EFFECTS OF STRAIN VARIATIONS ON AGING RESPONSE AND CORROSION PROPERTIES OF
THIRD GENERATION AL-LI ALLOYS

by
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ABSTRACT

Due to their high specific strength (strength/density) and specific stiffness (elastic modulus/density), Al-Li alloys are attractive alloys for structural aircraft applications. To produce contoured aircraft components from Al-Li wrought products, stretch forming prior to aging is a common manufacturing technique. The effects of different amounts of tensile straining (0-9%) on the mechanical, microstructural, and corrosion properties of two third generation Al-Li alloys (2099 and 2196) were investigated. In addition to typical characterization techniques, electron backscatter diffraction (EBSD), 2D micro-digital image correlation (DIC), and scanning Kelvin probe force microscopy (SKPFM) were used to examine site-specific effects of orientation, micro-strain evolution during straining, and surface potential on corrosion, respectively. Tapping mode atomic force microscopy (AFM) was also performed to study galvanic corrosion in artificial seawater (3.5% NaCl) as it occurred in-situ.

There was evidence of intergranular corrosion for 0% strain conditions, but the dominant form of corrosion was localized pitting for all specimens except Alloy 2196 strained 0%. Pitting initiated at grain boundaries and triple points. In many cases, pitting extended into particular grains and was elongated in the extrusion direction. Regions of high micro-strain preferentially corroded, and large, recrystallized grains in mostly unrecrystallized microstructures were detrimental to corrosion properties. Recommendations for improved thermomechanical processing and/or alloying to promote corrosion resistance of 2XXX series Al-Li alloys were investigated.
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CHAPTER 1: INTRODUCTION

Since the 1920s, Al-Li alloys have been studied extensively for structural aircraft applications. Aircraft designers are interested in Al-Li alloys due to the need for more fuel-efficient and high-performance engines and structures. A 1 wt% addition of Li to Al decreases density by approximately 3%, due to the low density of Li (0.53 g/cc), and increases the elastic modulus by approximately 6%. Extruded Al-Li alloys have been adapted for various applications in the fuselage such as crossbeams, wing stringers, and fuselage frames. Al-Li plate alloys have also been developed for structures such as wing panels [1].

While carbon fiber, boron fiber and non-metallic composites may offer an even greater reduction in density, the following makes Al alloys attractive: low acquisition costs, manufacturing experience, and utilization of existing manufacturing routes [2]. Li additions also lead to the formation of hardening precipitates, such as $\delta'(Al_3Li)$ and $T_1 (Al_2CuLi)$, which provide high strength and can promote fatigue crack growth resistance [3].

Al-Li alloys used in industry are manufactured with a minimum of 2.5% nominal strain to improve strength by providing dislocations as sites for precipitates to nucleate. To produce contoured aviation sections, up to 7% extra strain may be introduced into the alloys through stretch forming. The formation and distribution of precipitate phases in Al-Li alloys in grains and along grain boundaries are sensitive to the degree of strain imparted and it is known that second phase particles present in Al-Li alloys may contribute to general and localized corrosion [4].

The focus of this project is to identify the effects of different amounts of tensile straining (0-9%) and aging treatments on the mechanical, microstructural, and corrosion properties of two third-generation Al-Li alloys, namely 2099 (Alcoa 2003) and 2196 (LM/Reynolds/McCook Metals 2000). Table 1.1 provides compositions of these two alloys. In particular, it is of interest to identify microscale corrosion phenomena to elucidate corrosion mechanisms, pinpoint where corrosion initiates, and understand how corrosion proceeds.

| Table 1.1 - Target compositions of Al-Cu-Li alloys 2099 and 2196 [5] |
|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                | Avg wt% | Si  | Fe  | Cu  | Mn  | Mg  | Zn  | Ti  | Ag  | Li  | Zr  | Others (total) | Al  |
| 2099           | 0.05   | 0.07 | 2.7 | 0.30| 0.30| 0.70| 0.10| --  | 1.8 | 0.085| 0.15| Rem.          |     |
| 2196           | 0.12   | 0.15 | 2.9 | 0.35| 0.525| 0.35| 0.10| 0.425| 1.7 | 0.11 | 0.15| Rem.          |     |

1
The four pillars of materials science and engineering are processing, structure, properties and performance [6]. Figure 1.1 demonstrates the interrelationship between these four pillars and the project objectives and outlines the characterization techniques that are being utilized. In addition to typical characterization techniques (e.g. SEM, TEM, etc.), electron backscatter diffraction (EBSD), 2D micro-digital image correlation (DIC), and scanning Kelvin probe force microscopy (SKPFM) are being used to examine the effects of orientation, micro-strain evolution during straining, and surface potential on corrosion, respectively.

Furthermore, this research aims to answer three engineering questions. The first question is as follows: where does corrosion initiate and how does corrosion proceed in alloys 2099 and 2196? To address this question, samples of both alloys with various amounts of strain (0-9%) were thoroughly characterized in single, specific regions. For instance, micro-strain during tensile deformation was tracked
using 2D micro-digital image correlation (DIC). The orientations of grains were studied by electron backscatter diffraction (EBSD), and the impurity phases present were examined by backscattered imaging in a scanning electron microscope (SEM). Following DIC, EBSD and SEM, tapping mode atomic force microscopy (AFM) measurements were performed in solution to topographically monitor galvanic corrosion as it occurred in-situ. Ultimately, the goal was to relate corrosion initiation and the corrosion pathway to known attributes of the sample region, such as amount of strain, orientation of grains, and identity and location of impurity phases.

The second question is as follows: can corrosion be predicted? In addition to the previously-mentioned characterization techniques being utilized, scanning Kelvin probe force microscopy (SKPFM), which measures surface potential differences using an AFM, was performed prior to corrosion. Differences in surface potential due to second phase particles may lead to a reduction in resistance to localized corrosion (i.e. pitting and exfoliation corrosion). Surface potential values may aid in developing a pseudo-galvanic series and be used to predict corrosion resistance.

The last question the research aims to answer is: how can corrosion be prevented? This is the most difficult, and perhaps most important, question to tackle. Even though the project considerations can be simplistically summarized by Figure 1.1, it is important to recognize the complexity of the many interrelated factors contributing to corrosion. Assuming that galvanic corrosion of precipitates is the driving force for corrosion, the diagram in Figure 1.2 demonstrates that, even with this assumption, pinpointing a solution may not be straightforward. It should be pointed out that Figure 1.2 is still, most likely, an oversimplification.

The characterization involved in this research will aid in targeting key contributors of corrosion. It is the goal to back out realistic methods for mitigating corrosion, which may include the following: monitoring strain, processing to avoid or promote certain grain orientations, strategic alloying, or performing strategic heat treatments.
Figure 1.2 Causal diagram demonstrating the effects of many interrelated components on corrosion properties of Al-Li alloys.
CHAPTER 2: BACKGROUND

This chapter outlines the technical background for the current project. The first section provides a historical overview of the development and advances in Al-Li alloys. The following section describes relevant microstructural constituents which may form in third generation Al-Li alloys. Next, stretch forming and the effects of cold work prior to artificial aging are detailed, and two forms of corrosion (pitting and exfoliation) are described. Lastly, background is provided for relevant characterization techniques utilized as part of this research.

2.1 Historical Overview

The first additions of Li to Al were made by the Germans in the 1920s. The first commercial alloy, “Scleron”, had a nominal composition of Al-12Zn-3Cu-0.6Mn-0.1Li and claimed to have excellent wear, corrosion, and oxidation resistance with high tensile strength [7]. Shortly after the beginning of its production, Scleron was discontinued because the effects of Li additions to Al were not well understood, and alloys without Li seemed to have better properties. In 1945, Le Baron of Alcoa discovered Li could be added to Al-Cu alloys for strength, and Le Baron patented the first Al-Cu-Li alloys [8]. From 1955 until 1956, Hardy and Silcock identified the major Li-containing strengthening phases in Al-Cu-Li alloys, and the findings of Hardy and Silcock led to increased understanding and interest in Al-Cu-Li alloys [9].

In the 1950s, Alcoa realized that Li additions increased elastic modulus of Al alloys. Following this discovery, in 1958, Alcoa developed 2020 (Al-Cu-Li-Cd) which was used in the wings and horizontal stabilizers of the RA-5C Vigilante aircraft [10]. Even though 2020 had no failures in service, this alloy exhibited low ductility due to the following: planar slip, stress concentrations at high angle grain boundaries, nucleation of cracks at coarse Fe and Si-containing impurity constituents, and soft precipitate free zones [11]. To improve ductility, it was recommended that Fe and Si levels be lowered to reduce impurity constituents and Zr be added to maintain an unrecrystallized structure [11]. Following the development of 2020, the Soviet Union led the development of other first generation Al-Li alloys in the 1960s. Fridlyander et al. studied the Russian alloy VAD23, an alloy with a similar composition to 2020 and, in 1965, developed Al-Li-Mg alloys such as 1420 and 1421 [12]. These alloys were much less dense than conventional Al alloys (10-12% lighter than 2024) but were lower in strength [9].

Second generation Al-Li alloys were developed in the 1970s with a focus on reducing aircraft weight. To accomplish this goal, the second generation alloys generally contained above 2 wt% Li making them 8-10% less dense than conventional Al alloys. Some examples of second generation alloys include AA2090, AA2091, and AA8090. However, the second generation of Al-Li alloys was largely
unsuccessful due to several problems, namely, low short-transverse fracture toughness, high anisotropy due to strong crystallographic texture, low plane stress fracture toughness in sheet, and delamination fracture during manufacturing [3].

To address the challenges faced with the second generation Al-Li alloys, a third generation of Al-Li alloys was developed in the late 1980s and early 1990s. The third generation alloys contained a lower Li concentration (0.75-1.8 wt% Li) but were still 2-8% less dense than conventional Al alloys. The first alloy in this generation was Weldalite 049, with a high Cu/Li ratio and a nominal composition of Al-6.3Cu-1.3Li-0.4Ag-0.4Mg-0.14Zr [13]. Weldalite incorporated Mg and Ag to promote T₁ (Al₂CuLi) phase formation and Zr to refine the grain structure. As implied by its name, this alloy was designed to be weldable and one notable characteristic was that it could reach yield strengths of 700 MPa. Following the development of Weldalite, other third-generation alloys were developed, including the alloys of interest to this study, 2099 and 2196.

In some third generation Al-Li alloys, Ag is added for solid-solution and precipitation strengthening. In others, Zn is added for solid-solution strengthening and corrosion improvement [3]. In part, Al-Li alloys 2099 and 2196 were chosen for this study because 2196 contains less Zn than 2099 and 2196 has Ag additions, whereas 2099 does not contain Ag. It is of interest to determine the magnitude of the effects these alloying additions have on properties, including corrosion resistance.

2.2 Microstructural Constituents

Understanding the microstructural evolution and precipitation behavior of 2099 and 2196 during straining and aging is necessary to develop structure-processing-property relationships. Specifically, δ'(Al₃Li) and T₁ (Al₂CuLi) are perhaps the most important phases to consider in alloys 2099 and 2196 due to their strengthening effects and possible influences on corrosion. Many corrosion mechanisms have been proposed in these alloy systems but one of the most common, even among different types of corrosion, is anodic dissolution of a second phase. One goal of the research is to evaluate possible phases contributing to corrosion and the extent to which each phase contributes. This section provides background on the structure and formation of the various phases present in these alloys.

2.2.1 Dispersoids

β' (Al₃Zr) and δ' (Al₃Li) are two phases common in Al-Li alloys. The β' (Al₃Zr) phase forms during homogenization as a metastable spherical dispersoid phase and is used to inhibit recrystallization in Al alloys during hot working. The β' phase has the L12 crystal structure with a lattice parameter of...
0.408 nm with Al in the 3c positions and Zr in the 1a Wyckoff positions [14] and has a cube-cube orientation relationship with the Al (fcc) matrix [15].

The δ' (Al₃Li) phase is also a metastable, spherical dispersoid with the L1₂ crystal structure, a lattice parameter of 0.4010 nm with Al in the 3c positions and Li in the 1a positions [14], and also has the cube-cube orientation relationship with the Al (α-fcc) matrix [14], [16]. Due to their similar structures, the δ' dispersoids can grow epitaxially on β' dispersoids [17]. Often times, these phases are designated as having a “donut” appearance due to their core-shell structure. Although δ’ is a major strengthening precipitate, it is relatively soft and tends to be sheared by dislocations leading to coarse planar slip, low ductility, low fracture toughness, and poor fatigue properties [16]. The JEMS simulated crystal structure of δ’ is provided in Figure 2.1 along with a simulated selected area diffraction pattern along the [100] beam direction.

![Simulated JEMS unit cell of the δ’ dispersoid and Simulated JEMS diffraction pattern of Al+ δ’ along the [100]Al axis.](image)

### 2.2.2 Precipitates and Intermetallics

According to the literature, the following precipitates may also develop in artificially aged Al-Li alloys: β (AlZr), δ (AlLi), Θ’ (Al₂Cu), S’ (Al₂CuMg), T₁ (Al₂CuLi), and Ω (Al₂AgMg). Some of these precipitates form useful barriers to dislocation movement during slip and therefore strengthen Al-Li alloys while others do not and are undesirable. Of these, the main strengthening precipitate is T₁.

The β (AlZr) phase is an equilibrium phase that is not commonly observed in Al-Li alloys, but may form after extended heat treatments (far past typical heat treatments to peak hardness). The δ (AlLi) phase is another equilibrium precipitate that may form in Al-Li alloys aged for extended periods of time, especially in alloys with high Li concentrations. The formation of δ should be avoided because δ provides
no increase in strength and tends to precipitate at high energy sites, such as grain boundaries, resulting in precipitate free zones (PFZs) and brittle grain boundary fracture [18]. Because of its high Li content, the δ phase is also extremely reactive and can lead to localized pitting corrosion.

A common precipitation-hardening sequence in the Al-Cu alloy system is given by

\[ \text{GP zones} \rightarrow \theta'' \text{ (discs)} \rightarrow \theta' \text{ (plates)} \rightarrow \theta \text{ (Al}_2\text{Cu)} \]

[19]

While \( \theta'' \) and \( \theta \) are not commonly observed in aged commercial Al-Cu-Li alloys, \( \theta' \) plates are often present. The \( \theta' \) phase is tetragonal with lattice parameters of \( a=0.404 \) and \( c=0.580 \) nm [20]. Ma et al. found that the metastable, semicoherent \( \theta' \) phase was present in an Al-Cu-Li extrusion [16]. The orientation relationship of \( \theta' \) with the Al matrix is as follows: \{100\}_\theta //\{100\}_a \text{ and } <001>_\theta //<001>_a [17].

The orthorhombic metastable \( S' \) (Al\(_2\)CuMg) phase is known to form from GPB zones (Cu-Mg co-clusters) in Al-Cu-Mg alloys [14]. As a point of interest, \( S' \) is most prevalent in high Mg and low Cu alloys. In contrast, the alloys of interest to this study are low in Mg and high in Cu. Thus, while \( S' \) may form in Al-Cu-Li-Mg with low Mg and high Cu contents, the amount of \( S' \) is expected to be minimal. However, \( S' \) was observed in a selected area diffraction pattern (SADP) by Kumar et al. in an Al-Cu-Li-Ag-Mg-Zr alloy [21]. \( S' \) forms as laths along \{210\} habit planes and results in 420 streaks in \{100\}_Al and \{112\}_Al electron diffraction patterns [21] due to its thin dimensions.

