β Phase Growth and Precipitation in the 5xxx Series Aluminum Alloy System

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Dedications

This thesis is dedicated to my family – Thank you for all of your support and patience throughout the years. Without your love and understanding this work would not have been possible.

For the reader of this thesis:

I ask that you do not use this work to only seek answers, but to find the questions that have yet to be answered.
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Abstract

β Phase Growth and Precipitation in the 5xxx Series Aluminum Alloy System

Daniel Scotto D’Antuono

The 5xxx series aluminum alloys are commonly used for structural applications due to their high strength to weight ratio, corrosion resistance, and weldability. This material system is a non-heat treatable aluminum and derives its strength from a supersaturation of magnesium (3%), and from cold rolling. While these materials have many admirable properties, they can undergo a process known as sensitization when exposed to elevated temperatures (50-280°C) for extended periods of time. During this process, magnesium segregates toward the grain boundaries and forms the secondary precipitate β phase (Al3Mg2). When exposed to harsh environments such as sea water, a galvanic couple is formed between the Al matrix and the β phase precipitates. The precipitates become anodic to the matrix and preferentially dissolve leaving gaps along the boundary network, ultimately leading to stress corrosion cracking. While this problem has been known to occur for some time now, questions relating to nucleation sites, misorientation dependence, effect of prior strain, and preferred temperature regimes remain unanswered. The work contained in this thesis attempted to better understand the kinetics, growth, and misorientation dependence, of β phase precipitation using in situ transmission electron microscopy experiments which allowed for direct visualization of the precipitation process. Orientation imaging using a Nanomegas/ASTAR system (OIM in TEM) coupled with the in situ experiments, along with elemental STEM EELs mapping were used to better understand the diffusion of Mg and found low angle boundaries as potential sites.
for nucleation. The resulting STEM EELs experiments also showed that Mg is much more stable at the grain boundaries than previously thought. Concurrent bulk ex-situ studies were used to compare various heat treatments, as well as to failed in service material showing that the low temperature treatments yield the metastable \( \beta' \) phase more readily than the \( \beta \) equilibrium phase. The work here has identified the size, location, and kinetics of \( \beta \) phase formation as well as the effects of pre-strain (cold rolling) and boundary misorientation on precipitation showing that increases in dislocations speeds up sensitization and increases nucleation sites but does not increase overall precipitate size. This work also compared precipitate type (\( \beta \) vs. \( \beta' \)) showing that the metastable \( \beta' \) phase is more common in low temperature treated material and the main precipitate found in failed in service material. A comparison between the corrosion effects of the two precipitation showed that lower temperature treatments have a higher degree of sensitization further delineating between the two forms.
Chapter 1: Introduction and Motivation

1.1 Motivation

In recent years the 5xxx series aluminum alloy system has gained steam as a lightweight alternative [1] to steel due to its high strength to weight ratio and weldability [2, 3]. Despite these characteristics, when exposed to elevated temperatures for long periods of time the material can undergo the deleterious process known as sensitization which can lead to growth of the deleterious β phase (Al₃Mg₂). When the material experiences harsh environments such as sea water a galvanic couple is formed and stress corrosion cracking [4, 5] can occur. Growth of the secondary β phase (Al₃Mg₂) in the material has been known to be a problem for many years[6].

While there has been a push in recent years to better combat the sensitization process, the issues are still ongoing costing the navy millions of dollars per year with no permanent solution in sight [6]. The majority of studies in this area focus primarily on post treatment analysis and use relatively low resolution techniques to study the sensitization process. Due to this there is a clear lack of understanding in what actually goes on during the sensitization process in terms of precipitation mechanism. Also, the location of precipitation is mainly observed from etching and optical microscopy techniques and little information in regards to grain boundary character is reported.

Aside from general formation uncertainties, there is very little information on the effect of strain on the sensitization process. This idea is very important due to the fact that the material gains the majority of its strength through cold rolling along with Mg
additions [2]. Given all 5xxx series material is cold rolled to some extent it is important to see if other treatments can be implemented to improve overall sensitization resistance.

Finally there is a lack of consistency in the literature about the β phase formation in relation to the phase diagram. There appears to be two main ways to grow the β phase precipitation long times and low temperatures [5, 7-9] or accelerated heating and high temperature [10, 11] but both seem to yield the same type of precipitation. It is very rare for any article to delineate between the β equilibrium and its metastable precursor β’ (prime), thus leading to confusion on which form of the phase is most important. For instance, many works will refer to all precipitates as “β phase” despite being in temperature regimes where the metastable β’ is more likely. While both phases appear susceptible to corrosion and lead to stress corrosion cracking, it may be possible for one phase or more effectively sensitization treatment to cause more damage than the other.

While the previous approaches show what happens after sensitization has occurred there are still many questions yet to be answered. Groups have shown that low angle boundaries are effectively impervious to sensitization [12, 13] while high angle boundaries are the starting point of SCC [14, 15]. Conversely, early studies show that sensitization within the grain is possible and preferable as it reduced precipitation at the high angle boundaries [16]. Finally there are very few alternative treatments available for this alloy system besides the H116 treatment [17] and only a few attempts exist at reversing the corrosion process [18]. The results from this work will be used to answer the following key questions, as well as create a better understanding of sensitization in an attempt to mitigate the deleterious effects in the 5xxx series alloys.
Key Questions:

1. What is the location, time, temperature, and size of the precipitates during the sensitization process and what is its dependence on GB misorientation?
2. What role does prior strain play in the nucleation and growth kinetics of sensitization?
3. What is the main form of β phase contributing to corrosion (β vs β’) and what treatment approach mimics in service use the most?
4. What is the primary mechanism of precipitate formation?
5. Is remediation possible and what effect does it have on the final microstructure of the material?
6. What are the stability ranges of the precipitates and what temperature is required for Mg to be removed from the GBs?

In order to answer the above questions, a two-fold approach of in situ transmission electron microscopy and bulk ex situ processing will be implemented to fully understand the precipitation process including the location, size and kinetics of precipitation. Application of in situ heat treatments will also be used on bulk material in attempts to better improve corrosion resistance and mitigate the effects of sensitization in the 5xxx series alloy system. The following proposal will discuss a brief background on the 5xxx series alloy along with a review of previous work, which acts as motivation for this study, along with the procedure for answering proposed questions and initial findings.

1.2 Organization of Thesis

The organization of this thesis is as follows:

Background (Chapter 2) - This chapter will overview the current understanding of precipitation in the 5xxx series aluminum alloys system. It will begin with a brief overview and physical metallurgy of the alloy and what separates it from other Al alloy
series. The sensitization process will be explained and an overview of the subsequent phases which can form will be given. Key areas that have significant impacts on the sensitization process are also discussed including, precipitation location, effects of prior strain, the precipitation mechanism, effect of thermal treatment, the possibility of remediation and Mg segregation during the entire life cycle of precipitation.

**Methods (Chapter 3)** – This chapter will cover all experimental procedures and techniques used to acquire all data within this work. The majority of work is concentrated around either nanoscale in situ TEM observations as well as bulk ex situ studies. All sample preparation methods are explained in their entirety as well as all TEM experimental techniques.

**Grain boundary misorientation dependence of β (Chapter 4)** – In this chapter the initial observations of β growth and precipitate analysis during in situ heating TEM experiments are shown. The process of observing the precipitation and understanding the effect of location on factors such as size are explained. This chapter acts as a spring board for further in situ heating studies in this work.

