fine and continuous $\eta$ phase particles along the grain boundary while the $\eta$ phase particles are large and spaced at grain boundary in the as-received and T7 conditions.

Figure 6.13 A secondary electron image of a sectioned sharp IGC fissure prepared by FIB sectioning. The width of the sharp IGC fissure is around 200 nm.
Figure 6.14 Matching surfaces of a fractured sample indicate three distinct regions. A: selective grain attack from electrochemical pretreatment. B: sharp IGC fissures from humidity exposure. C: uncorroded ductile fracture region.
Figure 6.15 XPS spectra of Al, O and Cl on the layer of mud-cracking in the sharp IGC fissure area.
CHAPTER 7

CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

Intergranular corrosion (IGC) kinetics of 7xxx aluminum alloys were measured by the foil penetration technique in NaCl solution. Several AA7075 and AA7178 plates were used to study the influence of grain structure on the IGC kinetics. Heat treatment effects on the corrosion resistance of the material were characterized by polarization curves and the foil penetration data. A new approach was developed to duplicate the sharp IGC fissures in AA7178 and to quantify the rates. Several analytical approaches were taken to understand the sharp IGC mechanism and a statistical model was developed for IGC growth in AA7xxx. The following observations were made from the results of this work:

1. AA7xxx plates with grain aspect ratio greater than 1 were found to exhibit anisotropic localized corrosion kinetics, with kinetics in the S direction much slower than in either the L or T direction. Localized corrosion kinetics for an equiaxed AA7178 (with grain aspect ratio = 1) plate were independent of the orientation. The results suggest that localized corrosion kinetics strongly depend on the total IGC growth path.
2. A critical thickness associated with microstructural anisotropy was found to separate the localized corrosion kinetics in L direction from that in T direction on AA7xxx. For samples thinner than the critical thickness, the localized corrosion rates in T and L directions were similar.

3. Breakdown potentials were influenced by the heat treatment; however, they are independent of sample orientations. AA7xxx-T6 exhibits two breakdown potentials while AA7xxx-W and AA7xxx-T7 have only a single breakdown potential.

4. Generally, the higher the applied potential, the higher the current density and the faster the localized corrosion kinetics. However, the difference was less at high potentials. At potentials above −740 mV SCE, the effect of temper on the localized corrosion kinetics was not seen. At −750 mV SCE, the rate for T6 was slower than for T7, whereas the rate was slower for T7 during OCP exposure. W temper exhibited the fastest localized corrosion rate at both OCP and −750 mV SCE.

5. IGC morphology in AA7xxx is different in different environments. Selective grain attack forms in a NaCl solution and sharp IGC fissures form in a humid environment following a pretreatment.

6. A statistical model developed for IGC in AA7xxx explains well the influence of the microstructure on the localized corrosion kinetics in AA7178. This agreement was used to suggest that the mechanism for formation of the selective grain attack morphology is IGC/wake corrosion. This model does not work for rolled AA7075-T6, suggesting a different corrosion mechanism.
7. A new approach was developed to quantify sharp IGC fissure rates in humid environments. It provides the rates of long sharp IGC fissures. Each sharp IGC fissure is associated with a selective grain attack, which provides an aggressive environment for sharp IGC fissures to grow in humid environment.

8. Sharp IGC fissures grew with a rate that was constant with time over 1000 h, about 0.33 µm/h. Humidity from 96% to 58% RH has little effect on the sharp IGC fissure growth rates due to little connection of the local sites to the external environment. Sharp IGC fissures can even grow in a dessicator.

9. T6 temper exhibits a higher sharp IGC fissure rate than T7. TEM characterization at the grain boundary near a sharp IGC fissure shows that η phase particles are fine and continuous at the grain boundary in T6 and are coarse and spaced in T7.

10. The sharp IGC fissure growth is caused by stress corrosion cracking associated with stresses generated by the intergranular corrosion product.

7.2 Future Work

The present work on the IGC of 7xxx aluminum alloys has opened up several issues that are of interest for future study.