During artificial aging of Al-Cu-Li alloys, the T\(_1\) (Al\(_2\)CuLi) phase may form. T\(_1\) is an important phase in third generation Al-Cu-Li alloys such as 2099 and 2196 because it tends to be the most potent strengthening phase [22]. Many authors have reported space group and atom position data for T\(_1\). It is commonly accepted that the T\(_1\) phase is hexagonal with a P6/mmm space group. However, the atom positions reported vary [23]–[25] and are provided in Table 2.1. The most likely positions and occupancies were provided by Donnadieu et al. [25]. The orientation relationship of T\(_1\) to the Al matrix is given by the following: \{0001\}_T)/\{111\}_a; <1\overline{1}0\overline{1}>_T)/\langle1\overline{1}0\rangle_A; <1\overline{1}0\overline{1}>_T)/\langle1\overline{1}0\rangle_A and the T\(_1\) phase is known to form thin plates on \{111\} habit planes in the fcc matrix [17].

Additions of Ag to Al-Cu-Mg alloys with high Cu/Mg ratio cause nucleation of the \( \Omega \) (Al\(_2\)AgMg) phase. The \( \Omega \) phase is coherent and forms as uniformly dispersed thin plates on \{111\}_a planes [9]. Reporting on the \( \Omega \) phase has not been consistent; the \( \Omega \) phase has been described as monoclinic [26], hexagonal [3], orthorhombic [27], and tetragonal [28]. The most accepted structure was given by Knowles and Stobbs [27], who described \( \Omega \) as orthorhombic with lattice parameters of \( a=0.496 \) nm, \( b=0.859 \) nm, and \( c=0.848 \) nm. The orientation relationship of \( \Omega \) to the \( \alpha \) matrix is given as follows: \{001\}_\Omega//\{111\}_\alpha; \{010\}_\Omega//\{1\overline{1}0\}_\alpha; \{100\}_\Omega//\{1\overline{2}1\}_\alpha. \) However, an alternative hexagonal structure has received attention in the literature for Al-Cu-Li-Mg-Ag alloys. Rioja et al. [3], describe \( \Omega \) as isomorphous and isostructural with the T\(_1\) phase with Ag atoms substituting for Cu and Mg for Li.
The Ω phase is thought to precipitate on Ag-Mg co-clusters in Al-Cu-Mg-Ag alloys. Three dimensional atom probe (3DAP) studies report that Ag and Mg atoms form co-clusters in as early as 5 seconds when aging at 180°C [29]. However, in light of Ag-Mg co-clustering acting as a nucleation mechanism for Ω, it is not likely that Ω forms at all in Li-containing alloys. 3DAP studies conducted by Hono et al. [29] and Honma et al. [30] show no evidence of Ag-Mg co-clusters forming in alloys containing Li. Additionally, by comparing high-resolution TEM images of an alloy containing Li (1.25%) to an alloy with no Li, Ω was found only in the alloy without Li [31].

<table>
<thead>
<tr>
<th>#</th>
<th>Structure</th>
<th>Lattice parameter (nm)</th>
<th>Multiplicity/Wyckoff letter</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>1</td>
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<td>[23]</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>1b</td>
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<td>0</td>
<td>1/2</td>
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<td></td>
<td></td>
<td>2c</td>
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<td>0</td>
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<td></td>
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<td>2d</td>
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<td>2/3</td>
<td>1/2</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>6i</td>
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<td></td>
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<td>44.4% Al</td>
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<td>0</td>
<td>0.2363</td>
<td>55.6% Cu</td>
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</tbody>
</table>

If Ag-containing Ω does not form in Al-Cu-Li alloys, it is unclear why Ag is added to some third generation Al-Li alloys since Ag additions to Al-Li alloys without Mg do not aid in T₁ distribution [32]. However, in Al-Li alloys containing Mg, Ag additions are reported to increase the amounts of GP zones and T₁ [32]. Research by Khan et al. [33] supports the conclusion that Ag aids in T₁ formation in Mg-containing Al-Li alloys. One possible mechanism for the nucleation of T₁ is that Ag and Mg reduce stacking fault energy and promote {111}_Al stacking faults on which it is speculated that T₁ forms [34]. Additionally, 3DAP studies have reported segregation of Ag and Mg atoms at the T₁/α-Al interface [29], [35], suggesting that Ag plays a role in T₁ evolution. In part, alloys 2099 and 2196 were chosen because
2196 contains Ag additions whereas 2099 does not; one component of this research was to identify the effects of Ag on the properties of these alloys.

### 2.2.3 Impurity Constituent Phases

Fe, Si, Na, K, and Ca are common impurity elements in commercial aluminum alloys with Fe and Si being the most prevalent. These elements can form coarse impurity phases that develop during solidification and are insoluble in Al during solution treatments. Common impurity phases include \( \text{Al}_6(\text{Fe,Mn}) \), \( \text{Al}_2\text{Fe} \), \( \text{Al}_7\text{FeCu}_2 \), and \( \alpha-\text{Al}(\text{Fe,Mn,Si}) \) [19]. These impurity phases tend to be found on grain boundaries in wrought alloys and can be detrimental to mechanical properties, fracture toughness, and corrosion properties.

### 2.3 Stretch Forming and the Effects of Cold Work Prior to Artificially Aging

Stretch forming is a process of forming by the application of primary tensile forces. This technique is used extensively in the aircraft industry to produce parts with large radii of curvature, such as contoured sections of the fuselage frame. A diagram demonstrating the stretch forming process is provided in Figure 2.2 [36]. Stretch forming of Al-Li extrusions and plate product is performed prior to artificial aging and can add up to 7% additional deformation. Al-Li alloys 2099 and 2196 are typically provided with at least 2.5% nominal strain (T3-type temper); including the strain accumulated during stretch forming, the total amount of deformation can reach 9.5% in some areas of stretch formed components.

![Figure 2.2](image-url)  
**Figure 2.2** Representative diagram of the stretch forming process [36].
It is accepted that heterogeneous nucleation of $T_1$ precipitates occurs at dislocations, and in Mg-containing alloys, on octahedral loops and Mg-enriched $\{111\}$ GP zones [32]. To enhance $T_1$ precipitation by introducing dislocations, Al-Li alloys are often cold worked prior to artificial aging [37]. Straining prior to aging also promotes a more even distribution of the $T_1$ phase and reduces precipitation of $T_1$ at grain boundaries [38]. A study examining the effect of plastic deformation on $T_1$ precipitation demonstrates that deformation prior to aging speeds up $T_1$ aging kinetics, improves yield strength, and increases the total volume fraction of $T_1$ (Figure 2.3) [39].

![Figure 2.3](image)

**Figure 2.3** Effect of pre-deformation and aging at 190°C on (a) yield stress and (b) $T_1$ number density of an Al-2.45Li-2.45Cu-0.18Zr alloy [39].

Ringer et al. [37] suggested that deformation prior to artificial aging promotes $T_1$ formation at the expense of the $\delta'$ phase in Al-Cu-Li alloys and at the expense of $\delta$, $O'$, and $S'$ in Al-Cu-Li-Mg-Ag alloys. The volume fraction of $\Omega$ in an Al-Cu-Mg-Ag was found to decrease with cold work prior to artificial aging, which suggests that the nucleation mechanism for $\Omega$ is different from that of $T_1$. A potential explanation for the decrease in $\Omega$ is that dislocation movement disrupts the Ag-Mg clustering necessary for $\Omega$ formation [37]; it is speculated from 3D Atom Probe (3DAP) studies that Ag-Mg clusters act as nucleation sites for $\Omega$ precipitates [30]. However, in accordance with the previous discussion, $\Omega$ most likely does not form in alloys containing Li.

While cold working prior to aging does improve the strength of Al-Li alloys, too much cold work may be detrimental to mechanical properties. It is accepted that the effect of strain on aging response diminishes as the amount of cold work exceeds 4% [40]. Liang et al. discovered that increasing pre-
deformation beyond 5% in an Al-Cu-Li-Zr alloy containing Sc causes the T1 phase to coarsen, does not continue to increase strength, and decreases ductility [41]. It is also worth mentioning that, because strain can have a pronounced effect on the aging response of Al-Li alloys, inhomogeneous distributions of strain can cause local differences in strength [40] and potentially other properties, such as corrosion resistance.

One goal of this study is to examine the effects of strain on the mechanical and corrosion properties of 2099 and 2196 to evaluate improvement and degradation of properties based on the amount of strain received. In addition to measuring bulk strain across a gage section with an extensometer, micro-strain evolution was tracked using 2D micro-digital image correlation (DIC).

2.4 Corrosion

Due to the reactive nature of Li, the corrosion properties of third generation Al-Li alloys must be carefully examined, especially since the second generation alloys exhibited low stress corrosion cracking (SCC) thresholds in the long transverse (LT) and short transverse (ST) directions. In comparison, third generation Al-Li alloys have better corrosion resistance, especially for peak-aged and overaged tempers. SCC thresholds were greater than those of 7XXX series alloys, such as 7050-T7451, when tested by alternate immersion in salt water. Third generation Al-Li alloys also exhibit high exfoliation corrosion resistance [3]. However, further improvement of corrosion properties is desirable given that cladding needed for corrosion protection is unnecessary for Al alloys with sufficient corrosion resistance; low-strength cladding adds extra weight to aircraft components and decreases fatigue performance [9].

Third generation Al-Li alloys are sensitive to three forms of localized corrosion: pitting, intergranular attack, and exfoliation [10]. Modified ASTM acetic acid salt spray intermittent tests (MASTMAASIS) were performed on over 200 production lots of Alloy 2099, and all lots received ratings of P or EA [3], indicating pitting corrosion and exfoliation corrosion should be closely considered when evaluating corrosion resistance of third generation Al-Li alloys.

This research aims to identify the type(s) of corrosion present in aged 2099 and 2196 alloys with various levels of deformation prior to artificial aging. Furthermore, the mechanism(s) of corrosion must be understood in order to provide meaningful recommendations for corrosion improvement.

2.4.1 Pitting Corrosion

Pitting corrosion is a localized form of attack that is caused by the localized breakdown of a passive oxide film, such as Al2O3. This type of breakdown occurs at many different surface discontinuities, is often unpredictable, and results in relatively fast and localized penetration [42]. Alkaline solutions containing chloride are known to cause pitting in Al alloys and, for this reason, pitting
corrosion can be a problem for Al alloys in marine environments. For example, pitting corrosion was the only form of corrosion observed after 2099 was exposed to a seacoast environment for 19.1 years at Point Judith, RI [3].

Mechanistically, the interior of the pit acts as an anode and the exterior surface acts as a cathode. The interior of the pit becomes acidic from corrosion products, and the acidic content is maintained inside the pit because the pit provides a sheltered region where mass transport is difficult. The surrounding surface becomes the cathode by reduction of dissolved oxygen [42].

In appearance, pits may be shallow, elliptical, deep, undercut, or subsurface [43]. Pit shapes depend specifically on microstructure, chemistry, and environment. Additionally, pits may follow specific metallurgical features [42]. Considering third generation Al-Li alloys in commercial tempers (T83/T86), pits were elongated in the rolling direction when alloys were tested by ASTM G110 [44] and GB 7998-97 [45]. Elongated pitting is exemplified in Figure 2.4.

![Figure 2.4](image)

Figure 2.4  Elongated pitting corrosion morphology of 2099 in the T8 condition (aged at 150°C for 6 h) [45].

The elongated corrosion features sometimes observed in third-generation Al-Li alloys are pits and should not be confused with intergranular stress corrosion cracks (IGSCC). C-ring and mini direct tension SCC specimens under load showed the same elongated pits as direct tension specimens that were not loaded [44]. Furthermore, there were no SCC failures of 2X99-T86 samples loaded at 40 and 50 ksi for several years at Point Judith [46].

2.4.2  Intergranular and Exfoliation Corrosion

A second type of corrosion, exfoliation, occurs at the boundaries of the elongated grains that result from rolling or extruding during manufacturing. The main mechanism proposed to explain the onset
of intergranular corrosion in Al-Li alloys is the formation of galvanic couples between grain boundary precipitates, such as $T_1$ ($Al_2CuLi$) and precipitate free zones [47]. As corrosion at grain boundaries proceeds, larger volume corrosion products accumulate inside the grain boundaries and exert pressure on the outer grains causing them to be lifted from the metal surface (i.e., to exfoliate) [48]. An example is provided in Figure 2.5.

![Figure 2.5](image)

**Figure 2.5** Example of exfoliation corrosion in a peak-aged Al-Li alloy after immersion in EXCO solution (4.0 M NaCl + 0.5 M KNO$_3$ + 0.1 M HNO$_3$) for 96 h [49].

Constant immersion exfoliation corrosion (EXCO) testing was performed on 2$^{nd}$ generation Al-Li-Cu alloys [50] and Al-Li-Cu-Mg alloys [51], [52]. These findings suggested that the depth of attack and exfoliation corrosion susceptibility increases with artificial aging time. Thus, underaged conditions were least susceptible, peak-aged conditions were more susceptible, and overaged conditions were most susceptible to exfoliation corrosion. However, the visual ratings after EXCO testing fail to correlate with findings from natural environments.

Less aggressive MASTMAASIS tests used by Boeing and ALCOA are correlate well with tests performed in environments representative of in-service conditions, such as the tests performed by Colvin and Murtha [53]. It has been strongly recommended that investigators use MASTMAASIS testing instead of EXCO testing on Al-Li alloys when studying exfoliation corrosion behavior [9]. MASTMAASIS tests on peak-aged tempers exhibited little exfoliation corrosion susceptibility while underaged and overaged tempers were more susceptible.

In one study, third generation Al-Li alloys were shown to exhibit intergranular exfoliation corrosion for underaged tempers per ASTM G110 whereas peak-aged and overaged tempers were not susceptible to exfoliation corrosion and only exhibited pitting corrosion [44].
2.5 Characterization

In this research, advanced characterization techniques are utilized, and this section serves to help the reader gain familiarity and understand the fundamentals of a few of these techniques. In particular, electron backscatter diffraction (EBSD), 2D micro-digital image correlation (DIC), and scanning Kelvin probe force microscopy (SKPFM) will be discussed because these techniques are being used to examine the effects of orientation, micro-strain evolution during straining, and surface potential on corrosion, respectively. Lastly, tapping mode AFM in solution will be discussed since corrosion is being monitored in-situ by this method.

2.5.1 Electron Backscatter Diffraction (EBSD)

EBSD is a crystallographic characterization technique that takes place in a scanning electron microscope (SEM) equipped with an EBSD detector. EBSD relies on a combination of elastic and inelastic scattering of electrons within a specimen interaction volume. When electrons are directed onto a specimen from the SEM electron source, some electrons are inelastically scattered by atoms in the material, and many of the inelastically scattered electrons subsequently scatter at the Bragg condition for specific planes. The backscattered electrons form two Kikuchi lines per plane, and the spacing between the lines corresponds to the interplanar spacing of the planes. Two lines from the same planes are referred to as a Kikuchi band. Bands from different planes intersect according to their interplanar angles, and collectively, all of the bands intersecting for a given orientation are known as Kikuchi patterns (Figure 2.6). Kikuchi patterns are recorded on a phosphor screen of an EBSD detector and automatically analyzed by software to provide information about the crystal structure, orientation, and texture of the phases present in the specimen [54].

In this research, EBSD was used to collect inverse pole figure maps and image quality maps prior to and after straining. Inverse pole figure maps are used to discern grain orientations and image quality maps highlight grain boundaries and local strains that disrupt the perfect crystalline lattice and therefore degrade the quality of the Kikuchi patterns captured locally.

EBSD is also capable of identifying submicron areas of concentrated strain. It may be possible to evaluate elastic strain through image quality maps, and plastic strain by image quality, local misorientation, grain orientation spread, kernel orientation spread, kernel average neighbor misorientation, kernel average center misorientation, and/or reference orientation deviation [55].
2.5.2 2D Micro-Digital Image Correlation (DIC)

DIC is a technique for analyzing two or more images of the same area after some change and extracting a displacement field that relates the images [56]. For this research, 2D micro-digital image correlation is being used to determine deformation during straining. A DIC camera monitors in-plane displacement as a specimen is pulled in uniaxial tension to simulate the stretch forming process used in industry. The setup used is depicted schematically in Figure 2.7.