**Direct measurement of the effect of cold rolling on β precipitation kinetics (Chapter 5)**– This chapter continues within the same vein as the previous chapter but includes the effect of increased dislocation density and its impact on sensitization. This chapter helps to understand how dislocations introduced via cold rolling play a role in sensitization as well as their effect on size and growth rate of precipitates. Kinetic growth rates are calculated from precipitates formed during in situ heating TEM experiments and activation energies are also calculated and compared.
Atom probe tomography analysis of Mg pipe diffusion (Chapter 6) – This chapter utilizes techniques which allow for specific site analysis of β phase precipitation. Here grain boundaries and dislocations are analyzed for their localized Mg content in relation to precipitation. The relationship between the dislocations and the GB’s in terms Mg segregation paths during sensitization are discussed and observed. A more accurate mechanism of β phase precipitation is proposed.

Metastable precipitates as the predominant failure mechanism (Chapter 7) – This chapter switches up gears and begins to compare the effect of heat treatment approach (high vs low temperature sensitization). Effectively a direct comparison between the high temperature precipitate, β equilibrium and the low temperature β’ (metastable) is drawn. Failed in service material is characterized and compared to both in situ heating and ex situ bulk annealing regimes to confirm which is most accurate to the in service material. The corrosion mass loss results of the two regimes are compared and the need for a clear delineation between the β and β’ phases is discussed.

Effect of thermomechanical processing on microstructure and corrosion resistance (Chapter 8) - This chapter will show attempts to improve upon the current standard H116 treatment in the form of additional thermomechanical processing. Two different starting plates of material will be compared in terms of initial microstructure and the changes to said microstructure and corrosion properties caused by thermomechanical processing treatments. The importance of understanding the initial microstructure and the need for tighter specification on the H116 treatment are detailed here.
Impact of cyclic annealing on the remediation, precipitation, and corrosion properties of β (Chapter 9) – In this chapter the primarily focus explains what occurs during remediation, the stability of precipitates and the potential for regrowth upon re-sensitization treatments. In situ heating will be used to establish precipitate regime temperatures which will be adapted to bulk ex situ treatments for corrosion testing. It will be noted to what remediation temperature is necessary, the to which extent re-sensitization can occur and further describe precipitate stability ranges.

Localized changes in Mg concentration as a result of sensitization and remediation (Chapter 10) – This chapter will follow in the same line as the previous chapter repeating similar experiments but utilizing in situ heating EELs experiments to follow localized Mg concentrations throughout the remediation process. Mg changes will be observed along various stages during the remediation treatment. The work within this chapter will define what temperature ranges are required to full “heal” the material and if it is even a possibility.

Conclusions and Future Work (Chapter 11 and 12) – This chapter will summarize the primary findings of this work. The impact of this work on the future understanding of the precipitation process in the 5xxx series aluminum alloy system will be explained and future areas of study will be suggested.
Chapter 2: Background literature review

The information contained within this literature review has been focused around key principles which have been thought to have an impact on β phase precipitation within the 5xxx series alloy system. These primary areas of interest include: 1) A broad overview of the 5xxx series alloy and the impact of Mg additions, 2) The theory behind the precipitation process of β phase, specifically via pipe diffusion, 3) The effect of microstructure and location of precipitation and its impact on corrosion, and 4) The potential removal of precipitation and its impact on mechanical properties. The focus of this review is to summarize the current understanding of β phase precipitation and its corrosive effects.

2.1 The 5xxx series aluminum alloy system

The 5xxx series aluminum system is said to be a non-heat treatable alloy, which gains the majority of its strength through cold rolling as well as solute solution hardening (Magnesium additions) [19]. This alloy is composed primarily of Al and Mg and can be in a supersaturated solution at greater than 3% Mg and higher. The key alloys used in this system are 5083 and 5456 with ~4% and 5.5% Mg respectively [20]. In contrast to heat treatable alloys, like that of 2xxx, 6xxx, and 7xxx series which rely heavily on precipitation hardening to attain desired mechanical strength, the 5xxx series gains strength through solid solution hardening, dispersion hardening, and work hardening[21]. The quality of being considered non-heat treatable is due to lower levels of solute contained in the 5xxx series, but alloys containing higher levels of Mg can become heat treatable as well[22]. While alloying with Mg does lead to increases in strength, the most
notable impact is Mg’s ability to promote work hardening in the alloy[23]. The relationship between ultimate tensile strength and the amount of strain hardening provided by Mg additions is closely related to the Holloman-Stumpf equation:

\[
K_{\text{Mg}} = K_{\text{Al}} + H_{Mg} X_{Mg}^{2/3} \quad \text{where } X_{\text{Mg}} \text{ is atomic fraction of Mg}
\]

where its impact can be viewed in the figure below.

Figure 1 demonstrates that as more Mg is introduced into the alloy the ability for it to work harden increases, and thus the tensile yield strength also increases significantly. As a result of this, cold rolling is a very common processing treatment along with
manipulation of the Mg content. The most commonly used treatment to increase mechanical properties is that of the H116 treatment which entails a cold rolling reduction between 1/8 and 1/4 of full hardness[24]. It has to be mentioned that this is somewhat of a vague value and a very broad range which can potentially lead unforeseen issues like inconsistent corrosion resistance, when purchasing material. Aside from Mg a few other alloying elements are also included such as Mn, Fe, Cr, and Si, which act as agents to aid material production as well as improve weldability.

2.2 The Al – Mg phase diagram

The 5xxx series alloy system is considered to be a binary system allowing for a few possible equilibrium phases which are shown in the phase diagram below (Figure 2).

![Binary phase diagram of Al-Mg](image)

Figure 2: Binary phase diagram of Al-Mg[25]
While the phase diagram is not excessively complicated there are a few notable equilibrium phases shown within the plot which are: the Al solid solution, the Al₃Mg₂ or β phase intermetallic compound at ~37 wt% Mg, compound R, compound Al₁₂Mg₁₇, and solid solution Mg[21, 26]. The concentration of this work will be focused primarily on studying the β phase or more specifically the area in which Al + β phase occurs. According to the phase diagram Al+β phase precipitation is possible at temperatures ranging from 23°C to 450°C at the concentration of 3 up to 37.5wt% Mg respectively. As the Mg concentration increases the solvus temperature also increases and thus takes on a positive slope meaning that there is an increased ability for precipitation to occur[27]. The maximum solid solubility of Magnesium in Aluminum is 17.4wt% but typical concentrations for industrial use maintain around 5% due to loss of ductility at higher Mg levels. The more common 5083 and 5456 alloys contain between 4 and 5.5wt% Mg which when exposed to elevated temperatures allows for potential secondary precipitation. It is also to be mentioned that at Mg levels of ~5wt% the solvus temperature is 280°C. The process of the secondary β phase precipitation is known as sensitization and will be discussed next.

2.3 The Sensitization process

It is the general consensus that when exposed to elevated temperatures (50°C-200°C) [7] that the Mg segregation begins from supersaturated solution, (SSS) (>3%Mg or higher [2]), which ultimately results in formation of the β equilibrium phase [4, 28, 29]. The below equation illustrates the formation:
Equation 2: SSS $\rightarrow$ G.P zones $\rightarrow$ β”$\rightarrow$ β’$\rightarrow$ β equilibrium [21, 28-30].