1. This work found that IGC of 7xxx in a NaCl solution was in the form of selective grain attack. The detail of the mechanism of this attack is still not clear. It is interesting that once the attack is initiated, it consumes the grain matrix instead of continuing on the grain boundary to the next grain. The grain boundary is for some reason less susceptible to attack and acts as a barrier to further growth.
2. Morphology of the selective grain attack was observed under optical microscopes. The observed selective grain attack could be artificial due to poor resolution of in-depth focusing in an optical microscope. It is possible that corrosion attacks many sub-grain boundaries inside a grain and makes it look like attacking the whole grain under the optical microscope. Further work with SEM characterization is needed to find out the phenomenon.

3. The sharp IGC fissure rate was measured in thin foils in this work and was found to be independent of humidity of external environment. However, the corrosive solution inside the sharp IGC attack should be limited. It is questioned if the limited corrosive solution inside the narrow crack would dry out after traveling a longer distance than it was measured in this work.

4. Quantification of the sharp IGC fissure rates was performed at room temperature and the effect of temperature was not included in this study. Temperature would affect rate of localized corrosion and hydrogen-environment-assisted cracking. If as assumed in Chapter 6 the sharp IGC fissure mechanism includes hydrogen embrittlement, anodic dissolution and SCC, then the effect of temperature could play an important role in the sharp IGC fissure kinetics and is worthy of further exploration.
APPENDIX A

VARIATION OF CORROSION SUSCEPTIBILITY ACROSS AA7178 WINGSKIN PLATES

A.1 Introduction

It was brought to our attention that AA7178 wingskin plates have variation of corrosion susceptibility across the plate thickness. For instance, when etching an L section sample, which was cut through the whole thickness of the plate, the area near the top or bottom surface usually was darker than in the center (mid-plate area). This indicates that mid-plate area might be less susceptible to corrosion than the areas near the surface for this plate. Therefore, an investigation on the variation of corrosion susceptibility across plate thickness was carried out on two AA7178 wingskin plates.

A.2 Experimental

Two AA7178 wingskin plates were used in this study. Plate A was 8.5 mm thick, with no coating on the surfaces when received. Plate B was 5 mm thick; one side had a layer of gray coating and the other side had a Cr conversion coating. The microstructures were characterized by optical metallography after polishing and etching in Keller’s reagent.
Both plates were first polarized in air-bubbled 1 M NaCl at –725 mV SCE for 5 h to observe corrosion susceptibility. L oriented Samples covering the whole plate thickness were mounted in epoxy prior to testing. After polarization, they were cross sectioned in the T direction and examined under optical microscopy.

Polarization curves were performed in Ar-deaerated 1 M NaCl at a scan rate of 0.2 mV/s. Plate A was sliced to nine pieces across plate thickness. Each piece was measured on one side (S direction) except that one of the pieces on the surfaces was measured on both sides so as to obtain breakdown potentials in ten different locations across the plate thickness. Plate B was measured in two locations at the cross section (L direction): one half close to the gray coating and one half close to Cr coating.

Foil penetration experiments were performed on Plate A in the S direction. Foil samples were sliced using a diamond saw. The location of each sample relative to the top surface was recorded. All samples were ground mechanically and polished through a series of silicon carbide (SiC) papers (up to 800 grit) on both sides. A Teflon knife-edge O-ring with was used to define the exposed specimen area, which was 41 mm². The test solution was 1 M NaCl bubbled with O₂. All samples were first anodically polarized to –290 mV SCE for 1 s to initiate corrosion, followed by an immediate change to the desired applied potential.

A.3 Results and Discussion

Figures A.1 and A.2 show the corrosion susceptibility on Plates A and B across the plate thickness respectively. Plate A has more corrosion attack near the top and bottom surface than in the middle plate, indicating that the middle plate was less
susceptible to corrosion than near the surfaces. Plate B has most of corrosion attack on one side (near Cr coating surface). It should be noted that gray coating and Cr coating are mentioned here to identify the plate orientation and they were polished off before testing.

The grain sizes of both plates were analyzed in three perpendicular orientations (L, T and S). The grain size was measured using L and T sections. Each section was divided into ten equal parts from top to bottom for Plate A and five parts for Plate B. At least 20 grain size measurements were randomly made on each part. The grain sizes in L and S directions were measured in the T-section sample and the grain sizes in T and S directions were measured in the L-section sample.