In principle, DIC requires the use of a random grayscale intensity distribution, such as a speckling pattern. This pattern must deform together with the specimen surface. Pixel subset arrays, or facets, are
tracked from image to image during deformation, and each facet should contain several speckling features/particles. Facets are tracked instead of individual pixels because there is more variation in grayscale intensity from facets than from single pixels. This allows for a more unique identification of the deformed surface [58].

Full field strain measurements relate facets in a reference image (i.e. before strain) to the same facets after deformation and are used to determine strains (Figure 2.8). To compute full field strain measurements, vector displacement components are defined for each point within a facet. Points may be sub-pixel size; interpolation is used to determine a grayscale intensity level between pixels. Next, the displacement components can be solved for by using a cross-correlation criterion or sum-squared difference criterion. Optimal function parameters allow every point within a facet, in both the reference and deformed images, to be recognized [59].

![Figure 2.8](image.png)

Figure 2.8  Schematic relating a facet in (a) a reference image to (b) the same facet after deformation [58].

### 2.5.3 Scanning Kelvin Probe Force Microscopy

Scanning Kelvin probe force microscopy (SKPFM) has recently become a more widespread technique used in corrosion studies. The findings of [60]–[62] relate work function differences between various metals or within a given alloy (i.e. between a precipitate and the matrix) to corrosion behavior. SKPFM is performed in two scan passes on an atomic force microscope (AFM). During the first pass, the AFM measures and records the sample surface topography using the tapping mode. In the second pass, the tip is lifted a selected distance above the recorded surface topography and the Volta potential difference between the tip and sample is measured. The two measurements are then interleaved, i.e., the
two images, one of topography and one of Volta potential difference, are displayed simultaneously. The Volta potential difference is directly proportional to the work function difference. If the work function of the tip is known, a work function map of the material can be developed. Often times, Volta potential or work function measurements recorded from this technique are referred to as surface potentials.

During standard tapping mode AFM, the cantilever is vibrated near its resonant frequency by a piezoelectric element. For detection of the Volta potential difference and to avoid cross-talk of the two different feedback loops, the piezoelectric element is turned off and an oscillating AC voltage is applied directly to the cantilever tip. At this point, a DC voltage difference exists between the sample and the tip. The DC voltage on the tip is adjusted until the amplitude of oscillation is zero and the cantilever feels no oscillating force, indicating that the tip and sample are at the same DC voltage. At this point, the voltage on the tip is recorded [63].

These differences in work function due to second phase particles may lead to localized corrosion (i.e. pitting and exfoliation corrosion) [60]. See Figure 2.9. In this research, the SKPFM technique is being used to investigate work function differences caused by inhomogeneous strain, second phases, grain boundaries, etc.

![Figure 2.9](image.png)

**Figure 2.9** Potential difference across a second phase particle in AA2024 as measured by scanning Kelvin probe force microscopy [60].

However, it is important to recognize that the SKPFM measurements in air may not relate to the corrosion behavior that occurs due to the formation of galvanic couples in solution. Corrosion depends closely on the environment [64] such that, without performing SKPFM in a corrosive solution of interest, it may be irrelevant to compare work function data to corrosion behavior. Additionally, it is inherently difficult to conduct SKPFM in a corrosive solution because ions from an electrolyte can screen the field from a conductive AFM tip. Coaxial AFM tips have been developed to mitigate this problem [65] but are not yet commercially available.
Even if SKPFM could be performed in a corrosive solution with a coaxial AFM tip, the Volta potential difference found by SKPFM is directly proportional to corrosion potential only in the same electrolyte solution over a homogeneous metal without galvanic coupling [66]. Since this research aims to study micro-scale galvanic coupling, Volta potential differences may not relate to corrosion potential in this situation.

2.5.4 In-Situ Tapping Mode AFM

An alternate technique, in-situ tapping mode AFM, was used to study pitting and exfoliation corrosion behavior. In this method, tapping mode AFM topography scans are taken across a specimen surface in a corrosive solution (i.e. artificial seawater) after SKPFM measurements have been taken in air. The in-situ tapping mode topography scans should indicate, on a small scale (<30 nm), the site of corrosion initiation or pitting. If the topography scans are taken consecutively and quickly, the scans should also provide information about the rate of corrosion and the direction in which corrosion proceeds.

In-situ tapping mode AFM was performed on the same area examined by EBSD, DIC, SEM, and SKPFM. The location of initiation and advancement of corrosion may correspond to known orientation, strain, and/or microstructural features.
CHAPTER 3: EXPERIMENTAL METHODS

This chapter describes the experimental set-up for the primary experimental pathway and additional experimental procedures. Concerning the primary experimental pathway, specific regions were monitored throughout their thermomechanical history. This chapter details specimen preparation from the as-received material and provides information on characterization techniques and parameters. To support findings from the primary experimental pathway, additional experimentation was necessary, and the methods for these experiments are also described.

3.1 Primary Experimental Pathway

The effects of various amounts of strain (0-9%) in 2099 and 2196 were examined by characterizing single, specific regions. The site-specific examination serves as the primary framework for this study. As-received extrusions were sectioned into tensile bars and one 90 by 90 µm region on the surface of each tensile bar was tracked at various points throughout its thermomechanical history. Considering the temperature vs. time diagram in Figure 3.1, electron backscatter diffraction (EBSD) was performed following solution heat treatment. During straining, 2D micro-digital image correlation (DIC) was used to examine micro-strain evolution of the same region. Next, tensile bars were artificially aged by a two-step aging treatment, and the following techniques were performed, respectively: EBSD, backscattered electron (BSE) imaging, and scanning Kelvin probe force microscopy (SKPFM). Finally, the region of interest was examined by in-situ tapping mode atomic force microscopy (AFM) during corrosion.

In this section, the experimental procedure for each step of the process is described in detail.

3.1.1 Tensile Specimen Preparation

Extrusions of Alloy 2099 in the T83 (solution heat treated, cold worked, and peak aged) condition and Alloy 2196 in the T3511 (solution heat treated and stress relieved by minor amount of strain) condition were provided by Boeing. Tensile specimens were sectioned using an MSX saw and end-milled to achieve parallel sides. Twelve tensile specimens (6 for each alloy) were machined for the following strain conditions: 0, 1, 2, 3, 6, and 9%. Although initial dimensions were identical, specimens set aside for 6 and 9% strains were given a 50.8 mm (2 in) reduced gage section to prevent these specimens from fracturing in the tensile frame grips. The orientation of the tensile specimens with respect to the extrusion
direction is provided in Figure 3.2 and the geometry is detailed in Figure 3.3. The longitudinal direction corresponds to the tensile axis during straining.

![Figure 3.1](image1.png)

**Figure 3.1** Schematic temperature vs. time diagram indicating the thermomechanical processing steps as well as the sequence of characterization (gray) techniques used to analyze identical regions of the same specimen.

![Figure 3.2](image2.png)

**Figure 3.2** Extruded shape provided by Boeing indicating tensile specimen sectioning with respect to reference directions. Polished plane is highlighted in gray.
Figure 3.3 Tensile specimens for (a) 0, 1, 2, and 3% strain conditions and (b) 6, and 9% strain conditions with (c) specimen dimensions for 6 and 9% strain conditions labeled in mm. Disregarding the reduced gage section, dimensions for 0, 1, 2, and 3% specimens are the same as in (c).

Solution heat treatment and artificial aging times and temperatures were provided by Boeing and Alcoa per AMS 2772E. Solution heat treatment was performed at 549 °C for 2 h followed by a water quench. The furnace temperature was monitored using a Type K thermocouple and found to be within ±2.0 °C of the temperature reading on the furnace. After solution heat treatment, the short transverse-longitudinal (S-L) planes of the tensile specimens were mechanically polished because it was of interest to examine elongated pitting in the extrusion direction and the short transverse fracture toughness is of concern in Al-Li alloys. After many unsuccessful polishing attempts, instructions for mechanical polishing were established with help from both Weber Metal and George Vander Voort and are provided in Table 3.1.

<table>
<thead>
<tr>
<th>Step</th>
<th>Media</th>
<th>Polishing Cloth</th>
<th>Duration (min)</th>
<th>Lubricant</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grinding</td>
<td>800 grit SiC paper</td>
<td>N/A</td>
<td>10</td>
<td>Water</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>1200 grit SiC paper</td>
<td>N/A</td>
<td>15</td>
<td>Water</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>3 µm diamond suspension</td>
<td>Nylon</td>
<td>60</td>
<td>Alcohol based</td>
<td>150</td>
</tr>
<tr>
<td>Polishing</td>
<td>0.3 µm Al₂O₃ paste</td>
<td>Low napped synthetic rayon flock</td>
<td>5</td>
<td>DI Water</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>0.05 µm colloidal SiO₂</td>
<td>Low napped synthetic rayon flock</td>
<td>3</td>
<td>N/A</td>
<td>100</td>
</tr>
</tbody>
</table>
In between each polishing step, specimens were rinsed thoroughly with methanol, gently rubbed with methanol-soaked cotton balls, and briefly sonicated in methanol to ensure no residual SiC particles or polishing agents were transferred to the next polishing step. A typical surface following mechanical polishing is shown in Figure 3.4.

![Figure 3.4 Optical micrograph of surface of 2099 after mechanical polishing. Scratches, pits, and deformation from mechanical polishing are present but minimal.](image)

3.1.2 Final Polishing for Electron Backscatter Diffraction (EBSD)

After mechanical polishing, surface finishes of 2099 and 2196 were insufficient for high confidence interval EBSD imaging. Unfortunately, final polishing with 0.05 µm colloidal SiO₂ on a vibratory polisher led to severe pitting of 2196 and 2099.

Experiments were conducted to determine whether the surfaces of both alloys could be adequately prepared by electropolishing. As a first electropolishing attempt, samples ground to 1200 grit as well as mechanically-polished samples were exposed to a 30% HNO₃/70% methanol electrolyte held at -30°C. Voltages between 5 V and 20 V were applied to each sample, and the resulting surfaces were examined by optical microscopy. All sample surfaces were inadequate and appeared eroded and/or etched (e.g., Figure 3.5).

As a second attempt, the same electropolishing experiment was conducted using a 12.5% H₂SO₄/87.5% methanol solution at room temperature. Again, all sample surfaces were inadequate. Many samples were tarnished and had evidence of pitting and/or etching, as exemplified in Figure 3.6. Although the sample of Figure 3.6 is etched and pitted, this sample had the best surface finish of all samples electropolished in the 12.5% H₂SO₄/87.5% methanol solution.
Figure 3.5 Optical micrographs showing inadequate surface preparation of 2099 after electropolishing in 30% HNO₃/70% methanol electrolyte at -30°C with a voltage of 8.4 V. Samples were (a) mechanically polished to 0.05 µm and (b) ground to 1200 grit prior to electropolishing.

Figure 3.6 Optical micrograph showing inadequate surface preparation of 2099 after electropolishing in 12.5% H₂SO₄/87.5% methanol at 21°C with a voltage of 23 V for 3 s.

Due to the shortcomings of electropolishing, an alternate approach to final polishing was taken, and final polishing was performed in an FEI Helios NanoLab™600i DualBeam focused ion beam (FIB)/scanning electron microscopy (SEM) by ion milling. Tensile specimens were positioned according to Figure 3.7, such that mechanically polished surfaces (S-L planes) were 10° offset from parallel to the focused Ga⁺ ion beam. Regions of approximately 200 µm x 200 µm with depths of approximately 1 µm were milled into the mechanically polished area with an operating beam current of 33 pA and voltage of 20 kV.

Tensile specimens were milled away from edges or scratched regions to avoid curtaining and were polished with shallow depths at low currents to avoid excess milling. Examples of unacceptable and acceptable milling are shown in Figure 3.8.
Figure 3.7  Diagram of tensile specimen orientation during Ga⁺ ion polishing in (a) 2D and (b) 3D.

Figure 3.8  Secondary electron images taken after ion milling demonstrating (a) curtaining, (b) excess milling, and (c) shallow milling where (c) is the only acceptable preparation for EBSD.
3.1.3 Electron Backscatter Diffraction (EBSD) and Marking the Region of Interest

EBSD was performed in an FEI Helios NanoLab™ 600i DualBeam focused ion beam (FIB)/scanning electron microscopy (SEM) equipped with an EDAX “Hikari Super” 1400pps EBSD detector operating at 30 kV and 22 nA. Tensile specimens were secured to pin stubs with electrically conductive tape and mounted on a 70° tilt holder.

Following final polishing by ion milling, polished surfaces were aligned to face the EBSD detector and polished regions were brought to working distances of 6 mm. EBSD scans of approximately 150 µm x 150 µm were collected with a camera binning of 8 x 8 and step sizes of 0.3 µm using EDAX’s OIM™ Data Collection Software. The Hough parameters used for all scans are provided in Table 3.2.

Table 3.2 – Hough Parameters for EBSD in EDAX’s OIM™ Data Collection Software

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hough Type</td>
<td>Classic +</td>
</tr>
<tr>
<td>Hough Resolution</td>
<td>High</td>
</tr>
<tr>
<td>Binned Pattern Size</td>
<td>96</td>
</tr>
<tr>
<td>Theta Step Size</td>
<td>1</td>
</tr>
<tr>
<td>Rho Fraction</td>
<td>95%</td>
</tr>
<tr>
<td>Max Peak Count</td>
<td>7</td>
</tr>
<tr>
<td>Min Peak Count</td>
<td>3</td>
</tr>
<tr>
<td>Convolution Mask</td>
<td>9x9 (Medium)</td>
</tr>
<tr>
<td>Min Peak Magnitude</td>
<td>5</td>
</tr>
<tr>
<td>Min Peak Distance</td>
<td>15</td>
</tr>
<tr>
<td>Peak Symmetry</td>
<td>0.5</td>
</tr>
<tr>
<td>Vertical Bias</td>
<td>3%</td>
</tr>
<tr>
<td>Min Peak Magnitude</td>
<td>30</td>
</tr>
<tr>
<td>Max Band Width (% of Image)</td>
<td>10%</td>
</tr>
<tr>
<td>Max Angular Difference Between Edges</td>
<td>2.0°</td>
</tr>
</tbody>
</table>

After EBSD patterns were collected, tensile specimens were rotated 180° and tilted 60° to allow regions from where EBSD scans were collected to be imaged using the Ga⁺ ion column operating at low current (33 pA) in the FIB/SEM. At this point, EBSD scan regions could be easily identified by beam-related contamination (i.e. carbon deposition on the sample where the electron beam was scanning). Four fiducial markers of approximately 10 µm x 10 µm with depths of 5 µm were milled at the four corners of EBSD scans. Fiducial markers were milled to minimize the challenge of locating the same regions from technique to technique throughout the thermal processing route detailed in Figure 3.1. Fiducial markers served as guides to follow the regions of interest.
EBSD was performed a second time on each tensile specimen, directly following 2D micro-
digital image correlation (DIC) and artificial aging. Second EBSD scans were taken within the regions
marked by fiducial markers, and all scan parameters matched EBSD parameters used prior to DIC.

All EBSD maps were created using EDAX’s OIM™ Analysis Software. No post-scan software
clean-up was applied to any of the EBSD data reported as part of this research.

3.1.4 2D Micro-Digital Image Correlation (DIC)

Tensile specimens were loaded into an MTS Alliance RT/100 screw driven static test system with
the polished S-L plane of the tensile specimens facing parallel to the grips. Gage lengths during straining
were 25.4 mm (1 in), and total strain amounts across gage lengths were measured with an extensometer.

DIC was performed on the polished plane of the tensile specimens during deformation with a K-2
DistaMax Infinity Long-Distance Microscope equipped with a 20X Mitutoyo objective lens. The
microscope was mounted on a tripod and GOM’s Aramis software was used to analyze the images
collected by the microscope. The set-up is shown in Figures 3.9 and 3.10.