Note* Due to GP zones and β” only existing in alloys with concentrations higher than 13% [29, 31], they will not be discussed in this work.

In materials containing 13% Mg or higher it is possible to grow GP zones and β” precipitates but typically these are very rarely reported in alloys of lower Mg concentrations. Some works have shown that it may be possible to form these early stage precipitates[32] but the general consensus is that the β’ and particularly the β equilibrium phases are the primary phases of interest. While the nucleation and growth mechanism is not fully known it is well documented that the formation of β phase is temperature driven [33, 34]. As shown in the reaction above both β’ and β precipitations can form from the SSS with the β’ phase appearing first and leading to β equilibrium formation. The β’ phase is considered the lower temperature precipitate while β equilibrium the higher and their coexistence is sometimes reported as well[5]. It has been explained by Hamana et al.[30] that typically the β’ transforms into β equilibrium but at high temperatures and accelerated timescales formation of β equilibrium from the SSS is possible. Although it is very important the specific effects of the type of thermal treatment will be discussed in later parts of this work. In order to fully understand the precipitation process a comparison of the two constituent phases is necessary.

2.3.1 The metastable β’ phase

The metastable β phase is also commonly known as β’ phase and is the precursor to β equilibrium. It has been shown to precipitate from 50-200°C[7, 14] with 150°C being the main accelerating growth temperature[28]. It is said to take on a hexagonal structure with lattice parameters a=1.002nm and c=1.63nm [35, 36]. There is a general lack of
information of the exact structural information but is said to share complimentary structural atoms of the equilibrium phase[37]. This phase commonly forms at GB’s and is semi coherent to the matrix while being shaped as rods or plates [38]. The composition of the β prime phase is still up for debate but said to be close to Al$_3$Mg$_2$, the same as β equilibrium. In previous studies it has been mentioned as the main hardening precipitate [30] as well as in very early studies the primary contributing precipitate to corrosion [35]. Despite this, very rarely in recent works is this phase ever found or discussed, specifically in alloys 5083 and 5456.

2.3.2 Equilibrium β phase

The β equilibrium phase of the most commonly reported phase in the literature. The phase takes on a face cubic centered (FCC) structure with a lattice parameter of 28.2 angstroms [37, 39]. The growth is said to be incoherent [21, 40] with respect to the GB’s and occurs at temperatures of 200-300°C with dissolution at ~400°C [21] depending on Mg%. The precipitation commonly occurs heterogeneously like that of β’ but is said to occur at later stages of ageing[7, 21]. Again despite a different crystal structure the β equilibrium phase is said to have a very similar composition to that of β’ being Al$_3$Mg$_2$ as well [28, 29]. It should be noted that many early studies describe the composition of both β’ and β equilibrium as Al$_8$Mg$_5$ [41, 42] which can be somewhat confusing. When reviewing the literature one major point of confusion is the lack of delineation between the two precipitate types especially in works related to the 5083 and 5456 alloys. It appears that the most literature discussing β’ is that on alloys containing much higher Mg content. In many cases despite whatever heat treatment was applied to a given material the majority of works report observation of only β equilibrium phase precipitation.
2.4 β phase corrosion

2.4.1 Galvanic corrosion

Aside from the obvious changes to Mg distribution during sensitization, exposure to harsh environments (sea water) can create a galvanic couple between the β phase and matrix material [43]. Effectively galvanic corrosion occurs because the different phases, Al$_3$Mg$_2$ and α Al, have different electronegative potentials. The β phase takes on an anodic potential leading it to preferentially dissolve in relation to the matrix [44, 45]. This is made worse by the fact that the β phase precipitates grow by heterogeneous nucleation at dislocations, intermetallics, and primarily GBs [10, 11]. When in the corrosive environment the β phase preferentially dissolves leaving voids which can ultimately lead to intergranular stress corrosion crack formation [15]. As the precipitation occurs the Mg eventually segregates toward the grain boundaries forming along them. When exposed to the harsh environment the precipitates preferentially dissolve leaving pits along the grain boundary network. When these materials are then stressed the small pits along the grain boundaries open and grow leading to ultimate failure. It is clear that as the materials are exposed to elevated temperature along with harsh environments mechanical properties begin to decline rapidly over time[46].

2.4.2 Stress corrosion cracking

In order for stress corrosion cracking (SCC) to occur the material must be in a corrosive environment and some exterior force must be applied[47]. A schematic of the SCC process taken from Cormack[48] as shown in Figure 3.
Figure 3: Schematic of SCC in Al-Mg materials from Cormack [48].

The schematic illustrates the evolution of SCC within an Al-Mg alloy. First when exposure to elevated temperature occurs over time sensitization occurs at the grain boundaries of the material as described by the center image. As a tensile load is applied within a corrosive environment the β phase precipitates dissolve and intergranular stress corrosion cracking occurs. Upon further stress these cracks begin to connect and grow along the grain boundary networks and the material subsequently fails. Documentation of the effects of stress corrosion cracking is readily available in the literature [47]. This type of failure is mechanically assisted corrosion that allows the critical crack size to be reached at accelerated rates [49]. In comparison to fatigue crack growth, SCC not only has a contribution of crack growth from applied stresses but has additional stress contributions caused by corrosion [50]. Many examples of crack formation caused by SCC can be found within the literature [47, 51] as shown in Figure 4.
It is clear from these images that extreme damage can result from sensitization and subsequent SCC. As an effect many studies have been completed looking into understanding the process and causes of SCC in 5xxx series alloys. Work by Searles et al.[14] observed decreased ductility and mechanical properties as β phase levels increased. Jain, et al[52] explored the spreading of intergranular corrosion on surfaces of AA5083. Samples of 5083 were sensitized and underwent corrosion testing via emersion in 0.6 M salt water solution. It was found that precipitates would interact first forming pits and then connecting to form chain like networks at the grain boundaries [52]. A study by Frankel and Xia[53] investigated localized corrosion and SCC of friction stir welded aluminum. One of the key requirements for many uses of the 5xxx series alloy system is that the material must maintain strong mechanical properties after welding. This work compared the areas of the welds versus the as received 5454 material and found that the welded structures were much more susceptible to SCC. It was found that the welded samples had reduced ductility in chloride solution which does not bode well for applications in harsh environments. McMahon et al.[54] compared different treatments
H116, H131 and SHTQ and alloy compositions 5456 and 5083, to see what impact prior processing had on SCC response. It was explained that the H131 treatment had a 3/8 level of hardening vs. the H116 of 1/8 hardening. The SHTQ treatment was described to be a reprocessed H116 treatment which had an annealing treatment of 275°C for 10 hours and immediate water quenching. Upon comparison it was found that the H131 treatment was the most susceptible to SCC while the SHTQ treatment showed the least amount of susceptibility. Another interesting result is that according to the ASTM G67 results presented by this work the SHTQ reached a level of 40mg/cm² in 14 days while the 5456-H116 treatment only required 6.75 days to reach the same level of sensitization. None the less, these results show that starting material treatment condition can play a large factor in SCC mitigation.