Figures A.3 and A.4 are the grain size distributions in three perpendicular orientations for Plates A and B respectively. Both plates have anisotropic microstructures. Plate A has more elongated grains in the middle plate and more equiaxed grains near both surface. The length of the grain was decreasing from Cr coating side to gray coating side. The more elongated microstructure in Plate A is less susceptible to corrosion according to Figure A.1. However, the more elongated microstructure in Plate B is more susceptible to corrosion according to Figure A.2. Therefore, microstructure seems not directly related to corrosion susceptibility in this case.

Breakdown potentials of Plate A in ten different locations from top to bottom are shown in Figure A.5. The polarization curve was measured on each S-oriented sample at least twice with repolishing. In Figure A.5, the 2nd breakdown potential seems higher in the middle plate than near the surface. Generally speaking, a higher breakdown potential indicates more resistance to corrosion. For Plate A, it was shown from Figure A.1 that the middle plate is more resistant to corrosion.
Breakdown potentials of Plate B on the gray coating half and Cr coating half are shown in Figure A.6. Both 1st and 2nd breakdown potentials are higher on the gray coating half. It is also shown in Figure A.2 that this region is less susceptible to corrosion. Therefore, corrosion susceptibility on both plates is related to their breakdown potentials.

The localized corrosion kinetics of AA7xxx from the foil penetration experiments were found to follow the equation:

\[ d = A \times t^n \]  (1)

where \( d \) is the depth of the fastest localized corrosion site, \( t \) is time and \( A \) and \( n \) are constants. In order to show the difference of corrosion kinetics on different locations across the plate thickness, Eq (1) was rearranged to

\[ A = \frac{d}{t^n} \]  (2)

where \( n \) was taken as 1/4 according to the results in chapter 3. The larger the \( A \) value, the faster the corrosion rate. The variation of \( A \) with distance from the top surface is shown in Figure A.7. At the potential of –725 mV SCE, the corrosion kinetics were slower in the middle of the plate. The slower corrosion rates in the middle plate could be due to two reasons. (1) The middle plate is less susceptible to corrosion, as this region exhibited higher breakdown potentials. (2) Grains are more elongated in the middle plate so that the corrosion path would be more circuitous and longer if it travels in S direction (through thickness).

Experiments were also performed at the higher potential of –710 mV SCE and faster corrosion kinetics were found at the higher potential. However, the corrosion kinetics were essentially independent of position across the plate thickness at the higher potential of –710 mV SCE. It should be noted that –710 mV SCE is very high for this
material. It is possible that no difference was observed because the conditions were too severe. Figure A.8 shows two polarization curves, near top surface and in the middle plate. At –725 mV SCE, mid-section sample has a lower current density. However, at –710 mV SCE, both have similar current density.

A.4 Summary

It was found that AA7178 wingskin plates have variation of microstructure and corrosion susceptibility across the plate thickness. From Chapters 3 and 4, it was concluded that microstructure affects the total IGC path and the corrosion kinetics. However, it was observed that microstructure is not related to corrosion susceptibility. In Plate A, less susceptible to corrosion area has more elongated microstructure. Plate B is the opposite case. The variation of corrosion susceptibility seems to relate to the electrochemical properties (i.e. breakdown potentials) of the material. Those areas which are more susceptible to corrosion were found to exhibit lower breakdown potentials.
FIGURES

Figure A.1 Corrosion morphology of Plate A after exposure at a potential of –725 mV SCE in aerated 1.0 M NaCl for 5 hours. The plate S direction is horizontal and L direction is vertical. The L faces, or the top face in these images, were exposed.