Prior to straining, regions of interest were located using the K-2 DistaMax camera and speckled
with 0.05 µm Al₂O₃ non-agglomerated powder in ethanol using an airbrush powered by an air
compressor. Regions of interest were identified by four fiducial markers, as described in Section 3.1.3.
Figure 3.11 demonstrates the effect of speckling on image contrast. Upon speckling, 10 DIC images were
taken and run through the Aramis software. In the event that the software could not identify an
appropriate facet size or calculate a complete solution for each image, the speckling pattern was removed
with a cotton ball soaked in ethanol, and a new speckling pattern was applied.

During straining, the z-height was adjusted to incorporate the same microstructural and speckling
features as imaged prior to deformation. Images were taken at 20 evenly spaced strain increments, as
recorded by the macro-extensometer, per specimen. Many images (20-100) were taken for each strain
increment because vibrations caused the microscope to go in and out of focus. All of the images were
analyzed by the Aramis software, and only the highest quality image, allowing minimum facet size and
lowest interpolation area, was selected for each strain increment for the DIC analysis. Additionally, strain
maps from each increment were compared to previous and subsequent increments as a precaution against
inconsistent, false image artifacts. Outliers containing inconsistencies were excluded from consideration
for each strain increment. Upon completion of the DIC measurements, the speckling pattern was removed
from each specimen.

A simple strain rate sensitivity study was conducted to determine whether the pause during
straining to capture images at each strain increment had an effect on the total amount of stress received
for each strain condition. A constant strain rate of 0.09 in/min was compared to the inconsistent strain rate during DIC for 2099 and 2196 strained to 3% total strain, and the results are compared in Figure 3.12. Examining stresses at the same strains reveal that the stress achieved during the constant strain rate test and the stress throughout the DIC test are in close agreement. This indicates that strain rate sensitivity is not of concern in 2099 and 2196, and taking images at fixed increments is a valid experimental approach.

Figure 3.9 K-2 DistaMax Infinity Long-Range Microscope used for acquisition of DIC images.
Figure 3.10  Tensile specimen set-up for simultaneous straining and DIC imaging.
Figure 3.11  Microstructure of 2196 T4 tensile specimen prior to deformation imaged by (a) secondary electrons in a scanning electron microscope (SEM), (b) a K-2 Distamax camera with a 20X objective, and (c) a K-2 Distamax camera with a 20X objective after speckling the surface with Al$_2$O$_3$. 
Figure 3.12 Stress vs. strain for constant strain rates of 0.09 in/min and inconsistent strain rates during DIC testing. Strain rate sensitivity is not of concern in 2099 and 2196 since stress is similar at each strain.

3.1.5 Environmental Scanning Electron Microscopy (ESEM): Backscattered Imaging

Backscattered images were taken in an FEI Quanta 600i environmental scanning electron microscope (ESEM). Coarse Fe, Cu, and Mn-containing impurity phases appear lighter than the matrix when imaged in backscattered mode since elements of higher atomic number backscatter more strongly than elements with low atomic number.

Images were acquired for all strain conditions for both alloys after artificial aging, and the area of interest was identified by the ion milled fiducial markers described in Section 3.1.3.

3.1.6 Atomic Force Microscopy (AFM): Scanning Kelvin Probe Force Microscopy (SKPFM)

All AFM measurements were taken using an Asylum Research MFP-3D-Bio AFM. SKPFM measurements were taken using Version 14 of the Asylum Research AFM software by selecting SKPM under the Electrical category in the ModeMaster. BudgetSensors ElectriTap190-G conductive AFM probes were used. These probes are Si, coated on both sides of the cantilever with 5 nm Cr covered with 25 nm Pt, have tip radii less than 25 nm, and have resonant frequencies of approximately 190 kHz. Probes
were positioned to measure within areas of ion milled fiducial markers using the MFP-3D optical microscope.

Smaller specimens containing regions of interest were sectioned from larger tensile bars per Section 3.2.1. All specimens containing regions of interest were plasma cleaned with an EVACTRON CombiClean Decontaminator for 30 min prior to imaging with the AFM. The Decontaminator removes C deposition from electron backscatter diffraction (EBSD) as well as other contamination picked up during testing. Specimens were secured to an electrically insulated glass side with double-sided tape, and magnets were used to fix the glass slide to the AFM stage. Specimens were grounded to the AFM stage by an insulated wire that was attached to specimens with electrical tape and fixed to the AFM stage with a magnet, as demonstrated in Figure 3.13. Electrical grounding was connected far away from the conductive AFM probe to avoid cross-talk or electrical interference.

![SKPFM set-up showing specimen grounded to AFM stage.](image)

For SKPFM measurements, the AFM tip was biased 7 V. The nap/lift height during the second pass was 40 nm, and the largest scan size possible (90 µm x 90 µm) was acquired at a rate of 0.3 Hz within regions of interest. To precisely identify areas examined by SKPFM, optical images were taken showing cantilever positions above specimen surfaces at the beginning and end of each scan.

SKPFM measurements were taken in repulsive mode by keeping the phase signal below 90°, and the set-point voltage, drive amplitude, and integral gain were adjusted until trace and retrace signals closely matched without producing large oscillations/noise in the feedback loop.

### 3.1.7 Atomic Force Microscopy (AFM): In-situ Tapping Mode Topography during Corrosion

Tapping (AC) mode imaging in liquid was used to examine corrosion in-situ. The corrosive solution used was artificial seawater per ASTM D1141-98(2013). Olympus model TR800PB probes with
spring constants near 0.61 N/m, resonances frequencies of approximately 68 kHz, and silicon nitride tips with reflex coatings of 5 nm Cr covered with 50 nm Au were chosen due to their relatively high stiffness and Au coating for corrosion resistance in solution.

Specimens were prepared by sectioning with a slow speed diamond saw to thicknesses of approximately 1 mm. A small piece of low napped synthetic rayon flock held on with conductive tape was used to protect the region of interest during sectioning to prevent corrosion from the cutting lubricant, and the rayon flock was removed after sectioning. Specimens were rinsed with de-ionized water and isopropyl alcohol and plasma cleaned with an EVACTRON CombiClean Decontaminator for 30 min. Specimens were then glued, polished planes facing upwards, with a small dab of superglue to cylindrical Millipore petri dishes with diameters of 47 mm. Petri dishes were attached to the AFM stage with a magnetic petri dish holder, and the magnets of the holder were adjusted to keep petri dishes in place without allowing magnets to come in direct contact with the stage. The set-up is shown in Figure 3.14.

The same areas imaged by SKPFM were located using the optical images of probe positioning taken at the beginning and end of SKPFM imaging, as described in Section 3.1.6. One 90 µm x 90 µm scan was taken in air in traditional tapping mode. The set-point, drive amplitude, and integral gain were adjusted until the trace and retrace lines were in close agreement and the images collected appeared to match the topography images acquired during the first pass of SKPFM.

Once the initial parameters were set for tapping mode as described above, the AFM head was gently raised, the probe was pre-wet with a droplet of artificial seawater, and 2-3 mL of artificial seawater was added to the petri dish to entirely cover each specimen (Figure 3.15). A protective skirt holder was used to protect sensitive electronics in the AFM head (Figure 3.16). The AFM head was lowered into the solution in the petri dish, the laser was readjusted to maximize the sum signal, and the cantilever was retuned in solution before engaging the tip.
3.2 Additional Experimental Procedures

Additional experimentation was performed to support the findings of the primary experimental pathway. While the primary experimental pathway focused on single, specific regions, additional experiments examined other regions or samples. In this section, the sectioning of the tensile specimens...
after straining, Vickers hardness preparation, transmission electron microscopy (TEM) preparation, and bulk corrosion studies are described.

3.2.1 Tensile Specimen Sectioning

Provided that tensile specimens were strained to designated amounts between 0-9% and no specimens were loaded to failure, tensile specimens remained fully intact after straining. After 2D micro-digital image correlation (DIC) was performed during straining, specimens were sectioned parallel to the long-transverse reference direction, through the short transverse-long transverse (S-LT) plane, using an MSX saw. Regions of interest, marked with ion-milled FIB fiducial markers, were protected by a low napped rayon flock cloth held on with electrical tape to prevent scratches and corrosion during sectioning.

Each tensile bar was cut into seven sections, excluding material which was in the tensile frame grips. One section contained the area of interest and, concerning the remaining six sections, two sections were set aside for hardness measurements, two for transmission electron microscopy (TEM) foils, and two for bulk corrosion studies. From each original tensile bar, the section containing the area of interest, one section for hardness measurements, one section for TEM foils, and one section for bulk corrosion were artificially aged at 121°C for 12 h followed by 151°C for 48 h. The artificial aging treatment was designed to age alloys to peak hardness; the first step of the aging treatment at lower temperature promotes GP zone formation. The other sections were not artificially aged. Sectioning of the tensile specimens is demonstrated in Figure 3.17.

Figure 3.17 Diagram of tensile specimen sectioning.

3.2.2 Vickers Hardness

Samples of each condition were cold mounted in epoxy and left to harden overnight under vacuum. Samples were then mechanically polished according to Table 3.1. Between each grinding step,
samples were rinsed in methanol, gently rubbed with a cotton ball and methanol, and briefly sonicated in methanol to ensure no residual SiC particles were transferred to the next step in polishing. At least 10 Vickers hardness measurements were taken for each condition per ASTM E92 using a load of 500 lbs and a dwell time of 10 s.

3.2.3 Transmission Electron Microscopy (TEM)

Thin sections were cut parallel to the long transverse reference direction, through the short transverse-long transverse (S-LT) plane, with an MSX saw. These sections were then cut parallel to the short transverse reference direction, through short transverse-longitudinal (S-L) plane, to thin along the long transverse direction. The sections were secured to flat aluminum stubs with superglue and mechanically ground to 1200 grit on both sides of the S-L plane, carefully ensuring that the samples were sonicated in between the grinding of each side in acetone to remove all superglue. 3 mm discs were punched and any burrs were ground down to 1200 grit.

The specimens were individually polished using a twin-jet electropolisher in a 30% nitric acid/70% methanol solution at -25°C and 25 V. The TEM specimens were examined using a Philips CM12 TEM at 120kV accelerating voltage.

3.2.4 Bulk Corrosion

Alternate immersion corrosion tests were performed on all 24 sections set aside for bulk corrosion studies where each condition is fully described by Table 3.3. Sections were cut with a slow speed saw to create bulk corrosion samples of equal total surface area and equal polished surface area. Samples were immersed in artificial seawater per ASTM D1141-98 for periods of 10 min and dried for 50 min. After the drying cycle, samples were thoroughly rinsed with deionized water to remove remaining NaCl and corrosion byproduct resting on the surface. Samples were imaged using an FEI Quanta 600i environmental scanning electron microscope (ESEM) in secondary mode. In particular, it was of interest to identify exfoliation and pitting corrosion features.

Following 3 h of alternate immersion, bulk corrosion samples were left in artificial seawater for 15 additional hours, at which point, samples were again dried and rinsed and examined by ESEM.
Table 3.3 – Bulk Corrosion of 2099 and 2196

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Strain (%)</th>
<th>Artificially Aged?</th>
</tr>
</thead>
<tbody>
<tr>
<td>2099</td>
<td>0</td>
<td>Y</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>Y</td>
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<td>6</td>
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<tr>
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<td>N</td>
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<td>N</td>
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<tr>
<td></td>
<td>9</td>
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</tr>
<tr>
<td>2196</td>
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</tr>
<tr>
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<td>Y</td>
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<tr>
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<tr>
<td>2196</td>
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<td>N</td>
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<td>N</td>
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<tr>
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<td>9</td>
<td>N</td>
</tr>
</tbody>
</table>
CHAPTER 4: RESULTS

The research findings are described based upon the characterization technique performed. For the primary experimental pathway, specimens were characterized by electron backscatter diffraction (EBSD), 2D micro-digital image correlation (DIC), backscattered electron (BSE) imaging, scanning Kelvin probe force microscopy (SKPFM), and in-situ tapping mode atomic force microscopy (AFM). Additional experiments studied Alloy 2099 and Alloy 2196 by Vickers hardness and TEM. Lastly, bulk corrosion properties were evaluated.

4.1 Primary Experimental Pathway

The site-specific examination described in Section 3.1 serves as the primary experimental framework for this research. Identical regions of twelve specimens (6 for Alloy 2099 and 6 for Alloy 2196) were examined by EBSD prior to straining, DIC during straining, and the following techniques after straining and artificially aging: EBSD, BSE imaging, SKPFM, and in-situ tapping mode AFM during corrosion. Strain conditions of 0, 1, 2, 3, 6, and 9% were examined for both alloys. The purpose of this section is to present the findings and observations associated with each site-specific characterization technique performed.

4.1.1 Electron Backscatter Diffraction (EBSD) Prior to Straining

As described in Section 3.1.2, final polishing for EBSD was performed in a focused ion beam (FIB)/scanning electron microscope (SEM) by ion milling a shallow depth with a low beam current. Ion milling following traditional mechanical polishing dramatically improved the image quality (IQ) of EBSD patterns. Figure 4.1 compares inverse pole figure (IPF) maps overlaid on IQ maps prior to ion milling to IPF + IQ maps after ion milling, and the increase in image quality is significant. The improvement in image quality is demonstrated by a reduction of dark/gray regions as a result of ion milling and an improvement in IPF color contrast. As a result of ion milling, grain boundaries and subgrain boundaries were clearly visible in the IQ map, and grain orientations were easy to distinguish in the IPF map. In fact, no post-scan software clean-up was necessary following the shallow ion milling.
Polishing with Ga\textsuperscript{3+} ions may be of concern because Ga concentrates in specific regions of Al during FIB sample preparation [67], and Ga is known to cause liquid metal embrittlement of Al. Therefore, it is important to note that shallow FIB ion milling prior to EBSD did not appear to alter or degrade corrosion properties. Polished surfaces were topographically unaffected over long periods of time after ion milling, even after artificial aging. Additionally, samples prepared for bulk corrosion were only mechanically polished and were not ion milled, and the corrosion response in bulk corrosion samples was representative of the site-specific corrosion observed.

Elongated, unrecrystallized grains (<10 µm x 100 µm elongated grains) are the target microstructure in third generation Al-Li extrusions because unrecrystallized microstructures are known to provide the optimum combination of properties [3]. However, while many specimens exhibited the
expected unrecrystallized grain structure, the EBSD analysis of the initial tensile specimens revealed that there were inconsistent grain sizes throughout the 2099 and 2196 extrusions (Figure 4.2). Specifically, some specimens had relatively large grains (>25 µm) dispersed with the small grains. The source of these large grains is unclear and is likely due to recrystallization followed by abnormal grain growth. Significantly, both the unrecrystallized grains and large grains were relatively strain free. Regions of unrecrystallized grains contained low angle subgrain boundaries from recovery, and EBSD image quality was not degraded within large grains (i.e. dislocation density was relatively low within large grains). Abnormal grain growth attributing to these large grains could be related to Zr distribution since coherent β’ (Al3Zr) dispersoids are known to hinder recrystallization in Al-Li alloys.

Additionally, many specimens were completely large grained. These large, relatively strain free grains appeared to have undergone recrystallization and grain growth. Large, recrystallized grains are undesirable due to their lower strength and fracture toughness and will not exhibit the properties expected of the target fine-grain structures.

An attempt was made to find regions of unrecrystallized grains in the large grained tensile specimens by acquiring additional EBSD scans across the short transverse-longitudinal (S-L) planes. High aspect ratio EBSD scans were collected across the short transverse reference extrusion direction, and small grains were not consistently present, as demonstrated in Figure 4.3. The repeated observation of large grains indicates that they are not likely due to non-uniform Zr distribution. Additionally, since large grains were observed in multiple tensile specimens across the short transverse direction, the presence of large, recrystallized grains is also not likely a surface effect.