2.4.3 Corrosion Testing

Throughout the literature there are a few common ways for sensitization to be detected in materials which have been exposed to elevated temperatures with the most common being Nitric acid mass loss testing or ASTM G67 testing[55]. Here, samples are made according the ASTM specifications, measured, weighed, and emerged into nitric acid baths for 24 hours. After the bath the material is re-weighed and a value in terms of mg/cm² is calculated. The test yields a mass loss per unit volume which is used to determine the susceptibility of the material to cracking. While it is the most common form of sensitization detection many factors such as, β precipitate type, location, size of precipitates, precipitate location in relation to GBs are unknown. One other consideration is that of grain size which may have an effect on the testing. Theoretically very fine grained material will fall out easier than large pancake sized grains as it would talk longer
for etching of the perimeter of the grain to occur. While the test does yield a good starting point for understanding sensitization higher resolution techniques are required to fully understand precipitation within the material.

2.5 Key factors that impact β phase precipitation

Sensitization is effectively the segregation of Mg which leads to the secondary precipitation of β phase precipitates. It seems simple enough but through the literature there appears to be many factors which effect the formation, size, location, and growth kinetics of the β phase. Some of these factors include heat treatment approach, material properties such as microstructure or extent of H116 treatment, Mg concentration at the grain boundaries, and dislocation density to name a few. The goal of this section is to summarize some of the most important factors which lead to sensitization and their impact on sensitization. The key factors which will be expanded upon are:

1) The impact of grain boundary character on β phase precipitation
2) General microstructure evolution and Impact of Grain size
3) Effect of prior strain on precipitation
4) Effect of thermal treatment

2.5.1 The impact of grain boundary character on β phase precipitation

Polycrystalline materials are made up of many randomly oriented grains which are separated by grain boundaries. The geometric relationship between the two single crystal grains is very important when discussing precipitation. Grain boundaries are characterized according to five geometric parameters which include: three angles which characterize the orientation between the two grains, and two angles which describe the boundary plane inclination. The misorientation relationship is the most convenient way to
report these angles, made possible by relatively standard techniques such as electron back scatter diffraction. The other two angles, which describe the boundary plane, are typically not reported by this technique due to the extensive serial sectioning and iterative scanning required. Continuing on, the misorientation angle can yield two different classifications, either a high angle boundary (>15°) or low angle (<15°) boundary. The high angle boundaries can further be separated into: general high angle boundaries and special coincidence site lattice boundaries (CSLs or Σ# boundaries). Defining the grain boundary type and their distribution within the material is important as these boundaries can have a major impact on material properties.

Low angle boundaries are generally accepted as arrays of discrete dislocations which have aligned within a single crystal forming sub-grain boundaries. As the misorientation angle increases the space between dislocations decreases and subsequent overlap of dislocation cores occurs at angles of 15° and higher.[56] The two types of boundaries are reported to have varying mobility.[57] According to work by Winning et al. boundary mobility in aluminum bicrystals showed a dependence on misorientation angle and temperature. The mobility of high angle boundaries was found to be greater than low angle subgrains at temperatures of 200°C. This effect was intensified as the temperature was increased. While the diffusivity of the GBs was not observed movement of the boundaries was facilitated by diffusion as atoms are required to move atomic positions. Considering the differences in mobility, understanding the discrete interplay between Mg atoms and the grain boundaries based on angle is an interesting endeavor. Examples of a low (blue arrow) and high angle boundary (red arrow) are illustrated in soap bubble rafts below.
Figure 5: Rafts of soap bubbles exhibiting high (red arrow) and low angle grain boundaries (blue arrow)[34, 58].

Aside from general high angle boundaries there are special type boundaries, which include Σ# or otherwise known as coincidence cite lattice boundaries. These boundaries have been shown to improve properties such as embrittlement, stress corrosion cracking, and creep[59, 60]. The special CSL boundaries are displayed as Σ# with the number representing 1/# density of common lattice sites between grains. Boundaries with low CSL values are typically considered the primary boundaries which increase material properties with Σ3 or twin boundaries being the most desirable.

Thermomechanical processing is a standard procedure, first described by Watanabe[61], in an attempt to increase these special grain boundary types. This typically entails some form of deformation, usually cold rolling, and a subsequent anneal. This procedure can be
repeated multiple times to further improve the material or to assure full through thickness processing. One key aspect to this approach is that it is typically conducted on low stacking fault energy materials. Materials such as Steel and Cu have a higher propensity to form twin boundaries thus increasing the likelihood of forming special types of grain boundaries. While it is more difficult for aluminum alloys to form twins it is still possible for low value CSL boundaries to form[62].

Work by Davenport et al.[12] investigated the susceptibility of aluminum alloy 5182 to corrosion showing that low angle boundaries having the greatest resistance to attack compared to high angle. However, this work was also primarily based on low resolution techniques such as bulk etching, and atomic force microscopy, in regards to precipitate analysis at the grain boundaries. Due to this, there is high probability that precipitation at the low angle boundaries went undiscovered. Some other works have found that low angle boundaries <15° are indeed capable of sensitization and formation of fine particles does occur[15, 63, 64]. Also many early studies explain that initial H116 treatments were applied to the 5xxx series alloys to actually promote precipitation within the grain[19].

A study by Tan and Allen[13] observed the effects of thermomechanical processing on AA5083 in terms of corrosion resistance, grain boundary character, and special boundary or CSL distribution. The applied thermomechanical treatment was found to significantly increase the number fraction of Σ3, Σ7, Σ9, Σ15, and Σ23 type boundaries. It was found that due to the applied treatment that corrosion resistance was significantly reduced. It was concluded that while in comparison the low Σ value CSL
boundaries did increase it was not to the levels in which low stacking fault energy materials can achieve. The increase was shown only to be fractions of a percent increase in CSLs signifying a negligible impact on overall corrosion resistance and was mainly attributed to more equiaxed grain shapes and diminished texture. Yan et al. [65] investigated the dependence of precipitation on grain boundary character. It was found that the $\Sigma$ value had an impact on the thickness of $\beta$ precipitation along the boundaries. Boundary types $\Sigma 7$ and $\Sigma 21$ had average precipitate thicknesses of 2nm and 8nm respectively while higher sigma values of $\Sigma 37c$ and $\Sigma 39a$ had higher values of 45nm and 22nm respectively. This effect was attributed to the low energy of lower $\Sigma$ value boundaries as precipitation would be preferred at higher energy locations. Despite this low angle (lower energy boundaries) were still found to be susceptible to corrosion but did show better immunity compared to general high angle. Finally, sputtered Al-Mg with increased low $\Sigma$ boundaries was compared to standard bulk Al-Mg and found to have overall better corrosion resistance attributed to these boundaries. It was concluded that corrosion and $\beta$ precipitation was highly dependent on grain boundary character with misorientation angle, $\Sigma$ boundary value and adjacent boundary relationship the most important attributes.

Precipitation of $\beta$ phase occurs primarily at high angle grain boundaries but is also possible on pre-existing intermetallics [7, 10, 11] but the exact relationship between the grain boundary character and precipitation is still up for debate. In a TEM based study by Carroll et al. [10] $\beta$ precipitates were grown at 200°C for 24 hours appeared on both high angle and subgrain boundaries but misorientation was not mentioned. A similar study by Unwin and Nicholson [15] found that precipitation of $\beta$ phase was more difficult at low
angle boundaries than at random high angle GBs. The majority of literature considers low angle boundaries in this alloy system to be impervious to sensitization [12]. Tan and Allen [13] observed that material which was thermomechanically processed yielded a microstructure with a larger dislocation network and increased low angle boundaries showed higher corrosion resistance. In contrast, precipitation has been shown to be possible within the grain along dislocations and other defects, such as subgrains, which alloy developers have made use of in more corrosion resistant tempers (H116, H321, and H128) [20] A study by Zhang et al. [66] Zhang discussed the importance of misorientation on β phase precipitation and showed that high angle boundaries increased degree of sensitization (DOS) while low angle GBs lowered DOS signifying boundary misorientation has a significant impact on sensitization. The downside to the above literature is that there is no mention of the actual misorientation angle values and how they play a role in precipitation location, size, and kinetics.