Figure A.2 Corrosion morphology of Plate B after exposure at a potential of –725 mV SCE in aerated 1.0 M NaCl for 5 hours. The plate S direction is horizontal and L direction is vertical. The L faces, or the top face in these images, were exposed.
Figure A.3 Grain size distributions in three perpendicular orientations across Plate A thickness. Grains are more elongated in the middle plate.
Figure A.4 Grain size distributions in three perpendicular orientations across Plate B thickness. Grains are more elongated near Cr coating surface.
Figure A.5 Breakdown potential of Plate A measured in S sections across the plate thickness. The solution is Ar-deaerated 1 M NaCl and the scan rate is 0.2 mV/s.
Figure A.6 Breakdown potentials of Plate B measured in L section. The solution is Ar-deaerated 1 M NaCl and the scan rate is 0.2 mV/s.
Figure A.7 Foil penetration data for Plate A in S direction across plate thickness, at two different potentials.
Figure A.8 Anodic polarization curves of AA7178 OSU-10 plate in S direction at center of the plate and near the surface.
APPENDIX B

A STUDY ON CORROSION SUSCEPTIBILITY IN TWO AA7178 WINGSKIN PLATES

B.1 Introduction

KC-135 tankers have served in the US Air Force for decades and corrosion problems become more and more critical. A lot of R&D efforts have been put into anticipating the corrosion processes on these airplanes. One study was carried out in Daytona Beach, FL. [1] Samples cut from a retired airplane were exposed to the atmosphere near the coast to observe corrosion in such a severe environment. The behavior of two AA7178 wingskin plates has been of particular interest. The two plates were fastened side by side onto another plate, with many holes and fasteners on both plates. After one year exposure, one plate was found to have severe exfoliation corrosion on the surface around the fasteners and the other plate had very little corrosion. Compositional analysis showed that both plates were AA7178.

It is very interesting that similar plates behaved very differently in the same environment. In this work, more work was performed on these two plates, including examining composition, microstructure and their corrosion properties.
B.2 Experimental

Two AA7178 wingskin plates were used in this study and were labeled as good and bad plates. The good plate is 4.0 mm thick and it exhibited little exfoliation corrosion after one year exposure at Daytona Beach. The bad plate is 4.6 mm thick and it exhibited a lot of exfoliation corrosion after one year exposure at Daytona Beach.

The composition of both plates was analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) on a Perkin Elmer Optima 3000. The microstructures were characterized by optical metallography after polishing and etching in Keller’s reagent.

Polarization curves were performed in Ar-deaerated 1 M NaCl at a scan rate of 0.2 mV/s. Samples were prepared in three perpendicular orientations (L, T and S). Samples in S direction were measured on top surface, ¼ of plate thickness from top surface, mid-section and bottom surface.

Corrosion kinetics on both plates were measured in O₂ bubbled 1 M NaCl at –725 mV SCE by the foil penetration technique. Corrosion rates were only measured in the S direction. After the foil penetration experiment, samples were cross sectioned and corrosion morphology was examined under an optical microscope.

B.3 Results and Discussion

Table B.1 lists the composition of both plates measured by ICP-OES. Samples were cut from top surface, mid-section and bottom surface for each plate. Both plates have very similar composition, except that good plate has higher contents of Mn and Fe.
Grain sizes of both plates were analyzed in three perpendicular orientations. The grain size was measured using L and T sections. Each section was divided to five equal parts from top to bottom. At least 20 grain size measurements were randomly made on each part. The grain sizes in L and S directions were measured in the T-section sample and the grain sizes in T and S directions were measured in the L-section sample.

Figures B.1 and B.2 are the grain size distributions in three perpendicular orientations for the good and bad plates, respectively. Both plates have anisotropic microstructures. The good plate has more elongated grains in the middle plate and more equiaxed grains near both surface. The bad plate has uniform grain size distribution across the plate thickness. Overall, the grain sizes in the bad plate are larger than in the good plate. Figure B.3 shows the microstructure near the top surface of both plates.

The breakdown potentials of both plates on L and T sections are shown in Figure B.4. There seems to be no difference in the breakdown potentials measured on the L and T sections between the two plates. Figure B.5 shows the breakdown potentials on S sections in different locations across the plate thickness. Breakdown potentials are also similar between the two plates except higher breakdown potentials were observed in the mid-plate of the good plate.

Figure B.6 shows the corrosion kinetics of both plates in O$_2$ bubbled 1 M NaCl at –725 mV SCE. Although the data are scattered, it is apparent that bad plate has a higher corrosion rate than good plate, which is consistent with the Daytona exposure results. A power law, \( d = A \times t^n \), was tried to fit the data to obtain \( n \) value. The power law was then rearranged to \( A = \frac{d}{t^n} \). The larger the A value, the higher the corrosion rate. Figure B.7 shows the re-plotted data with A vs. sample location across the plate thickness.
Both plates showed similar corrosion kinetics across the plate thickness. There is no difference in the corrosion rate for different locations through the thickness.