Recrystallization to produce large grains could be the result of non-uniform deformation, strain rate, or temperature throughout the initial part during the extrusion process. However, the extrusion processing parameters for these alloys, such as initial shape, extrusion ratio, temperature, and ram speed are proprietary and were not provided. Furthermore, attempting to identify the one or more factors contributing to these large grained regions was considered outside the scope of this project. However, in order to prevent the accumulation of experimental variables and uncertainty, attempts were made to exclude the large grained samples from the test matrix as much as possible. As a result, additional tensile specimens were sectioned from the as-received extrusions and examined by EBSD, DIC, and SEM. The large grained specimens were not further examined. However, it is important to note that variations in grain size may play a significant role in the corrosion properties of these alloys.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Small Grains</th>
<th>Mixed Small and Large</th>
<th>Large Grains</th>
</tr>
</thead>
<tbody>
<tr>
<td>2099</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>2196</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 4.2 Inverse pole figure maps overlaid on image quality maps (grayscale) acquired by EBSD revealing microstructure of 2099 and 2196 extrusions that were comprised of small grains, mixed small and large grains, and large grains.
Figure 4.3  Large-area inverse pole figure map overlaid on image quality map (grayscale) acquired by EBSD. Note the presence of large, recrystallized grains. The improvement in image quality near the center of the longitudinal direction is due to shallow ion milling. No post-scan software clean-up was applied.

4.1.2  2D Micro-Digital Image Correlation (DIC)

As a first attempt, DIC was performed on mechanically polished and chemically etched specimens. Etching was accomplished by immersing specimens for 15 s in Keller’s reagent (Table 4.1) immediately following a colloidal silica final polish, and specimen were thoroughly rinsed in warm de-ionized water after etching.

<table>
<thead>
<tr>
<th>Table 4.1 – Keller’s Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constituent</td>
</tr>
<tr>
<td>H$_2$O</td>
</tr>
<tr>
<td>HNO$_3$</td>
</tr>
<tr>
<td>HCl</td>
</tr>
<tr>
<td>HF</td>
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</tbody>
</table>

Etched specimens were considered because it was of interest to easily identify strain along and within specific grains; Keller’s reagent highlights grain boundaries and overlaying strain maps calculated by DIC is straightforward when grain boundaries are visible in the images acquired. However, etching contrast made it difficult to achieve a random grayscale intensity distribution, and etching artifacts
appeared to influence the strain calculated by the DIC software. The undesirable influence of etching contrast is highlighted in Figure 4.4. Dark regions resulting from etching and speckling consistently appeared lower in strain. Additionally, for site-specific examination, it was necessary to perform corrosion studies on the same region examined by DIC. Etching is expected to impact corrosion resistance, especially at etched features, such as grain boundaries in this case.

As a result of these findings, subsequent DIC analyses were performed on polished and speckled surfaces following EBSD, i.e., no specimens were etched. In order to identify the area of interest in which EBSD was performed, four ion milled fiducial markers were made using a focused ion beam (FIB) to mark the EBSD scan region. These fiducial markers were then located using the DIC camera.

Axial strain accumulation was examined by DIC for both alloys in all strain conditions of interest (1, 2, 3, 6, and 9%). An example of the type of information acquired for each specimen is demonstrated in Figure 4.5, which displays axial strain results for a 2099 specimen strained from 0-5.6% total strain. Micro-strain determined by DIC measurements should be in close agreement with macro-strain measurements determined by an extensometer during uniform straining, prior to the onset of localized deformation (i.e. necking). As expected, the total strain accumulation for each strain increment, shown in the histograms of Figure 4.5, closely matched the extensometer readings across the gage length. Figure 4.5 indicates that the DIC results are in good agreement with the macro-strains achieved and demonstrates that DIC has the ability to accurately resolve micro-scale strain and to examine localized variations in strain.

In addition, the DIC measurements matched the expected amount of strain received, based on microstructural orientations of grains prior to straining. The amount of strain expected in each grain relates to the Schmid factor of each grain, and the Schmid factor term, \(\cos(\lambda)\cos(\theta)\), is related to resolved shear stress by Equation 4.1:

\[
\tau = \sigma \cos(\lambda) \cos(\theta)
\]

where \(\tau\) is the resolved shear stress, \(\sigma\) the applied stress in tension, \(\lambda\) the angle between the tensile axis and the slip direction, and \(\theta\) the angle between the tensile axis and slip plane normal. Once \(\tau\) is greater than \(\tau_{CRSS}\), the critical resolved shear stress, slip should occur on that particular slip system. Therefore, grains of higher Schmid factor are expected to experience slip at lower applied stresses and should receive more strain/deformation for a given total applied strain.

Accordingly, grains and regions of higher Schmid factor received more strain, as calculated by DIC. Conversely, regions of lower Schmid factor corresponded to regions of lower measured strain. This relationship is demonstrated in Figure 4.6 for Alloy 2099 after straining to 3% total strain. Since Schmid
factor is traditionally defined for single crystals, it is important to note that the reverse relationship held true when examining Taylor factor since Taylor factor is inversely proportional to Schmid factor.

Not only is strain related to initial grain orientation prior to deformation, but the amount of strain received is also based on other microstructural aspects, such as grain size. Considering specimens containing one or more large, recrystallized grains, the strain was clearly concentrated in the large grains. Large grains are softer and can accommodate more slip because less grain boundary area is present to disrupt and/or prevent movement of dislocations. As expected, the strain calculated by DIC was higher in large grains as demonstrated in Figure 4.7 and Figure 4.8. Note that the DIC software was unable to calculate strain at the edges of the strain maps because there was a loss of resolution at image edges due to the DIC camera zoom bellows.

Overall, DIC was capable of measuring micro-strain due to the following factors: micro-strain evolution closely matched bulk extensometer strain readings, grains with higher Schmid factors corresponded to higher micro-strains, and large, soft grains received higher micro-strains. Strain was monitored by DIC for both alloys in all strain conditions.

4.1.3 Electron Backscatter Diffraction (EBSD) After Straining

EBSD was performed a second time on all regions of interest after straining and aging. Inverse pole figure (IPF) maps were generated to observe changes in grain orientation from straining, and image quality maps (IQ) were generated to observe topographic features brought about by surface relief during straining. Notice the changes in grain orientation as a result of straining in Figure 4.9.

4.1.4 Backscattered Imaging of Impurity Phases

Upon artificial aging, constituent impurity phases were examined by scanning electron microscopy (SEM). Backscattered electron (BSE) imaging was employed to highlight the impurity phases because they have a higher average atomic number than the Al matrix.

Prior to examining regions of interest, separate specimens, not subject to the primary experimental pathway, were examined by BSE imaging (Figure 4.10). In both alloys, impurity phases of approximately 5 µm or larger were present at grain boundaries and triple points.

Energy dispersive spectroscopy (EDS) was used to determine which impurity elements contribute to the coarse impurity phases (1.0 µm in diameter or larger) in Alloys 2099 and 2196. It was found that the impurity phases present typically contained Fe, Cu, and Mn (Figure 4.11).
Figure 4.4 DIC attempt of Alloy 2099 showing (a) etched microstructure prior to speckling and deformation, (b) speckled microstructure after straining 3.5% along the tensile axis, (c) axial strain map calculated by DIC after straining 3.5%, and (d) overlay of images presented in (b) and (c). Nonrandom intensity distribution caused the dark regions circled in (b) to consistently appear lower in strain, as circled in (c) and (d).
Figure 4.5 Axial strain maps and strain histograms calculated by DIC for total strains, as measured by an extensometer, of (a) 0.8%, (b) 1.6%, (c) 2.4%, (d) 3.2%, (e) 4.0%, (f) 4.8%, and (g) 5.6%.
Figure 4.6   Examination of the same region of Alloy 2099 showing (a) strain map after straining 3%, (b) image quality map prior to deformation highlighting grain boundaries, (c) strain map overlaid on image quality map prior to deformation, and (d) Schmid factor map overlaid on image quality map prior to deformation. In general, regions of higher Schmid factor, circled with dashed lines in (a), (c), and (d), accumulated more strain, and regions of lower Schmid factor, circled with solid lines in (a), (c), and (d), received less strain.
Figure 4.7 Examination of the same region of Alloy 2196 showing (a) strain map after straining 6%, (b) image quality map prior to deformation highlighting grain boundaries, (c) strain map overlaid on image quality map, and (d) Schmid factor map overlaid on image quality map. Large grains and regions of higher Schmid factor accumulated more strain as expected.
Figure 4.8 Examination of the same region of Alloy 2099 showing (a) strain map after straining 6%, (b) image quality map prior to deformation highlighting grain boundaries, (c) strain map overlaid on image quality map, and (d) Schmid factor map overlaid on image quality map. Large grains and regions of higher Schmid factor accumulated more strain as expected.
Figure 4.9 IPF maps overlaid on IQ maps for (a) 2099 prior to deformation, (b) identical region shown in (a) after straining 2% and artificially aging, (c) 2196 prior to deformation, and (d) identical region shown in (c) after straining 1% and artificially aging.
Figure 4.10  BSE images where impurity constituents appear light due to higher mass. All specimens were solution heat treated, strained, and artificially aged where (a)-(c) are Alloy 2099 strained 0%, 6%, and 12%, respectively and (d)-(f) are Alloy 2196 strained 0%, 6%, and 12%, respectively.
Next, BSE imaging was performed on specimens of both alloys in all strain conditions after artificial aging. Images were taken within regions of interest, marked by the ion milled fiducial markers per Section 3.1.3. It should be noted that these regions were the same regions examined by EBSD prior to straining, DIC during straining, and EBSD again after straining and artificial aging. Examples of BSE images acquired are provided in Figure 4.12.

Not surprisingly, the impurity phases within the regions of interest largely populated grain boundaries and grain boundary triple points. In particular, large impurity phases were often located at triple points, as demonstrated in Figure 4.13.

The goal of taking BSE images was to determine whether or not impurity phases play a significant role on corrosion initiation or overall corrosion properties in third generation Al-Li alloys. Impurity elements such as Fe, Cu, and Mn have different galvanic potentials than Al, and are expected to contribute to galvanic corrosion. However, the extent of their contribution to corrosion depends on their corrosion potential (i.e. size of impurity phases and magnitude of galvanic potential difference), environment, and time in corrosive solution. Additionally, other factors, such as precipitation, amount of strain, or grain size may contribute more significantly to corrosion.
Figure 4.12  BSE images of (a) 2099 strained 1% and (b) 2196 strained 2% where impurity constituents display lighter contrast due to higher average atomic number. Ion milled fiducial markers in the four corners mark where initial EBSD scans were taken.

Figure 4.13  BSE images taken after deformation overlaid on image quality maps collected prior to deformation of (a) 2099 strained 2% and (b) 2196 strained 1% where impurity constituents display lighter contrast due to higher average atomic number and grain boundaries appear dark due to low EBSD image quality. Large impurity phases at triple points are indicated with arrows.
4.1.5 Atomic Force Microscopy (AFM): Scanning Kelvin Probe Force Microscopy (SKPFM)

Initial SKPFM measurements were taken using a Digital Instruments Dimension 3100 AFM in interleave mode. Surface potential measurements were taken on a γ/γ′ Ni-based superalloy and Al-Li alloy 2196 to evaluate the capability of the instrument (Figure 4.14). Even though the feedback loops for topographic and surface potential measurements are separate, topography appeared to greatly influence surface potential. Topography may have altered surface potential readings because sharp changes in topography could have brought the AFM tip closer to the surface laterally, even when the nap/lift height in the z-direction remained constant. Another possibility is that the feedback loops in the DI Dimension 3100 AFM were not operating properly.

Figure 4.14 Comparison of (a), (c) topographic maps to (b), (d) surface potential maps collected by SKPFM using a Dimension 3100 AFM where (a), (b) were taken on a γ/γ′ Ni-based superalloy and (c), (d) were taken on Alloy 2196 strained 3% and artificially aged.

All subsequent measurements were collected using an Asylum Research MFP-3D-Bio AFM. The effects of topography on surface potential were not pronounced when the MFP-3D-Bio AFM was used and indicates that the feedback loops for topography and surface potential were operating independently.
and that the nap/lift height chosen (40 nm) was appropriate. As an example, the height features in the topographic map of Figure 4.15 for Alloy 2099 strained 3% and artificially aged do not appear to directly impact the surface potential measurements of the same region.

![Topographic Map](image1.png)

![Surface Potential Map](image2.png)

![3D Overlaid Image](image3.png)

**Figure 4.15** SKPFM of Alloy 2099 strained 3% and artificially aged showing (a) topographic map (b) surface potential map and (c) 3D overlaid image of (a) and (b). Height does not appear to significantly influence surface potential.

In an effort to verify the validity of the SKPFM technique, SKPFM was performed on materials with known work functions. One SKPFM scan of 50 µm x 50 µm was taken on pure Ni polished to a mirror finish and one 50 µm x 50 µm scan was taken on a pure Y polished to a mirror finish. Ni and Y were chosen because their work functions are established, i.e., Ni has a relatively high work function (5.04-5.35 eV) while Y has a relatively low work function (3.10 eV) in comparison to other elements. The median surface potential reading (i.e. $V_{DC}$ applied by the lock-in amplifier to zero the oscillation amplitude of the AFM tip) for the Ni scan was $0.213 \pm 0.0569$ V and the median potential for the Y scan was $0.508 \pm 0.0569$ V. The surface potential values recorded relate linearly to the work function difference between the conductive AFM tip and the sample surface. Since the work function for Ni and Y are known, the work function of the tip was solved for and found to be $\sim 6.71$ eV.
Next, a SKPFM scan was taken across a smooth P-doped CdTe/Au interface (Figure 4.16). The interface boundary was distinct, and the surface potential of P-doped CdTe was greater than that of Au. Since the work function of Au (5.10 eV-5.47 eV) is closer in value to that of the tip (~6.71 eV) than the work function of Ni (5.04 eV-5.35 eV), the median surface potential in the Au region should be less than the median surface potential recorded for pure Ni (0.213 ± 0.0569 V). In agreement, the median surface potential in the Au region was found to be 0.138 ± 0.0125 V. The ability of the SKPFM to clearly plot differences in surface potential between the two materials demonstrates the surface potential resolution of the technique.

![Figure 4.16](image.png)

Figure 4.16 Surface potential map acquired by SKPFM of a P doped CdTe/Au interface in (a) 2D and (b) 3D where 3D features correspond to height. There is a distinct change in surface potential across the interface.

SKPFM was performed within the regions of interest for both alloys for all strain conditions after specimens were examined by backscattered electron (BSE) imaging. For many specimens, a trend between surface potential and axial strain determined by DIC existed, and higher surface potentials were associated with regions of higher strain. Figures 4.17 and 4.18 illustrate these findings for Alloy 2099 strained 9% and artificially aged and 2196 strained 1% and artificially aged.

Even though, for some specimens, the surface potential appeared to directly correlate with the axial strain achieved, the SKPFM results were not always straightforward to interpret. For instance, surface conditions and minor contamination appeared to considerably alter the surface potentials, as demonstrated in Figure 4.19. In spite of the fact that experimental caution was taken when examining identical regions to avoid contamination, surface imperfections were still present on several specimens. Thus, measurements taken by SKPFM should be carefully considered in order to prevent making conclusions that are based on surface rather than material attributes.
4.1.6 Atomic Force Microscopy (AFM): In-situ Tapping Mode Topography during Corrosion

Following SKPFM, regions of interest from both alloys (2099 and 2196) in all strain conditions (0, 1, 2, 3, 6, and 9%) were examined by AFM in tapping mode as the regions corroded in artificial seawater per ASTM D1141-98. As a verification of the technique, a VLSI calibration grating with a nominal 10 µm x 10 µm pitch pattern with nominal depth of 180 nm was imaged in de-ionized water (Figure 4.20). The measured dimensions of the calibration standard agreed with the reported dimensions, indicating that the AFM cantilever was properly tuned in fluid and accurately tracked topography during the scan. The pitch standard scan demonstrated that the instrument is capable of taking high resolution topography scans in solution.