2.5.2 General microstructure evolution and Impact of Grain size

Since the primary source of strength in aluminum alloys comes from cold work grain refinement and control of microstructure is an important process to discuss. This involves slowing the recrystallization process down, so smaller sized grains remain intact leading to higher strength as described by the Hall-Petch relationship. When a material is cold rolled it results in formation of dense tangles of dislocations which form wall like structures around areas that are almost free of dislocations. The hardness of this material is high due to the dislocation density and the interaction between the dislocations of the crystal.
The following section details the steps of recovery and recrystallization in terms of 5xxx series alloy. A more in-depth examination can be found in chapter 3 of Phase Transformations in Metals and Alloys by Porter and Easterling[58]. The first stage is the introduction of dislocations into the system via cold rolling. During this process, some energy can be stored at lower temperatures in the form of point defects within the crystal lattice. The added dislocations can also rearrange themselves during this stage into structures known as low-angle boundaries as described in the section above. The next step of this movement is recovery, which involves lowering the energy of the dislocations even further by means of climb. The low-angle boundaries are formed, and the dislocations in the tangles are rearranged due to a higher temperature. The reason for this is that there is a larger thermal activation needed in order for longer-range diffusion of the point defects to occur. The final stage is recrystallization, which occurs when the metal is heated above a critical temperature when new grains, which are mostly free of dislocations, are produced. Large-angle grain boundaries with a misorientation greater than 15 degrees are produced. The grain structure starts off small but begins to grow as the process continues. This further lowers the energy of the crystal due to the fact that the area of the grain boundary is reduced.
Figure 6: Schematic displaying the various stages of recovery, recrystallization and grain growth.[67]

Figure 6 above displays each stage of the recovery and recrystallization process from cold rolling to grain growth brought on by annealing. A general schematic showing the relationship between strength, hardness and ductility vs the various stages of the process is also given. It is clear that as dislocations are recovered strength and hardness levels drop dramatically but ductility increases. So by controlling the balance between amount of cold work and resulting microstructure is imperative to assuring proper mechanical properties and material performance.

High temperatures allow for the migration of grain boundaries to reduce the number of grains and increase grain diameter (grain growth). During grain growth the grain boundaries move toward their center of curvature. This results in an overall reduction in the size of smaller grains. This reduction of the smaller grains is influenced
by the relative size of the surrounding grains. Over time large grains will start to move in on the smaller grain. This causes the center grain to form concave grain boundaries toward its center. This leads to the smaller grain to only have three sides which make it more unstable thus reducing the ability of the cell to have larger curvature. Also the larger grain boundaries can hold more dislocations due to the larger surface area leaving them with a larger driving force. Eventually the smaller cells disappear and the larger grain boundaries become larger as the driving force in the material is released. In other words, as the material recrystallizes the grain boundaries move away from the center of curvature. The pressure difference caused by curved boundaries is to create a free energy or chemical potential that is used to drive atoms across the grain boundary. This energy difference pulls the grain boundary toward the grain of higher free energy.

![Figure 7: Example of energy gap for an atom to migrate from one grain to another during grain growth][58]
In order for the atoms to migrate and grow grains they must overcome the energy gap by means of thermal activation as shown in the figure above.

Aside from complex analysis of grain boundaries simple concepts such as grain size, caused by the process discussed above, and texture have also been shown to have an impact on sensitization and corrosion in 5xxx series alloys. As discussed mentioned above in Tan et al. the grain texture and size played a very significant role in lowering corrosion resistance. Grain refinement through thermomechanical processing has been implemented successfully in improving corrosion response [68-70]. While grain refinement is possible through chemistry changes[71] thermomechanical treatments provide a way to achieve different properties for specialized applications post material production. A review article published by Ralston and Birbilis[69] does an excellent job of summarizing the effect of grain size on corrosion covering many materials. It is clear from this review that there is no unified theory in relation to grain size. Depending on the material larger grain boundary sizes can either hurt or help corrosion resistance but it is clear that general changes to grain size in materials of the same composition can have a major impact on corrosion potential. Work by Zhang et al.[68] specifically on AA5083 observed the corrosion response in relation to grain size comparing a wide range of grain sizes. The samples compared in this study were: a severely plastic deformed material via ECAP processing material with average grain size of 1.2µm, a high pressure torsion processed material of grain size 241nm, a cryo-rolled sample with 6.9µm grains, and a 77.3% cold rolled plate with grain size 50µm. The degree of sensitization (DoS) values were reported showing that for the ECAP samples DoS increased as a result of reduction of grain size conversely, the DoS of the rolled samples decreased as grain size was
reduced. It was concluded that while grain size does contribute to corrosion resistance other factors such as misorientation are also important in terms of controlling DoS. It was also suggested that knowing the starting material microstructure is important when fabricating structures and performing procedures such as welding which will have a localized effect on the material and thus further effect corrosion resistance.

2.5.3 Effect of prior strain on precipitation

As discussed previously the 5xxx series alloy system derives its strength through Mg additions as well as increases in dislocation density from cold work. Early work by Dix et al.[16] discussed the effects of additional cold work on the sensitization process and emphasized that there was a tradeoff between strength and corrosion resistance. This review showed that a material having a lower Mg content could sensitize just as fast as a material with a higher Mg content when additional dislocations were added via cold rolling. Work by Gonsky and Furrer [72] expressed that precipitation at the GBs could be enhanced by intrinsic defects but even more so by those which were extrinsic.

2.5.4 Effect of thermal treatment

While any form of Mg segregation and β phase precipitation is viewed as sensitization it is still not understood which form is most applicable to materials exposed to in-service conditions. Current studies attempt to mimic precipitation by two different approaches: A low temperature anneal at very long exposure times, or a high temperature treatment on an accelerated time scale. β equilibrium phase formation, as discussed previously, is said to occur at 200-300°C but some studies show β equilibrium precipitates at ageing conditions below 200°C [5, 7, 9]. A study by Goswami et al. [8]
observed β precipitation in a 5083-H116 alloy that was homogenized at 250°C for 10hrs and aged at 100°C for times ranging from 3-90 days. Although the sensitization treatment was very short only β equilibrium precipitates were found in the alloy. Zhu et al.[5] had similar findings in 5083-H131 which was aged at 70°C for 1 year and 175°C for 15 days yielding β phase characterized by STEM and eds.

On the other hand, the literature also exhibits examples of β precipitation at very high temperatures at shorter aging times. Carroll et al. [10] observed β equilibrium phase growth at GB’s and subgrains in 5083 after 24 hours at 200°C. Fuller et al. [11] showed precipitate growth at the GBs after 72 hours at 288 and 300°C in modified 5754 (higher Mg content) aluminum.