The bad plate has larger grain dimensions. However, as was discussed in Appendix A, grain dimension has little connection to corrosion susceptibility. Corrosion susceptibility is much more linked to the electrochemical properties (breakdown potentials) of the material. However, the two plates exhibit similar breakdown potential. Therefore, it is still not clear what causes bad plate to be more susceptible to corrosion than good plate.

Grain dimension would affect corrosion kinetics if the corrosion attack is intergranular in nature. From Figures B.1-B.3, it is suggested that the good plate would have shorter IGC path in S direction due to the finer grains. However, the corrosion rate in the good plate is slower than in the bad plate. One of the reasons could be due to corrosion susceptibility of the bad plate. There could be other possible reasons, such as corrosion mechanism.

Figures B.8 and B.9 are cross sections of the foil penetration samples. Figure B.9b shows that corrosion attack in bad plate was along grain boundaries, while Figure B.8b indicates good plate has pitting along certain grains. It was discussed in Chapter 4 that there might be two possible localized corrosion mechanisms for AA7xxx: pitting corrosion and IGC/wake attack. Based on the corrosion morphology in Figures B.8 and B.9, the good plate seems to follow the pitting corrosion mechanism and bad plate has IGC/wake attack.
B.4 Summary

Two AA7178 wingskin plates with different corrosion susceptibility were studied. The grain sizes of the two plates are different; however, this is not likely the reason behind the different corrosion susceptibility. Composition and breakdown potentials are more related to the corrosion properties of the material. However, both plates have similar composition and breakdown potentials. It is still not clear at this time what is the main reason causing the bad plate to be more susceptible to corrosion.

Localized corrosion kinetics are higher in the bad plate than in the good plate. The localized corrosion mechanism in the good plate is more like pitting corrosion, while IGC/wake attack is found in the bad plate.

REFERENCES

Table B.1 Composition of good and bad AA7178 plates quantified by ICP-OES. Samples were analyzed near top and bottom surfaces and in the middle plate.
FIGURES

Figure B.1 Grain size distributions in three perpendicular orientations across good plate thickness. Grains are more elongated in the middle plate.

Figure B.2 Grain size distributions in three perpendicular orientations across bad plate thickness. Grains are uniform distributed across the plate thickness.
Figure B.3 Microstructure of (a) good plate and (b) bad plate near the top surface.
Figure B.4 Breakdown potentials of good and bad plates measured in L and T sections. The solution is Ar-deaerated 1 M NaCl and the scan rate is 0.2 mV/s.

Figure B.5 Breakdown potential of good and bad plates measured in S sections across the plate thickness. The solution is Ar-deaerated 1 M NaCl and the scan rate is 0.2 mV/s.
Figure B.6 Localized corrosion kinetics of good and bad plates in S direction.

Figure B.7 Re-plot of Figure B.6 with A vs sample location across the plate thickness.
Figure B.8 Cross section of good plate after foil penetration experiment. (a) non-etched; (b) etched.

Figure B.9 Cross section of bad plate after foil penetration experiment. (a) non-etched; (b) etched.
APPENDIX C

CORROSION MORPHOLOGY OF AA7XXX IN HIGH MAGNIFICATION

An AA7075-T6 plate was purchased from Alcoa in 2000. This plate was re-heat treated to the W, T6 and T7 tempers in 2003. The work on AA7075 reported in Chapters 3-5 was from the re-heat treated material. The localized corrosion kinetics on the as-received AA7075-T6 was measured in 2001. Figure C.1 shows the localized corrosion kinetics of the as-received AA7075-T6.