Regions of interest were continuously scanned, and scans were saved as corrosion proceeded. Two forms of corrosion occurred during the in-situ experiments: intergranular corrosion and pitting corrosion. Intergranular corrosion only occurred in specimens that were not strained (0% strain conditions) and intergranular corrosion did not occur in strained and artificially age specimens. For Alloy 2099 in the 0% strain condition, pitting corrosion was the dominant corrosion mechanism. However, there was some evidence of intergranular corrosion, supported by Figure 4.21. Notice that this region is relatively limited, as indicated by the micron bars.

Intergranular corrosion was the primary form of corrosion for Alloy 2196 in the 0% strain condition. Distinct grain boundaries were evident in the AFM images acquired during corrosion due to the deterioration of these boundaries, and the findings are displayed in Figure 4.22.

Specimens of all other strain conditions exhibited pitting corrosion. One advantage of acquiring AFM scans in-situ was that growing pits could be monitored over time. An example of a widening pit is presented in Figure 4.23. Corrosion byproduct formed in and around the edges of pits and, as corrosion proceeded, the byproduct escaped from pits, resulting in larger pits. The growth of pits was directional, and in general, pits grew along the extrusion direction.

For most specimens, appreciable corrosion events happened quickly, and oftentimes these events occurred within 30 min of immersion in artificial seawater. Visible corrosion events were observed in the AFM optical microscope and spread across the scanned regions (90 µm x 90 µm) within seconds. Signs of pitting initiation were apparent in the topographic AFM images, and pitting initiation was typically observed at several locations within the regions of interest. After initiation, the pits grew at comparably sluggish rates. Pitting initiation and growth is exemplified in Figure 4.24.
Figure 4.17  (a) SKPFM map of Alloy 2099 after 9% strain and artificial aging, (b) strain map acquired by DIC after 9% strain, and (c) overlaid image of (a) and (b). Note that regions of higher strain correspond to regions of higher surface potential.
Figure 4.18  (a) SKPFM map of Alloy 2196 after 1% strain and artificial aging, (b) strain map acquired by DIC after 1% strain, and (c) overlaid image of (a) and (b). Regions of higher strain correspond to regions of higher surface potential.
Figure 4.19  Alloy 2196 after straining 2% and artificial aging (a) surface potential map acquired by SKPFM, (b) secondary SEM image, and (c) overlaid image of (a) and (b). Surface contamination clearly contributed to the observed surface potential.

Figure 4.20  3D topography of VLSI pitch standard in de-ionized water.
Figure 4.21 Identical region of Alloy 2099 after solution heat treatment and artificial aging where (a) is a topographic image acquired by AFM after immersion in artificial seawater for 2.25 h, (b) is an inverse pole figure map overlaid on an image quality map acquired by EBSD prior to corrosion, and (c) is an overlaid image of (a) and (b). Dark black pits are present in addition to less severe intergranular corrosion.

Figure 4.22 Identical region of Alloy 2196 after solution heat treatment and artificial aging where (a) is a topographic image acquired by AFM after immersion in artificial seawater for 2.3 h, (b) is an inverse pole figure map overlaid on image quality map acquired by EBSD prior to corrosion, and (c) is an overlaid image of (a) and (b). Grain boundary corrosion is evident in contrast to the observations in Alloy 2099.
Figure 4.23 Growing pit in Alloy 2099 strained 5.6% and artificially aged monitored by in-situ tapping mode topography as corrosion proceeds from (a)-(f) over a period of 3.25 h. The growing pit and corrosion byproduct escaping from the pit are labeled in (a).

Figure 4.24 AFM topography scans of an identical region of Alloy 2196 strained 2% (a) in air prior to corrosion (b) after immersion in artificial seawater for 15 min, and (c) after immersion in artificial seawater for 4.25 h.
There were many experimental challenges faced during the in-situ AFM corrosion studies. Tuning the AFM cantilever in fluid was not always straightforward since, in many cases, multiple resonance peaks existed. Additionally, corrosion byproduct and hydrogen gas evolution interacted with the AFM probe, and sometimes disturbed the tapping mode measurements (Figure 4.25). In particular, corrosion byproduct that stuck to the cantilever caused the tip to withdraw or prevented accurate scanning. When corroding for long periods of time, there were drastic changes in surface height and roughness, but scan parameters can only be adjusted manually. Without adjustment, continuous scanning often failed. Lastly, AFM tips dull with use, and continuous scanning regularly lead to a loss in image resolution.

### 4.2 Additional Experimentation

Additional experiments were conducted to gather complementary information about the alloys of interest and support the findings of the primary experimental pathway. Vickers hardness measurements were performed to examine the effects of aging and straining on properties, transmission electron microscopy (TEM) was used to study precipitation hardening, and bulk corrosion studies were conducted to verify the findings of the site-specific corrosion studies. The results are described in the following sections.

#### 4.2.1 Vickers Hardness

Vickers hardness measurements were performed on Alloys 2099 and 2196 before and after artificial aging (AA) for 60 h for various amounts of strain. The results are plotted in Figure 4.26. Hardness measurements taken prior to AA are labeled “2196, no AA” (solid trend line) and “2099, no AA” (dashed trend line) for alloys 2196 and 2099, respectively, and straining was performed directly after
solution heat treatment for these conditions. For the artificially aged conditions labeled as “2196, AA” (solid trend line) and “2099, AA” (dashed trend line), straining was performed directly after solution heat treatment and prior to AA for 60 h.

Additionally, measurements were taken for 2099 and 2196 in post-strained conditions. A post-strain treatment consists of solution heat treating, quenching, AA, and straining after AA. For example, the “2009, AA+6%” condition represents the hardness of alloy 2099 after solution heat treating, AA for 60 h, and post-straining 6% after AA. Thermomechanical processing for post-straining treatments is provided in Figure 4.27. Post-strained hardness conditions are labeled as individual data points in Figure 4.26. Hardness measurements were also taken for the as received (AR) alloys. Alloy 2196 was received in the T3511 condition and 2099 was in the T83 condition. As expected for age hardenable alloys, the hardness values for 2099 and 2196 were greater for every strain condition after AA for 60 h compared to the hardness prior to AA. The hardness values prior to AA increased as the amount of strain increased. Similarly, the hardness after AA increased with amount of pre-strain up to approximately 9%. Beyond 9% pre-strain, the hardness appeared to level off or even drop slightly.

Data points for post-strained conditions of both alloys were not easily obtained. Many samples broke in the tensile frame grips during post-straining because AA increased the strength of the samples enough to significantly reduce ductility. Only three post-strained samples did not break in the grips for each alloy, and these samples represent the post-strained data shown in Figure 4.26. To obtain additional post-strained data points, it would be necessary to machine tensile samples with reduced gauge sections to ensure local stresses in the grips would not cause failure.

Examining the post-strained conditions for both alloys together, it is possible to deduce that post-strained hardness closely followed pre-strained hardness after AA. In fact, the hardness values of 2099 and 2196 in the 3% pre-strained and aged condition were almost identical to those of 2099 and 2196 in the “AA+3%” post-strained condition. These results demonstrate that the increase in hardness with increase in strain for all conditions may largely be due to strain hardening from straining and not to an increase in the number, volume, or distribution of strengthening precipitates formed during aging.

While Vickers hardness measurements may support findings of the density and distribution of Al-Cu-Li strengthening precipitates, such as T₁ (Al₂LiCu), additional characterization is necessary for identifying and quantifying the phases present, and comparing or predicting alloy properties.
Figure 4.26  Vickers microhardness versus amount of pre-strain for Alloys 2099 and 2196. Error bars show a 95% confidence interval. Each data point represents the average of 10 hardness indents.
Figure 4.27  Temperature vs. time diagrams for (a) pre-strained and aged conditions and (b) post-strained conditions.
Additional Vickers hardness measurements were taken to produce hardening curves of Alloys 2099 and 2196. The hardening responses during the AA treatment of alloys pre-strained to various degrees are plotted in Figure 4.28. The aging times and temperatures were per AMS2772E (121°C for 10-14 h, 151°C 42-54 h). The results indicated that peak hardness for a 12% strain condition was reached before AA was completed according to AMS2772E, i.e., after approximately 46 h.

![Figure 4.28](image)

Figure 4.28 Aging curves for Al-Li alloys 2099 and 2196 according to amount of pre-strain prior to AA. The first 12 hours of aging were performed at 121°C while the remaining 48 h were conducted at 151°C. Error bars show a 95% confidence interval. Each data point represents the average of at least 10 hardness indents.

4.2.2 Transmission Electron Microscopy (TEM)

Bright field images, dark field images, and selected area diffraction patterns (SADPs) were taken to identify the precipitates in the 2099 and 2196 alloys which were pre-strained up to 12% and artificially aged for 60 h. \( T_1 (\text{Al}_2\text{LiCu}) \) and \( \delta' (\text{Al}_3\text{Li}) \) were present in both alloys for all pre-strained conditions aged for 60 h. \( \delta' (\text{Al}_3\text{Li}) \) was present in all conditions including prior to artificial aging, whereas \( T_1 (\text{Al}_2\text{LiCu}) \) was not present for either alloy prior to artificial aging (AA).

Figure 4.29 contains a SADP taken down the \([011]_\text{Al}\) zone of Alloy 2099 after SHT, no pre-strain, and AA for 60 h. Superlattice reflections from the \( \delta' \) phase and precipitate reflections from the \( T_1 \) phase
were visible in addition to matrix reflections. Likewise, reflections from both T\textsubscript{1} and δ’ were present in Alloy 2196 after solution heat treatment, 6\% pre-strain, and AA for 60 h (Figure 4.30).

![Figure 4.29](image1)

**Figure 4.29**  Calculated (a) and experimental (b) SADPs of Al-Li alloys containing the δ’ and the T\textsubscript{1} phase along the [011\textsubscript{Al}] axis. The calculated pattern in (a) is taken from the literature [16] and the experimental pattern in (b) is from Alloy 2099 (SHT, 0\% strain, AA 60 h).

![Figure 4.30](image2)

**Figure 4.30**  Calculated (a) and experimental (b) SADPs of Al-Li alloys containing the δ’ and the T\textsubscript{1} phase along the [001\textsubscript{Al}] axis. The calculated pattern in (a) is taken from the literature [23] and the experimental pattern in (b) is from Alloy 2196 (SHT, 6\% strain, AA 60 h).

To further demonstrate the presence of T\textsubscript{1} and δ’ in the alloys shown in Figures 4.29 and 4.30, dark field images of the δ’ and bright field images of T\textsubscript{1} were taken. Centered dark field images of the δ’
precipitates were taken using a 100 $\delta'$ reflection in Figure 4.31. Note that $\beta'$ ($\text{Al}_3\text{Zr}$) cores enveloped by $\delta'$ ($\text{Al}_3\text{Li}$) shells were observed along with smaller $\delta'$ precipitates.

![Figure 4.31](image)

Figure 4.31  Centered dark field images of (a) 2099 (SHT, 0% strain, AA for 60 h) and (b) 2196 (SHT, 6% strain, AA for 60 h) taken using a 100 superlattice reflection near an $<011>$ matrix orientation. Note that the $\delta'$ precipitates appear bright whereas the $\beta'$ cores appear slightly darker due to mass contrast.

Bright field images from the same grain taken near the $<011>$ of the matrix (Figure 4.32a) revealed the thin T$_1$ plates that were oriented approximately 70.5° apart, consistent with them lying on the {111} habit planes that are parallel to the beam. These thin precipitates generated the 111 streaks in the SADP in Figure 4.29. The fringes seen in Figure 4.32a correspond to the thin T$_1$ precipitates that lie on the other {111} planes that are inclined in this orientation.

While T$_1$ ($\text{Al}_2\text{LiCu}$) was present in both alloys after AA, no T$_1$ ($\text{Al}_2\text{LiCu}$) superlattice reflections were seen in diffraction patterns of 2099 and 2196 prior to AA for 60 h. Only $\delta'$ ($\text{Al}_3\text{Li}$) reflections were present in the unaged conditions (e.g., Figure 4.33).

TEM was further employed to examine samples aged for 46 h (12 h at 121°C and 34 h at 151°C). An aging time of 46 h was chosen because the Vickers hardness measurements for samples strained 12% prior to aging demonstrated that peak hardness occurred after 46 h of AA instead of 60 h. For higher strain amounts, such as 12%, the number of strengthening precipitates is expected to be greatest around 46 h. Also, the corrosion resistance is expected to be highest for peak aged tempers.

When examined in the TEM, the $\delta'$ ($\text{Al}_3\text{Li}$) phase was present after 46 h of aging. Figure 4.34 is a centered dark field image highlighting the $\delta'$ ($\text{Al}_3\text{Li}$) phase.
Pre-straining should influence the amount and distribution of the $T_1$ ($Al_2LiCu$) precipitates since $T_1$ ($Al_2LiCu$) heterogeneously nucleates on dislocations, and the dislocation density of a material increases with cold work. However, it is of interest to determine the magnitude of this effect. The results in Figure 4.26 indicate the hardness increased with pre-strains up to about 9%, after which hardness remained relatively constant or decreased slightly. It may be useful to determine the amount of $T_1$ ($Al_2LiCu$) at various pre-strains and relate it to the hardness measurements taken.

To relate $T_1$ ($Al_2LiCu$) formation to the amount of pre-strain, it is important to know the relative amount of deformation which has occurred in the specific grains of interest during pre-straining. In a highly textured material, most grains should incur similar amounts of deformation because they will have similar orientations and Schmid factors prior to deformation. EBSD was performed on a bulk sample of 2099 in the T4 temper. The resulting pole figures demonstrate that the 2099 sample was highly textured (Figure 4.35). Figure 4.36 is an inverse pole figure map where the texturing is also apparent. This sample was subsequently sectioned into tensile bars, strained various amounts, artificially aged, and used to make TEM foils. Although $T_1$ ($Al_2LiCu$) formation was examined in several grains, most grains should have experienced similar amounts of deformation with similar precipitation in each grain for the same pre-strain condition due to the strong initial texture of the starting material in the T4 temper.

To examine the difference in precipitate formation between the various pre-strain amounts, bright field images of $T_1$ ($Al_2LiCu$) near $B$=[111] were taken (Figure 4.37). Many images were taken for each
pre-strain condition; images were taken in different grains, at different magnifications, and at various 
degrees of tilt from B=[111]. The images in Figure 4.37 are representative of precipitate distributions for 
the respective pre-strain values, and the images were taken at similar magnifications.

Figure 4.33  SADP of 2196 in the T4 condition (no AA) taken down the $[\overline{1}1\overline{2}]_{\text{Al}}$ zone axis. Indices in 
italics represent $\delta'$ superlattice reflections while those bolded represent primary 
reflections from the matrix.

Figure 4.34  Centered dark field image of $\delta'$ (Al$_3$Li) in 2099 (SHT, 0% strain, AA for 46 h) taken 
using $g=100$ (reflection used is shown in the SADP) near $B=[011]$. 

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Figure 4.35  Pole figures showing pole densities of 2099 in the T4 condition with \( \{112\}<111> \) Cu orientation texture. (a) (111) pole figure demonstrating the [111] extrusion direction, ED, and (b) (112) pole figure demonstrating the (112) extrusion plane.

Figure 4.36  Inverse pole figure map of 2099 in the T4 condition. The similar coloring is representative of a (112) extrusion plane according to the inverse pole figure legend.
By visual inspection of the TEM images obtained in Figure 4.37, it was concluded that the amount of $T_1$ ($Al_2LiCu$) increased significantly from a 3% pre-strained condition to a 6% pre-strained condition. However, by visual inspection alone, it was difficult to see a difference between the amount of $T_1$ ($Al_2LiCu$) in the 6% pre-strained condition and the 12% pre-strained condition. These findings agree with the pre-strained and aged hardness results for 2099 plotted in Figure 4.26. The increase in hardness between 3% and 6% pre-strains was greater than the increase in hardness between 6% and 12%. This may have occurred because the volume fraction of $T_1$ ($Al_2LiCu$) increased more significantly between the 3% and 6% pre-strains.