Again while both approaches seem to form β phase precipitation it is not always clear what type of precipitation is present be it β’ or β. This idea can become confusing when surveying the literature which consistently labels all precipitation as “β phase” despite heat treatment applied. Some of the difficulty in distinguishing the two phases is also brought on by the composition being the same as well as low resolution techniques used for characterization. While the general consensus is that β equilibrium is the main cause of sensitization some[29, 30, 35] have argued that the β’ phase is most likely the main cause of corrosion.

2.5.4.1 Segregation of Mg during sensitization

While it is well understood that sensitization is strongly temperature driven[28] the exact mechanism of precipitate formation is not fully known. Despite previous TEM studies, there is a lack of information about the local chemistry changes, specifically at the GB’s, during sensitization. Searles et al. [14] observed a Mg depletion from 4.4 to
3.5wt% after sensitization at a boundary with no visible precipitate. This result supports the collector plate mechanism proposed by Aaron and Aaronson [73] where solute diffuses to the GB and then quickly feeds precipitates. On the other hand, Goswami and Holt [8, 9] observed no depletion of Mg via EDS line scans. It was also observed that the growth rate of the precipitates during both nucleation and coarsening were faster than the bulk diffusion of Mg which later led to the conclusion that pipe diffusion was enhancing the bulk diffusivity of Mg [8]. These ideas will be discussed in further detail in the following section.

2.6 Mg segregation mechanisms

Sensitization is effectively the segregation of Mg atoms toward the grain boundaries over time. In order to fully understand the process it is necessary to discuss concepts pertaining to segregation. In general, segregation occurs in systems which contain inhomogeneities within the solid material[74]. Areas such as grain boundaries, defects like dislocations and vacancies, intermetallics, and free surfaces, can act as sites for solute atoms to lower their Gibbs free energy of the system[75]. Due to these differences in energy and composition, solute atoms are attracted to these areas. One of the most important locations pertaining to segregation is that of the grain boundaries. Localized segregation of solute to the grain boundaries can be brought on by effects such as temperature, radiation, or chemistry imbalance, and has a tendency to lead to embrittlement and ultimately failure[76, 77]. The problem of grain boundary diffusion is a very complex one, contingent on many factors and processes. The most simplistic way this process can be explained is that atoms must move from the matrix to the grains and diffuse within the boundary. The process of the solute reaching the grain boundary alone
can be very complicated. Theories of bulk diffusion\cite{78} and pipe diffusion\cite{8, 33} have been used to explain transport of solute to the grains, but a lack of physical evidence of these phenomena still remain. Magnesium is an oversized solute being 12\% larger than aluminum and is also substitutional. Thus as it is driven to the boundary by thermal exposure allowing for the energy of the system to be minimized\cite{78}. Applying these ideas to aluminum, Goswami et al.\cite{7} conducted TEM experiments to resolve the mechanism and growth of $\beta$-phase in 5083 alloy. As-received samples were tested against bulk sensitized samples at 175$^\circ$C for 10 days. The As-received sample did not exhibit any $\beta$-phase but the annealed As-received did show $\beta$-phase precipitates as expected. It was observed that the $\beta$-phase formed at the aluminum grain boundaries and on the Mn particles found in the matrix. The $\beta$-phase precipitates were measured to be 50-190nm in thickness and calculations were conducted to compare the theoretical thickness with the observed thickness of the precipitates. The equation was based off the bulk diffusivity of Mg in Al and the resulting calculated upper limit was found to be 20nm which was did not agree well with actual measured precipitate sizes. As this example suggests, bulk diffusion is not the only mechanism involved in $\beta$ phase formation. Due to this, focus on the primary contributor to Mg diffusion has shifted from bulk diffusion to that of pipe diffusion via dislocations, which will be discussed next.

The most generally accepted mechanism for Mg transport to the grain boundaries is that of pipe diffusion. The mechanism of pipe diffusion in metals has been proposed for a number of years but with little physical evidence \cite{33, 79}. Pipe diffusion effectively is defined as a narrow high diffusivity path (dislocation) within a matrix of a lower diffusivity which acts as a pathway for solute diffusion\cite{58, 79, 80} depicted in Figure 8.
Pipe diffusion allows for increased mobility of atoms along disordered cores of dislocations. It has been shown in similar alloys that atoms can be transported at rates orders of magnitude faster than by bulk diffusion alone [33, 78]. Work by Goswami et al.[8] observed that in Al-7.5 Mg material which was severely plastically deformed, the sensitization process was greatly enhanced by increases in vacancies and dislocations from processing. While pipe diffusion is likely the mechanism or at least a major part of it, the theory has yet to be fully confirmed in the 5xxx series alloy.

The topic of what occurs after solute reaches the boundaries is still open for debate as once the solute has reached the grains new mechanisms begin to take over. The general assumption when discussing what happens within the GB on the atomic level is that solute atoms move by exchanges with vacancies but more recent results show that interstitial sites can also play a role as well[81, 82]. Grain boundaries can be thought of as vacancy sinks that lower the overall concentration of vacancies[83]. When energy is added to the system this natural gradient of vacancies to the grain boundaries can aid in

**Figure 8: Illustration of dislocations through a matrix acting as pipes or diffusion pathways[58]**
solute segregation. As vacancies travel along the grain boundaries solute atoms (In the case of this thesis Mg) can also be carried along the boundaries. Typically when discussing Mg segregation along the boundary the collector plate mechanism is generally described as the primary mode of transportation[84]. Here, solute diffuses from the matrix to the grain boundary and the boundary acts as a collector of the solute ultimately taking on the form of a plate[85]. The solute travels along the grain boundary toward the location of nucleation from both sides of the boundary increasing both the length and the width of the precipitate as shown in Figure 9.

![Diagram](image)

**Figure 9:** Example of the lengthening and thickening of a collector plate type precipitation at a grain boundary[85].

### 2.7 Sensitization remediation

In order to combat the deleterious effects of sensitization some steps have been taken to reverse precipitation in these alloys. One such process is known as remediation in which removal or reversal of the precipitation process can be done by heating the material up above the solvus point and dissolution occurs due to the instability which is driven by the localized chemistry imbalance[86]. In the case of aluminum, the material is brought up to the solidus temperature (~280°C) to remove the β phase and redistribute
the Mg within the matrix. While this approach has shown potential at removing the sensitization [18, 87] the effects are temporary when re-exposed to heat [17, 18].

Thermomechanical treatments have also been implemented [13, 88] similar to grain boundary engineering in steel and have shown some signs of improved corrosion resistance but a permanent solution has yet to be found.

This process can have many names but is typically referred to as remediation, desensitization, sensitization reversal, or precipitate dissolution. While it may appear to be so, this process is not simply the reversal of the nucleation and growth process, rather the process is more complex. In the literature a few attempts have been made to reverse the precipitation at the GBs and improve corrosion resistance of sensitized material. Chen et al. [89] developed a thermal process to improve corrosion resistance in AA5456-H116. Sensitized in service ship material was annealed at 250°C for times of 10, 30, 60, and 180 minutes. Microhardness, NAMLT (Nitric acid mass loss testing aka. ASTM G67), and electrochemical measurements were taken comparing the various treatments as shown in Figure 10.