Comparing Figure C.1 to Figure 3.8 (the localized corrosion kinetics of the re-heat treated AA7075-T6), it was found that corrosion rate is slower in L direction, faster in T direction and similar in S direction after re-heat treatment. The critical thickness to separate corrosion rates in L and T directions did not change; it was still around 170 µm. The re-heat treatment seems not to change the grain dimensions of this plate, but might have changed its corrosion behavior to some extent, which could be due to dissolving and re-precipitating the strengthening particles. The exact difference between the as-received and re-heat treated AA7075-T6 is not clear.
In chapter 4, two possible mechanisms for selective grain attack (SGA) were proposed: pitting corrosion and IGC/wake attack. The pitting corrosion type was found in re-heat treated AA7075-T6 and was described as consuming the grain but not bridging to neighboring grains. It is more pronounced in the as-received AA7075-T6. Figures C.2 and C.3 show the cross sections of the as-received AA7075-T6 in three perpendicular orientations after foil penetration experiments. Samples were also etched by Keller’s reagent to reveal the grain boundaries. Figures C.2 and C.3 show very clearly that attack was along selected grains and the attack tips are blunt.

Figures C.4 and C.5 are cross sections of AA7178 wingskin samples. The attack tips are sharper than those in the as-received AA7075-T6 and seem to be along the grain boundaries. They were suggested to follow IGC/wake attack mechanism in Chapter 4.

Corrosion morphology was observed by optical microscopy. The disadvantage of optical microscopy is its poor resolution in depth. Corrosion attack on the cross section, whether shallow or deep, would look like a big hole if not on the focused plane. A few samples were examined by scanning electron microscopy (SEM). Figures C.6 and C.7 show the comparison of corrosion morphology observed by optical microscopy and SEM. Selective grain attack seems to involve many sub-grain boundary attack.
Figure C.1 Localized corrosion kinetics of as-received AA7075-T6 in O$_2$ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure C.2 Cross sections of as-received AA7075-T6 foil penetration samples. Corrosion path is along L direction. (a) non-etched; (b) etched.

Figure C.3 Cross sections of as-received AA7075-T6 foil penetration samples. Corrosion path is along T direction. (a) non-etched; (b) etched.
Figure C.4 Cross sections of wingskin AA7178 foil penetration samples. Corrosion path is along L direction. (a) non-etched; (b) etched.

Figure C.5 Cross sections of wingskin AA7178 foil penetration samples. Corrosion path is along T direction. (a) non-etched; (b) etched.
Figure C.6 Cross section of AA7178 wingskin sample after foil penetration experiment in 1 M NaCl at OCP for 29 days. (a) Corrosion morphology under optical microscopy; (b) Corrosion morphology under SEM.
Figure C.7 Cross section of AA7178 wingskin sample after electrochemical pretreated in 1 M NaCl at –725 mV SCE and high humidity exposure. (a) Corrosion morphology under optical microscopy; (b) Corrosion morphology of marked area in (a) under SEM. Selective grain attack seems to involve many sub-grain boundary attack.
APPENDIX D

TEMPER EFFECT ON EQUIAXED AA7178

The temper effect on the localized corrosion kinetics in AA7075 was discussed in Chapter 5. This appendix describes the work on the temper effect in equiaxed AA7178.

The heat treatment cycle for this plate is shown in Figure D.1. Equiaxed AA7178 plate has no obvious working directions, but was still labeled as L, T and S according to the nominal dimensions of the plate so as to identify the sample orientation. Figure D.2 shows the microstructure of equiaxed AA7178 in different tempers. Grain sizes of equiaxed AA7178 are identical in different orientations and are not affected by artificial aging.

Foil penetration experiments were performed on this material to measure the corrosion kinetics. Experiments were conducted in O₂ bubbled 1 M NaCl at –725 mV SCE. The localized corrosion kinetics of equiaxed AA7178 in different orientations are shown in Figures D.3-D.5 in each temper separately. The localized corrosion rates for this material were found to be independent of orientation.
Since the localized corrosion rates are independent of orientation, data in different orientations were combined together for each temper and were re-plotted in Figure D.6 to see the effect of temper. The results show that localized corrosion rate in T7 is faster than that in T6, and is a little slower than that in W. The result is consistent with the observation on AA7075 that T7 has a higher localized corrosion rate than T6 in a NaCl solution.