4.2.3 Bulk Corrosion

Bulk samples, sectioned from the tensile specimens used during the primary experimental pathway, were corroded in artificial seawater by alternate immersion for 3 h and direct immersion for an additional 15 h. Of the scanning electron microscopy (SEM) images acquired, SEM images taken following the entire 18 h of corrosion were most informative and indicative of expected corrosion features.

Prior to artificial aging, both alloys primarily exhibited intergranular corrosion for all strain conditions (Figure 4.38). The intergranular corrosion observed was not uniform across the entire sample surface but occurred locally. In addition to intergranular corrosion, Alloy 2099 in the 9% strain condition (Figure 4.38c) had some evidence of elongated pitting corrosion, and the elongated pitting was on the order of the expected grain size.
Figure 4.38 Corrosion after 18 h of (a) Alloy 2099 strained 0%, (b) Alloy 2099 strained 3%, (c) Alloy 2099 strained 9%, (d) Alloy 2196 strained 0%, (e) Alloy 2196 strained 3%, and (f) Alloy 2196 strained 9%. Samples were solution heat treated prior to straining but were not artificially aged.

Upon artificial aging, pitting corrosion was the dominant corrosion mechanism for both alloys in all strain conditions (Figure 4.39). Low strain conditions had some evidence of intergranular corrosion, and intergranular corrosion was most apparent in the 0% strain conditions. In some cases, severe grain boundary corrosion was seen within regions of elongated pitting (Figure 4.39c), indicating that pitting or
general corrosion occurred both inter- and intragranularly. Uniform corrosion on the surface was also prominent in Alloy 2196 in the 9% strained and artificially aged condition.

Figure 4.39 Corrosion after 18 h of (a) Alloy 2099 strained 0%, (b) Alloy 2099 strained 3%, (c) Alloy 2099 strained 9%, (d) Alloy 2196 strained 0%, (e) Alloy 2196 strained 3%, and (f) Alloy 2196 strained 9%. Samples were artificially aged.
Elongated pitting corrosion was observed in all artificially aged samples strained at least 1\% (Figure 4.40). This observation is consistent with the literature discussed in Section 2.4.1. The pitted region in Figure 4.40 also contains what appears to be deep grain boundary corrosion. These findings suggest that intergranular corrosion and pitting corrosion are not always separate phenomena.

Figure 4.40 Corrosion after 18 h of Alloy 2196 strained 2\% and artificially aged. Elongated pitting with severe grain boundary corrosion is observed.
CHAPTER 5: DISCUSSION

This chapter serves to address the three engineering questions posed in the introduction. The first engineering question was as follows: where does corrosion initiate and how does corrosion proceed in Alloys 2099 and 2196? The first section of this chapter considers this question by discussing the location of corrosion. The second engineering question posed was: can corrosion be predicted? The second section of this chapter evaluates scanning Kelvin probe force microscopy (SKPFM) as a method for predicting corrosion. The third and final question posed was: can corrosion be prevented? The last section of this chapter poses possibilities for corrosion prevention.

5.1 Location of Corrosion

The site-specific in-situ atomic force microscopy (AFM) study aimed to locate corrosion initiation and determine how corrosion proceeds over time. The AFM topographic information was compared to information collected from previous characterization techniques performed on identical regions in order to determine which microstructural aspects influence corrosion properties most significantly.

As discussed in Section 4.1.6, intergranular corrosion was observed for both alloys in the 0% strain condition, and intergranular corrosion was most severe in Alloy 2196 (Figures 4.21 and 4.22). The dominant corrosion mechanism in all specimens other than Alloy 2196 in the 0% strain condition was localized pitting corrosion.

Comparing the AFM topographic maps to image quality (IQ) maps collected by electron backscatter diffraction (EBSD) prior to straining, deep pitting was often present along grain boundaries and at grain boundary triple points. One example is provided in Figure 5.1 for Alloy 2099, which was strained 3% and artificially aged. Pitting is represented by dark features in the AFM topographic image after corrosion because pits advance into the depth of the surface and become low topographic features. Furthermore, pitting initiation pathways appear light due to corrosion byproduct escaping the surface as corrosion proceeds. Deep pitting is visible at grain and subgrain boundaries and triple points, and pitting initiation extends along grain boundaries.

Additionally, discrete pits in Alloy 2099 after straining 9%, artificially aging, and corroding for 9 h in artificial seawater, also formed at grain and subgrain boundaries and grain boundary triple points (Figure 5.2).
Figure 5.1  Grain boundary pitting in Alloy 2099 in the 3% strain and artificially aged condition where (a) is an AFM topographic image taken in air prior to corrosion, (b) is an AFM topography image taken in artificial seawater after corroding the region for 15 h, (c) is an IQ map acquired by EBSD prior to deformation highlighting existing grain and subgrain boundaries, and (d) is an overlay of (b) and (c). The resulting image in (d) demonstrates that pitting occurs at grain and subgrain boundaries.

As a third example, rows of pits developed along the elongated grain boundaries of Alloy 2196 after straining 2%, artificially aging, and corroding for 4 h in artificial seawater. As shown in Figure 5.3, pits and corrosion byproduct match the grain boundary locations established in the IQ map collected from
the same region prior to deformation. Although pitting initiated at grain boundaries, it is important to note that several pits grew out from grain boundaries into adjacent grains.

![Figure 5.3](image)

**Figure 5.3** Grain boundary pitting in Alloy 2196 in the 2% strain and artificially aged condition where (a) is an AFM topographic image taken in air prior to corrosion, (b) is an AFM topography image taken in artificial seawater after corroding the region for 4 h, (c) is an IQ map acquired by EBSD prior to deformation highlighting existing grain boundaries, and (d) is an overlay of (b) and (c). Pits and corrosion byproduct are primarily along grain boundaries.

Upon pit formation at grain boundaries, pitting growth appeared to be influenced by the amount of micro-strain received during straining. As is apparent in Figure 5.4, the location of the deepest elongated pit corresponded to the region of the highest localized strain, represented by the strain map acquired by 2D micro-digital image correlation (DIC). Secondary pitting was also observed in regions of relatively high strain.

The relationship between local strain and pitting held true for many specimens; localized pitting correlated with regions of higher strain, even when severe, deep pitting was not observed. For example, for Alloy 2196 strained 9%, artificially aged and corroded for 1.5 h in artificial seawater, the areas of highest strain, indicated in red in the strain map, showed evidence of shallow pitting (Figure 5.5), even when the time of exposure to seawater was relatively short (1.5 h). The pits appeared elongated along the tensile direction, i.e., along the same direction the grains were elongated.
Alloy 2099 in the 3% strained and artificially aged condition where (a) is an AFM topography image taken in air prior to corrosion, (b) is an AFM topography image taken in artificial seawater after corroding the region for 15 h, (c) is the axial strain map calculated at 3% final strain by DIC, and (d) is an overlaid image of (b) and (c). Deep pitting is indicated with arrows in (b).

Highly localized strain also appeared to be a good indicator of uniform corrosion in addition to localized corrosion. Considering the specimen of Alloy 2099 after straining 6%, artificially aging, and corroding for 1.5 h in artificial seawater, high localized strain occurred within a valley of the broader surface of interest, as demonstrated in Figure 5.6. The depth of this feature indicates that uniform corrosion may have occurred at this location. However, this conclusion is somewhat speculative because the valley mentioned existed in the AFM topographic image prior to the onset of corrosion, and the depth was not significantly altered after corrosion occurred for 1.5 h.
Figure 5.5  Alloy 2196 in the 9% strained and artificially aged condition where (a) is an AFM topography image taken in air, prior to corrosion, (b) is an AFM topography image taken in artificial seawater after corroding the region for 1.5 h, (c) is an axial strain map calculated at 9% final strain by DIC, and (d) is an overlaid image of (b) and (c). Pitting corrosion is circled in (b).

A more convincing example of higher strain corresponding to uniform corrosion is provided in Figure 5.7 for Alloy 2099 after straining 1%, artificial aging, and corroding in artificial seawater for a longer period (19.25 h). In this specimen, there was some evidence of deep pitting, but a sizable region of corrosion was more uniform in appearance. Both pitting and uniform corrosion occurred in regions of relatively high strains, indicated by red coloring in the strain map provided.

One reason a specific region may have accumulated more strain than neighboring grains is due to grain size. In general, large grains received more strain during deformation because large grains do not provide as much grain boundary resistance to dislocation movement. This trend was discussed in Section 4.1.2. Since, in general, areas of higher strain corroded, it would be expected that large grains would also preferentially corrode. Experimentally, this expectation held true.

Large grains appeared to exhibit dramatic pitting and uniform corrosion. Figure 5.8 considers microstructural aspects of the specimen shown in Figure 5.6. The region that possibly exhibited uniform corrosion, shown in the AFM topographic map after corrosion, occurred at and within a single, large grain.
Figure 5.6  Alloy 2099 in the 6% strained and artificially aged condition where (a) is an AFM topography image taken in air prior to corrosion, (b) is an AFM topography image taken in artificial seawater after corroding the region for 1.5 h, (c) is an axial strain map calculated at 6% final strain by DIC, and (d) is an overlaid image of (b) and (c). Pitting corrosion is circled in (b) and the possible location of uniform corrosion is outlined by a dashed line in (b).

The effect of grain size on corrosion was even more apparent in the specimen shown in Figure 5.7. The microstructural influence on corrosion is examined in Figure 5.9, and the considerable area of uniform corrosion occurred in one, original large grain. Not only did the large grain completely corrode, but the corrosion continued to advance from the large grain into the surrounding smaller grains.

Severe pitting also occurred preferentially in large grains, as observed in Alloy 2196 strained 6%, artificially aged, and corroded for 3 h in artificial seawater (Figure 5.10). Individual, deep pits were observed within the largest grain in the site-specific region examined, and the severity of the pitting is apparent by the scale of the AFM topographic image.

Backscattered electron (BSE) images were taken from regions of interest to identify impurity phases in each specimen. The BSE images were compared to the AFM topography measurements from corrosion to determine whether impurity phases play an important role on corrosion properties of third generation Al-Li alloys. Although secondary impurity phases are known to lower corrosion resistance, this effect was minimal or nonexistent in the relatively short-term AFM corrosion studies conducted as
part of this research. Corrosion did not seem to specifically occur at sites of impurities, and the presence of impurities did not appear to alter the overall corrosion resistance. For example, the large pits in Figure 5.11 do not directly align with the impurity phases in the BSE images from the same region.

Impurities did not appear to influence corrosion in other specimens as well, including 2196 strained 9% and artificially aged, shown in Figure 5.12. Elongated pitting did not consistently initiate near or follow regions populated by impurity phases.

As a final example, the presence of impurity phases did not noticeably contribute to corrosion in Alloy 2196 strained 2% and artificially aged (Figure 5.13). Elongated pitting was very evident in this specimen but was not associated with these impurity phases.

In summary, intergranular corrosion was prevalent in both alloys in the 0% strain condition, and intergranular corrosion was the dominant form of corrosion for Alloy 2196 in the 0% strain condition. For all specimens except Alloy 2196 in the 0% strain condition, pitting corrosion was dominant. Pitting corrosion initiated at grain boundaries and, for many specimens, independent pits occurred along grain and subgrain boundaries and at triple points. Localized pitting and generalized corrosion also occurred in regions of high local strain produced during straining, and higher local strain consistently led to lowered corrosion resistance. As expected, based on the axial strain observations, large grains were highly detrimental to corrosion properties given that they corroded and pitted preferentially when compared to the smaller, unrecrystallized grains. Lastly, impurity phases identified by BSE imaging did not appear to significantly influence general corrosion or pitting behavior.

5.2 Prediction of Corrosion by Scanning Kelvin Probe Force Microscopy (SKPFM)

The SKPFM technique was implemented to determine whether or not surface potential measurements relate to corrosion. In the event of a real relationship, one of the research goals was to develop a pseudo-Galvanic series based on surface potentials from SKPFM to aid in predicting where corrosion occurs and how quickly corrosion proceeds.

In specimens where surface potentials from SKPFM closely matched strain (refer to Section 4.1.5), regions of high potential appeared to corrode at the expense of low potential regions. However, in many specimens, the relationship between surface potential and corrosion properties was less obvious. For instance, when considering Alloy 2099 strained 1%, artificially aged, and corroded for 19.25 h in artificial seawater, the corroded regions were loosely associated with regions of relatively high surface potential (Figure 5.14). These regions are circled with solid lines in Figure 5.14. However, this trend was inconsistent as some regions with low surface potentials still corroded preferentially; one such region is circled with a dashed line in Figure 5.14.
As mentioned in Section 4.1.5, surface contamination influenced surface potential measurements. In addition to contamination, minor scratches occasionally played a role in surface potential readings. In Figure 5.15, high potentials appear aligned with scratches/linear features of the AFM topography images for Alloy 2099 strained 6% and artificially aged. Even when ignoring this, a relationship between corrosion and surface potential for this specimen was not easily distinguished.

Oftentimes, linear or almost-linear features of high surface potential did not appear to be associated with scratches or visible surface defects detected by AFM or SEM. One of these features is pointed out in Figure 5.16. Subsurface deformation from polishing may have influenced the surface potential measurement in this case. Again, no obvious relationship between surface potential and corrosion existed in Alloy 2196 strained 9% and artificially aged (Figure 5.16).

In a couple of cases, a reverse trend between surface potential and corrosion was observed, i.e. regions of relatively low surface potential corroded instead of regions of high potential (e.g., Figure 5.17). Contrary to the findings for most specimens, low surface potentials were associated with high strains for the specimen examined in Figure 5.17.

For all specimens, DIC strain maps were more effective at predicting corrosion than surface potential maps. High micro-scale strain consistently led to greater corrosion, whereas micro-scale surface potential measurements were inconsistent. Even in cases where regions of high surface potential received high strains, the relationship between strain and corrosion was more apparent than the relationship between surface potential and corrosion.

In spite of the fact that surface potential maps did not provide dependable results for accurately predicting corrosion on a micro-scale, statistical information was collected for entire SKPFM scans (90 µm x 90 µm) to examine broader, not site-specific, corrosion implications. Under the assumption that surface potential differences directly relate to voltage potential differences during corrosion (i.e. galvanic potentials), large differences in surface potential theoretically promote galvanic corrosion. To quantitatively examine the extent of surface potential variation within a scan, the arithmetic average of the absolute values of deviation from the mean surface potential was calculated for each specimen. This surface potential calculation is the SKPFM equivalent to an average roughness calculation for topographic measurements and is given by:

$$R_a = \left( \frac{1}{n} \int_{i=0}^{n} |y_i| \right)$$  \hspace{2cm} 5.1

where $R_a$ is the variation in surface potential (i.e. average roughness of the surface potential measurement), $n$ is the number of surface potential data points, and $y$ is the surface potential deviation.
from the mean. The calculated results are plotted in Figure 5.18. Larger variations in surface potential (higher $R_a$) should have lower galvanic corrosion resistance and vice-versa. Therefore, $R_a$ calculations from SKPFM predicts 0% strain conditions have the worst corrosion resistance and macro-strains between 0% and 3% have the best corrosion resistance for both alloys. This is in agreement with the literature and qualitative corrosion data obtained from the in-situ AFM measurements during corrosion. The large error associated with this calculation may be due, in part, to surface potential outliers from contamination or scratches. Nonetheless, any conclusions drawn from the surface potential average roughness calculations should be evaluated with considerable caution.