![Figure 10: Plots of Vickers hardness vs thermal treatment, NAMLT vs. exposure time and electrochemical measurements from Chen et al. [89]](image-url)
The overall hardness values exhibited a significant drop at temperatures over 250°C or at thermal exposures treatments longer than 30 minutes. The loss in hardness at the range of 20-250°C was attributed to recovery while treatments of 250-350°C hardness losses were driven by recrystallization and finally coarsening occurred at temperatures above 400°C (Figure 10 Left). A treatment at 250°C for 30 minutes was chosen to minimize hardness decreases while lowering the degree of sensitization as shown in the NAMLT results plot (Figure 10 center) also as a result of this treatment corrosion potentials fell to more reasonable levels (Figure 10 far right). While the lowering of hardness values is a negative, no tensile testing was completed which is the primary requirements for knowing if material can be used in service or not[20]. Work by Kramer et al.[18] sought to develop a method for localized reversal of sensitization using a heated steel plate which could be used in the field.
A stabilization plot was developed (Figure 11 Left) by Kramer[18] using work from Dix et al.[16] and Scamans et al.[90] to separate the regimes of sensitization, stabilization and annealing. By following this plot the necessary thermal treatment based on weight % Mg is easily visualized. In order to understand the extent of softening and mass loss in 5456 plate the material was first sensitized at 150°C for 24 hours and was exposed to a temperature range of 200-340°C for 24 hours to reverse the sensitization. Consequently it was found that unlike the previous study annealing did not occur below 300°C and it was

Figure 11: Left: A stabilization plot developed by Kramer et al[18] from work by[16], Right: Effect of exposure temperature on Mass loss and tensile yield strength.[90]
also found that above 225°C mass loss due to sensitization dropped dramatically (as shown in Figure 11 right). Another key finding is that once the material that was desensitized and subsequently re-exposed to a sensitization treatment, the values of mass loss returned to their original state. While it does appear that sensitization can be reversed there is not a catch all treatment which can be applied. It is clear that understanding of the starting material is required otherwise things like mechanical properties may be greatly impacted. Also missing from the above literature is a major lack of general electron microscopy showing the sensitization i.e. if precipitation is actually being removed/dissolving or if there is some other mechanism occurring (grain growth, dislocation recovery) leading to the lower mass loss. While these studies are steps in the right direction there is still a lot of room for improvement.

2.5 In situ heating in TEM

The addition of analytical holders such as the Gatan heating holder has greatly expanded the abilities of the TEM. Heating holders have been used extensively to examine dynamic processes such as precipitate phase transformations [34, 91-96], grain boundary phenomena[97, 98], and pipe diffusion[33]. In general, standard TEM concentrates on post analysis but analytical holders have given researchers the ability to directly view phenomenon in real time. Garg and Howe[92] observed the secondary precipitation of the omega phase in Al-Cu-Mg-Ag. Three sample types were used of varying heat treatments and then heated in situ at 10°C/Min from 0°C to 400°C. The results showed that nucleation of the omega phase was uniform with no preference for the defects and had preferential growth along the <112> direction. Furthermore, it was
observed that thickening of the omega phase plates (seen in Figure 12 plate “D”) occurred faster by dislocation dissociation.

**Figure 12:** Micrographs at 400°C taken 5 min apart showing thickening and growth of γ precipitate (Arrow marked “D” in the images)[92]

From this study they were able to show that the omega precipitates had a preferred orientation and that dislocations aided the thickening of the phase plates. An experiment like this without in situ heating would be much more complex if completed in the bulk. Many samples would have to be investigated at various stages of aging requiring comparison of many precipitates, whereas in the case, the direct growth of precipitates was observed by looking at a single precipitate. While in situ heating is a major advantage there are some unique downsides which need to be considered such as thin film effects. Since the material is extremely thin issues like thermal gradients and surface
diffusion can lead to false observations. Due to this it is imperative that if it the give
phenomenon can be tested in the bulk that the ex situ data should be compared to see any
inconsistency. One such work by Thomas and Whelan[99] observed thin film effects in
Al-Cu alloy. They found that Al-Cu precipitates were found in the thinnest part of the
TEM foil near the center hole of the sample. When the sample was observed at thicker
areas away from the hole no precipitates were found. This study alone shows that careful
consideration and restraint is required by researches using these techniques, and that
when possible, complementary ex-situ bulk work is indispensable.

2.6 Summary of current understanding

It is clear from the above that sensitization readily occurs within the 5xxx series
aluminum alloy system but there are some glaring omissions from our current
understanding. It has been discussed that there is a difference between precipitation on
high and low angle boundaries but without relation to size or preferred location of
precipitation. The impact of prior strain on precipitation is not well understood despite it
being a key factor contributing to the admirable mechanical properties of the material.
Further, the process of sensitization is typically described using low resolution techniques
and always after the precipitation has occurred. Temperature regimes within the literature
overlap and precipitation is placed in an umbrella of β phase despite heat treatment
regime, a symptom of using lower resolution techniques. Due to these issues the
approach of this work has focused on a total reexamination of the β phase precipitation
using high resolution in situ TEM to better understand the location, size, kinetics,
temperature regimes, and Mg diffusion throughout the lifetime of β precipitate.
Chapter 3: Experimental Methods

3.1 Material Selection

Aluminum alloy 5456-H116 was the primary material used for the enclosed studies. This material was provided by Alcoa through the naval surface warfare center Carderock. The material is provided in the form of 0.25” plate in the H116 condition meaning the material was rolled between 1/8 and 1/4 of full hardness [24]. The composition of the material is shown in the Table 1 below:

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Mg</th>
<th>Mn</th>
<th>CR</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance</td>
<td>5.0</td>
<td>0.63</td>
<td>0.08</td>
<td>0.19</td>
<td>0.1</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Composition of AA5456-H116 used as primary material within this work.

Due to the H116 treatment there are extensive subgrain network and a significant amount of dislocations within the material (Figure 13a). As commonly reported in other works[21, 44] many intermetallic precipitates are present such as Al-(Mn, Cr, Fe) plates in Figure 13b and long rod shaped Al₆Mn precipitates as shown in Figure 13c. Despite being new material and considered unsensitized some preexisting Mg rich β’ precipitates were found in the As received material. It should also be noted that some Mg₂Si intermetallics were also found but were a very rare occurrence.
Figure 13: Low mag TEM bright field images of (a) subgrain and dislocation structures in starting material. (b) Al-(Mn, Cr, Fe) intermetallic plate (c) example of very common Al₆Mn rods (d) preexisting Mg rich β’ precipitates. (Right) EBSD scan of starting material microstructure.

AA5083-H116 plate was acquired for bulk processing and corrosion experiments. Two different plates of 5083–H116 were purchased, one provided by Carderock naval surface warfare center (plate A, 0.5” thick), and the other purchased through McMaster-Carr Supply Company (plate B, 3/8” thick). This alloy is another very commonly used version but generally contains lower levels of Mg (~4%). The nominal composition of these materials is shown in the Table 2 below:

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Mn</th>
<th>Cr</th>
<th>Fe</th>
<th>Si</th>
<th>Zn</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>AA5083</td>
<td>4.0 – 4.9</td>
<td>0.4 – 1.0</td>
<td>0.05 – 0.25</td>
<td>0.40 max</td>
<td>0.40 max</td>
<td>0.25 max</td>
<td>Bal</td>
</tr>
</tbody>
</table>

Table 2: Composition of Selected Aluminum Alloy (wt. %)[20]
This material was mainly used for some bulk thermomechanical processing experiments as well as bulk corrosion studies. Aside from Mg content of the material it was very similar to the 5456-H116 material above.