Figures D.2-D.5 show that both the microstructure and localized corrosion rates for equiaxed AA7178 are isotropic, independent of temper. However, the morphology of the localized corrosion attack observed after the foil penetration experiments varied slightly depending on temper. In W temper (Figure D.7), the localized corrosion attack is pitting, attacking the grains. In T6 temper (Figure D.8), the localized corrosion attack is intergranular.
**FIGURES**

Figure D.1. Heat treatment cycle AA7178.

<table>
<thead>
<tr>
<th>7178</th>
<th>L section</th>
<th>T section</th>
<th>S section</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>T6</td>
<td>![Image]</td>
<td>![Image]</td>
<td>![Image]</td>
</tr>
<tr>
<td>T7</td>
<td>![Image]</td>
<td>![Image]</td>
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</tr>
</tbody>
</table>

Figure D.2. Microstructure of equiaxed AA7178 in different tempers and different orientations. Artificial aging does not affect grain size.
Figure D.3 Localized corrosion kinetics of equiaxed AA7178-W in three orientations in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.

Figure D.4 Localized corrosion kinetics of equiaxed AA7178-T6 in three orientations in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure D.5 Localized corrosion kinetics of equiaxed AA7178-T7 in three orientations in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.

Figure D.6 Localized corrosion kinetics of equiaxed AA7178-W, -T6 and in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by linear curve fitting.
Figure D.7 Corrosion morphology of equiaxed AA7178-W. Attack is pitting. (a) non-etched; (b) etched.

Figure D.8 Corrosion morphology of equiaxed AA7178-T6. Attack is along grain boundaries. (a) non-etched; (b) etched.
APPENDIX E

MORE RESULTS ON TEMPER EFFECT IN AA7075

The effects of temper on the corrosion resistance at AA7075 were addressed in Chapter 5. Some results not showing in Chapter 5 are included in this appendix.

Figure E.1 shows the microstructure of AA7075 in different tempers. Grain dimensions were not affected by artificial aging.

It was mentioned in Chapter 5 that effects of temper on the localized corrosion kinetics of AA7075 become evident at potentials of –750 mV SCE and lower. Comparisons on the localized corrosion kinetics in different tempers at higher potentials are shown in Figures E.2-E.6.

Corrosion morphology in NaCl solution is the form of selective grain attack, regardless of applying potential. Figure E7-E9 show the selective grain attack in AA7075-W, -T6 and –T7 in NaCl solution at different potentials.
Figure E.1 Microstructure of AA7075 in different tempers and different orientations. Artificial aging does not affect grain size.
Figure E.2 Localized corrosion kinetics of AA7075-W, -T6 and T7 in S direction in O₂ bubbled 1 M NaCl at –700 mV SCE. Kinetics are shown by power curve fitting.

Figure E.3 Localized corrosion kinetics of AA7075-W, -T6 and T7 in S direction in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure E.4 Localized corrosion kinetics of AA7075-W, -T6 and T7 in L direction in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.

Figure E.5 Localized corrosion kinetics of AA7075-W, -T6 and T7 in T direction in O₂ bubbled 1 M NaCl at –725 mV SCE. Kinetics are shown by power curve fitting.
Figure E.6 Localized corrosion kinetics of AA7075-W, -T6 and T7 in L direction in O₂ bubbled 1 M NaCl at –740 mV SCE. Kinetics are shown by power curve fitting.

\[ d = A \cdot t^n \]

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>n</th>
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</thead>
<tbody>
<tr>
<td>W</td>
<td>0.268</td>
<td>0.665</td>
</tr>
<tr>
<td>T6</td>
<td>0.246</td>
<td>0.181</td>
</tr>
<tr>
<td>T7</td>
<td>0.232</td>
<td>0.449</td>
</tr>
</tbody>
</table>

Figure E.7 Corrosion morphology of AA7075-W in L direction in 1 M NaCl at different potentials. (a) -725 mV SCE; (b) OCP.
Figure E.8 Corrosion morphology of AA7075-T6 in L direction in 1 M NaCl at different potentials. (a) -725 mV SCE; (b) OCP.

Figure E.9 Corrosion morphology of AA7075-T7 in L direction in 1 M NaCl at different potentials. (a) -725 mV SCE; (b) OCP.
BIBLIOGRAPHY


E.H. Dix, In "Acceleration of the Rate of Corrosion by High Constant Stress" ed., edited by (1940)