5.3 Possibilities for Corrosion Prevention

Based on the findings of this research, there are many possibilities to explore in order to reduce or eliminate corrosion. For example, in-situ atomic force microscopy (AFM) tapping mode measurements during corrosion demonstrated that both alloys in the 0% strain conditions underwent intergranular corrosion. This is in agreement with the bulk corrosion studies, which also showed that intergranular corrosion was an issue in unstrained and artificially aged specimens. Intergranular corrosion in third generation Al-Li alloys has been commonly attributed to $T_1$ ($Al_2CuLi$) precipitation at grain boundaries; it is known that $T_1$ heterogeneously nucleates at grain and subgrain boundaries and within grains during artificial aging. Unstrained specimens, with lower dislocation densities within the matrix, tend to preferentially precipitate $T_1$ at grain and subgrain boundaries [21], [41]. It is accepted that boundary and subgrain boundary dissolution occurs by localized galvanic attack of Cu-containing precipitates, such as $T_1$, and that $T_1$ acts as a local anode during corrosion [68], [69]. Straining introduces matrix dislocations and provides heterogeneous nucleation sites for $T_1$ precipitation within grains. Numerous studies have shown that straining prior to aging promotes the precipitation of $T_1$ within grains [3], [21], [69]. Therefore, to reduce or eliminate intergranular corrosion, it appears that alloys should be strained prior to aging.

Interestingly, Alloy 2196 in the 0% strain condition exhibited more severe intergranular corrosion than Alloy 2099. It is speculated that Ag additions in the presence of Mg promote $T_1$ formation in 2XXX series Al-Li alloys, and it is possible that the Ag additions in 2196 enhanced $T_1$ formation on grain boundaries when Alloy 2196 was not strained. If Ag does increase the volume fraction of $T_1$ along grain boundaries when 2196 is not strained, Ag should not be added if any regions of the components will not receive strain during stretch forming processes. Additionally, it is known that Zn additions lower the galvanic potential of the matrix because Zn additions cause grain boundary precipitates to be closer to the potential of the matrix [45]. Alloy 2099 contains more Zn, which could explain why Alloy 2099 is less
susceptible to intergranular corrosion than Alloy 2196. As a consideration, more Zn could be added to Alloy 2196.

The AFM corrosion results in combination with axial strain maps acquired by 2D micro-digital image correlation (DIC) demonstrated that corrosion occurs in regions of relatively high strain. It is anticipated that T₁ precipitates at dislocations, and regions of high strain should contain more dislocations. Therefore, regions of high strain should also accumulate more T₁ during aging, and the presence of T₁ may cause specific grains or regions to act as preferential anodes compared to the surrounding matrix. The contribution of T₁ to corrosion is in agreement with the bulk corrosion studies performed. Unaged specimens are not expected to contain age-hardening precipitates, such as T₁, and the majority of the unaged specimens exhibited intergranular corrosion, not localized attack corresponding to regions of high micro-strain. High strain conditions for unaged specimens (Figure 4.38c) had some evidence of elongated pitting, which suggests high, localized micro-strain (without T₁ precipitation) can also influence corrosion resistance. It is probable that, in artificially aged specimens, regions of high micro-strain corroded as a result of a combined effect of T₁ precipitation and high micro-strain accumulation.

One possibility to prevent large differences in micro-strain from grain to grain is to promote texture during primary processing. If grains are all of similar orientation prior to straining, it is expected that most grains will incur a similar amount of strain during deformation. However, texture can be detrimental due to anisotropy in other properties, such as fracture toughness and tensile properties. A method to develop texture only at the surface to prevent pitting initiation as a result of Na⁺ exposure without degrading other properties would be ideal. A couple of possibilities for creating a surface texture are to add a recrystallization heat treatment or to explore compositionally graded alloys where elements known to promote texture, such as Zr (effective at pinning grain boundaries), are compositionally higher near the surface.

It was also shown in this study that large, recrystallized grains among unrecrystallized grains preferentially and severely corroded by uniform and pitting corrosion and were extremely detrimental to corrosion properties. Although some Zr is added to 2099 and 2196 to prevent recrystallization during processing, it is possible that the amount of Zr or other recrystallization inhibitors (Cr, Sc, La, etc) should be increased. Additionally, dynamic recrystallization could possibly be prevented by better controlling the temperature, extrusion ratio and ram speed during extrusion.

Lastly, surface potential average roughness values calculated from scanning Kelvin probe force microscopy (SKPFM) measurements predicted that corrosion resistance is highest for strains between 0% and 3%. However, it is important to point out that the error in this calculation was significant.
Figure 5.7  Alloy 2099 in the 1% strained and artificially aged condition where (a) is an AFM topography image taken in air prior to corrosion, (b) is an AFM topography image taken in artificial seawater after corroding the region for 19.25 h, (c) is an axial strain map calculated at 1% final strain by DIC, and (d) is an overlaid image of (b) and (c). Pitting corrosion is indicated with an arrow (b) and uniform corrosion is outlined by a dashed line in (b).
Figure 5.8 Corrosion of one, single large grain in Alloy 2099 strained 6% and artificially aged. Images shown are (a) an AFM topography image taken in air prior to corrosion, (b) an AFM topography image taken in artificial seawater after corroding the region for 1.5 h, (c) IQ map acquired by EBSD prior to deformation, and (d) overlaid image of (b) and (c).
Figure 5.9  Corrosion of one, single large grain in Alloy 2099 strained 1% and artificially aged. Images shown are (a) an AFM topography image taken in air, prior to corrosion, (b) an AFM topography image taken in artificial seawater after corroding the region for 19.25 h, (c) IQ map acquired by EBSD prior to deformation, and (d) overlaid image of (b) and (c).
Figure 5.10  Deep, severe pitting concentrated in a single, large grain of Alloy 2196 strained 6% and artificially aged. The pitting is examined by comparing (a) an AFM topography image taken in air, prior to corrosion, (b) an AFM topography image taken in solution after corroding for 3 h in artificial seawater, (c) IQ map acquired by EBSD prior to deformation, and (d) overlaid image of (b) and (c).
Figure 5.11 Comparison of impurity phases to corrosion features in Alloy 2099 strained 0% showing (a) an AFM topography image taken in artificial seawater after corroding for 6 h 40 min, (b) impurity phases (lighter due to mass contrast) imaged by BSE, and (c) overlaid image of (b) and (c). Dark pits in (a) do not closely match impurities, several of which are circled in (b)-(c).
Figure 5.12 Comparison of corrosion features to impurity phases in Alloy 2196 strained 9% and artificially aged where (a) is an AFM topography image taken after corroding the specimen in artificial seawater for 1.5 h, (b) is a BSE image from this region, and (c) is an overlaid image of (a) and (b). Regions containing impurities did not appear to corrode preferentially, and several of these specific regions are circled in (b)-(c).
Figure 5.13 Comparison of corrosion features to impurity phases in Alloy 2196 strained 2% where (a) is an AFM topography image taken after corroding the specimen in artificial seawater for 4 h, (b) is a BSE image from this region, and (c) is an overlaid image of (a) and (b). Regions containing impurities did not corrode, and several of these specific regions are circled in (b)-(c).
Figure 5.14 Identical region of Alloy 2099 strained 1% and artificially aged showing (a) an AFM topography image taken in air prior to corrosion, (b) an AFM topography image taken in artificial seawater after corroding for 19.25 h, (c) surface potential map acquired by SKPFM, and (d) overlaid image of (b) and (c). Two areas of relatively high surface potential are circled with solid lines and one region of low surface potential is circled with a dashed line in (c)-(d).
Figure 5.15  Identical region of Alloy 2099 strained 6\% and artificially aged showing (a) an AFM topography image taken in air, prior to corrosion, (b) an AFM topography image taken in artificial seawater after corroding for 1.5 h, (c) surface potential map acquired by SKPFM, and (d) overlaid image of (b) and (c). Clearly surface scratches/features influence surface potential but may not lead to enhanced chemical attack.
Figure 5.16 Identical region of Alloy 2196 strained 9% and artificially aged showing (a) an AFM topography image taken in air, prior to corrosion, (b) an AFM topography image taken in artificial seawater after corroding for 1.5 h, (c) surface potential map acquired by SKPFM, and (d) overlaid image of (b) and (c). A high surface potential feature not associated with a known defect is identified with a double-sided arrow in (c).
Figure 5.17  Identical region of Alloy 2196 strained 6% and artificially aged showing (a) an AFM topography image taken in air, prior to corrosion, (b) an AFM topography image taken in artificial seawater after corroding for 1.5 h, (c) surface potential map acquired by SKPFM, (d) overlaid image of (b) and (c), (e) overlaid surface potential and image quality map, and (f) overlaid axial strain and image quality map. Contrary to most specimens, regions of low surface potential corroded and regions of low surface potential were high in strain.
Figure 5.18 Surface potential average roughness as a function of total strain amount in Alloys 2099 and 2196. Based on the data plotted, corrosion resistance is expected to be greatest between 0% and 3% strains, indicated by the drop in surface potential average roughness. Error bars account for the entire spread in calculated average roughness across all AFM retrace scan lines evaluated.
CHAPTER 6: SUMMARY AND CONCLUSIONS

The primary experimental pathway for this research revolved around thoroughly characterizing single, site-specific regions of third generation Al-Li Alloys 2099 and 2196 to investigate and understand micro-scale corrosion properties. Alloys were characterized by electron backscatter diffraction (EBSD), 2D micro-digital image correlation (DIC), backscattered electron (BSE) imaging, and scanning Kelvin probe force microscopy (SKPFM) in order to determine the effects of microstructure and grain orientation, localized strain received during straining, impurity phases, and surface potentials on corrosion, respectively. Micro-scale corrosion was studied by tapping mode atomic force microscopy (AFM) to observe topographic changes as corrosion occurred in-situ.

Mechanical polishing of Alloys 2099 and 2196 is difficult because these alloys have a relatively soft Al matrix and relatively hard strengthening precipitates, and these alloys contain Li, which is chemically active. To adequately prepare alloy surfaces for EBSD, shallow ion milling was performed in a focused ion beam (FIB) using a low beam current, and ion polishing significantly improved EBSD image quality.

EBSD revealed inconsistent grain sizes throughout Al-Li extrusions. Small, unrecrystallized grains are the desired microstructure. However, many regions contained large, recrystallized grains; in some sections, recrystallized grains were the dominant microstructure. Although tensile specimens with completely recrystallized grains were experimentally excluded, several regions of interest considered contained at least one large grain.

Another finding of this research is that DIC is capable of tracking micro-strain evolution. Local strain measured by DIC matched macro-strain imparted, as recorded by a bulk extensometer. Initial grain orientation was taken into consideration, and as expected, grains with higher Schmid factor received higher local strain during straining. Initial grain size also played a role in the evolution of micro-strain, and strain locally accumulated in large, soft grains.

Surface potential measurements from SKPFM were not straightforward to interpret. In general, high surface potential related to high strain, but this trend was not consistently observed, and in some cases, regions of low strain were higher in surface potential. Surface potential measurements were highly sensitive to contamination, defects, and scratches, and the influence of surface flaws on surface potentials did not aid in predicting corrosion. The magnitude of overall corrosion resistance was evaluated by calculating surface potential average roughness, and the average roughness calculations predicted highest corrosion resistance for strains greater than 0% but less than 3%. This prediction should not be considered absolute because the calculation error was substantial.
Several major conclusions arose as a result of the in-situ AFM topography measurements:

1. There was evidence of intergranular corrosion for both alloys in the 0% strain condition. Pitting corrosion was the dominant corrosion mechanism for all specimens except Alloy 2196 strained 0%.

2. Pitting initiated at grain boundaries and individual pits commonly developed at grain and subgrain boundaries. Pitting commonly proceeded to grow into specific grains.

3. Regions of high micro-strain preferentially corroded. High micro-strain resulted from grain orientation prior to deformation and grain size. With this, the presence of large grains among smaller, unrecrystallized grains was highly detrimental to corrosion properties. Large grains were locally targeted and deteriorated by pitting and uniform corrosion.
CHAPTER 7: FUTURE WORK

Due to time constraints associated with combining many advanced characterization techniques, the sample size for this research was limited. For each strain condition, only one specimen of each alloy was subjected to the primary experimental pathway. To increase the statistical significance, it would be prudent to repeat the experiments. Examining many specimens of the same alloy in the same strain condition (% macro-strain) could aid in developing a meaningful quantitative description of corrosion, indicative of the type and extent of corrosion expected for each strain. With experimental repetition, it may also be possible to accurately calculate the minimum orientation deviation between grains or the minimum micro-strain gradient required to initiate corrosion.

Although numerous studies have confirmed the expected amount and type of precipitation in third generation Al-Li alloys, transmission electron microscopy (TEM) could be further employed to quantitatively identify amounts of precipitates, such as T₁(Al₂CuLi) and δ’ (Al₃Li), at grain boundaries and within grains. In particular, focused ion beam (FIB) lift-outs could be taken in regions of high and low micro-strain to confirm whether T₁ is more prevalent in grains of higher strain. Additionally, the amount of T₁ at grain boundaries is of interest, particularly in the 0% strain conditions, because it is speculated that T₁ at grain boundaries is the cause of intergranular corrosion.

One important finding of this research was that regions of high micro-strain preferentially corroded. Both the amount of deformation/dislocations and the amount of T₁ precipitation is expected to be higher in regions of higher micro-strain. To reduce the galvanic corrosion potential between neighboring grains, one possibility is to ensure grains receive a similar amount of strain during straining. One way to achieve this is through texture because heavily textured materials have grains of similar orientation (i.e. similar Schmid and Taylor factors prior to deformation). However, texture leads to anisotropy in mechanical properties. A technique to promote surface texture without encouraging sharp texture in the interior of extrusions would be ideal. One idea for future work is to explore recrystallization texture (for these alloys, recrystallization textures of cube, Cu, and Goss (G) are common) by heat treating the surface of extrusions. Another possibility would be to experiment with compositionally graded alloys where elements known to promote texture, such as Zr (effective at pinning grain boundaries), are compositionally higher near the surface.

Since regions of higher micro-strain preferentially corroded, the presence of large, recrystallized grains in a mostly unrecrystallized microstructure was detrimental to corrosion properties because large grains accumulated more micro-strain during straining. To prevent corrosion, it may be necessary to control extrusion parameters or increase the content of recrystallization inhibitors.
In this research, EBSD was used to identify completely recrystallized regions within Alloy 2099 and Alloy 2196 extrusions upon solution heat treatment (T4 temper condition). Although recrystallized regions were not studied in-depth, large grains are detrimental to strength and ductility and do not provide the optimum combination of properties in these alloys. Thus, even without taking corrosion properties into consideration, future research should be conducted to understand the independent and combined effects of extrusions parameters such as temperature, extrusion ratio, and ram speed on dynamic recrystallization in order to prevent recrystallization. Computational modeling could be helpful in predicting optimal extrusion parameters.
CHAPTER 8: REFERENCES


Figure 9.1 Alloy 2099, 0% strain. (a) IPF + IQ map, (b) Secondary SEM image, (c) BSE image, (d) Surface potential map, (e) AFM topography prior to corrosion, and (f) AFM topography after corroding in artificial seawater for 6.67 h.
Figure 9.2  Alloy 2099, 1% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 1% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 19.25 h.
Figure 9.3  Alloy 2099, 2% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 2% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 7.7 h.
Figure 9.4  Alloy 2099, 3% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 3% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 15 h.
Figure 9.5
Alloy 2099, 6\% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 6\% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 1.5 h.
Figure 9.6  Alloy 2099, 9% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 9% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 9 h.
Figure 9.7 Alloy 2196, 0% strain. (a) IPF + IQ map, (b) Secondary SEM image, (c) BSE image, (d) Surface potential map, (e) AFM topography prior to corrosion, and (f) AFM topography after corroding in artificial seawater for 2.33 h.
Figure 9.8  Alloy 2196, 1% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 1% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 15.17 h.
Figure 9.9  Alloy 2196, 2% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 2% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 4 h.
Figure 9.10  Alloy 2196, 3% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 3% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 14 h.
Figure 9.11  Alloy 2196, 6% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 6% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 3 h.
Figure 9.12  Alloy 2196, 9% strain. (a) IPF + IQ map prior to straining, (b) Schmid factor map prior to straining, (c) axial strain map at 9% strain, (d) IPF + IQ map after straining and artificial aging, (e) BSE image, (f) Surface potential map, (g) AFM topography prior to corrosion, and (h) AFM topography after corroding in artificial seawater for 1.5 h.