In an attempt to compare real world sensitization treatments to lab sensitized, samples of failed in service 5456-H116 from Naval Surface Warfare Center Carderock were supplied. This material was taken from the intake area of a ship which had failed due to formation of stress corrosion cracks.

The final material used in this work was a 12” x 12” x 0.25” inch fully recrystallized 5456-H116 aluminum plate. This material acted as a baseline for material which has minimal subgrains and dislocations.

![Figure 14: Bulk As received 5456-H116 fully recrystallized plate](image-url)
3.2 Material preparation

3.2.1 TEM sample preparation

All TEM samples from this work were produced in the same manner for all TEM experiments. Coupons were cut from the bulk material (however processed) using a Buehler IsoMet high speed saw with a Silicon carbide blade. All samples unless noted otherwise were taken from the long transverse direction as shown in Figure 15 below.

![Figure 15: Image illustrating TEM sample location from bulk. Red dotted line represents where coupon was cut.](image)

The samples were cut to a thickness of 1-2mm and mounted to an aluminum puck with superglue. An important point is that typically crystal bond is used for TEM sample preparation which requires ~120°C to melt but due to the high temperature range superglue was used to avoid possible sensitization. The samples were ground on both sides using 320, 400, 600, and 800 SiC sand paper to a final thickness of 40-50µm. In order to assure the final thickness of 50µm digital micrometer was used. The sample and aluminum puck were then submerged in acetone and left for 24 hours or until the sample was free. A Gatan disk punch system (model 659) was used to punch 3mm size TEM disks. The samples were then ion milled to final TEM transparency using a Fishione
Model 110 ion mill. It should be noted that the thickness of 40-50µm was necessary for three main reasons: 1) It was found that if the sample was too thin even when in the range of 30-40µm it was very common for the sample to curl up on itself during ion milling 2) When the sample was too thin the samples would mill too quickly and layering would occur rather than a graduated wedge shape at the hole 3) If the sample was too thick aside from taking much longer to mill the area around the hole would be too thick due to the ion mill beam being blocked at lower milling angles. After much trial and error the best recipe was found to be as follows:

<table>
<thead>
<tr>
<th>Step</th>
<th>Time</th>
<th>Voltage</th>
<th>Current</th>
<th>Rotation</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3-4 Hours</td>
<td>5kv</td>
<td>5mA</td>
<td>360°</td>
<td>15°</td>
</tr>
<tr>
<td>2</td>
<td>2-3 Hours</td>
<td>5kv</td>
<td>5mA</td>
<td>360°</td>
<td>12°</td>
</tr>
<tr>
<td>3</td>
<td>30 min</td>
<td>4.5kv</td>
<td>5mA</td>
<td>360°</td>
<td>10°</td>
</tr>
<tr>
<td>4</td>
<td>20 min</td>
<td>4kv</td>
<td>5mA</td>
<td>360°</td>
<td>8°</td>
</tr>
<tr>
<td>5</td>
<td>10 min</td>
<td>3kv</td>
<td>5mA</td>
<td>360°</td>
<td>6°</td>
</tr>
<tr>
<td>6</td>
<td>5 min</td>
<td>1.5kv</td>
<td>5mA</td>
<td>360°</td>
<td>4°</td>
</tr>
</tbody>
</table>

| Table 3: Ion mill sample preparation recipe |

No significant signs of improvement were found when samples were milled using low temperatures via liquid nitrogen vs. room temperature so the practice was discarded.
The main adjustments were usually made to the first two steps depending on sample thickness. If the samples were on the thicker side longer times should be used. Effectively step 1 was used to create the center hole in the sample with step 2 acting as the first stage of sample thinning. Steps 3-6 were used as a way to clean up the sample with step 3 also aiding in some thinning. The best samples were those in which step 1 generated a tiny hole where only a little light was able to pass through with step 2 opening the hole and further thinning the specimen. The final steps which were optional 5-6 were used to help clean up the sample and remove some re-deposited material from the thin area. Despite these final steps some re-deposition was possible ranging from excessive to minimal.

While the TEM sample preparation was very time consuming the approach was necessary compared to other standard TEM preparation like that of FIB or Electropolishing. This approach allowed the observation of samples which had already been sensitized and maintained the precipitates with minimal disturbance. As with most TEM based techniques this procedure was hit or miss but yielded a 70% success rate. Electropolishing was attempted with varying concentrations of nitric acid in methanol, a very common aluminum electrolyte,[100] using a Struers TenuPol-5, but in every case the β precipitates were completely dissolved at the grain boundaries thus the procedure was discarded for ion milling.

3.2.2 Bulk SEM preparation for EBSD

Samples of aluminum were processed, cut and made to fit into 1.5inch round standard mounting cups. Release agent was applied to the mounting cups and a two part low temperature slow cure epoxy (Buehler epoxicure2) mounting resin was used. After a 24 hour cure the samples were remove from the cups and grinding and polishing was
completed. The same approach was taken for all samples in which EBSD was to be conducted. Samples were polished by hand using MetaServ 250 Twin polishing wheel with the complete procedure in Table 4 below.

<table>
<thead>
<tr>
<th>Step</th>
<th>Grit</th>
<th>Time</th>
<th>Wheel Speed</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>320 grit SiC</td>
<td>1-2 min</td>
<td>150-250 RPM</td>
<td>optional</td>
</tr>
<tr>
<td>2</td>
<td>400 grit SiC</td>
<td>1-2 min</td>
<td>150-250 RPM</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>600 grit SiC</td>
<td>1-2 min</td>
<td>150 RPM</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>800 grit SiC</td>
<td>2-5 min</td>
<td>150 RPM</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1200 grit SiC</td>
<td>5-10min</td>
<td>150 RPM</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9µm Diamond</td>
<td>10-15min</td>
<td>150 RPM</td>
<td>optional</td>
</tr>
<tr>
<td>7</td>
<td>3µm Diamond</td>
<td>10-15min</td>
<td>150 RPM</td>
<td>Trident cloth Sonicate after</td>
</tr>
<tr>
<td>8</td>
<td>1µm Diamond</td>
<td>10-15min</td>
<td>150 RPM</td>
<td>Microcloth Sonicate after</td>
</tr>
<tr>
<td>9</td>
<td>0.03 Colloidal</td>
<td>2 Hours</td>
<td>50-70% Power</td>
<td>Vibro polish dilute with water 1:1</td>
</tr>
</tbody>
</table>

Table 4: Bulk grinding and polishing protocol
Step 1 was optional but was primarily used to remove any epoxy that had covered the sample while mounting. It was also used to create a new flat surface to avoid any damaged areas from saws or other processing procedures. Steps 2-4 continued to help create and maintain a flat even surface. In cases of more difficult to work with material, samples which had a lot of intermetallics or contained higher level of work hardening, additional grinding time was required. Steps 5-9 begin the polishing phase of the procedure. At 800 grit some small scratches are visible but at 1200 grit the majority of scratches from the surface are removed and a matte finish should be observed. A few tiny scratches were sometimes seen in an optical microscope but the samples were taken to the next polishing step. Steps 6-8 utilized water based diamond suspension particularly MetaDi Supreme polycrystalline diamond suspension by Buehler. The 9 µm diamond in step 6 is optional but can also be interchanged with the 1200 grit SiC paper in step 5 with no adverse effects. At step 6 like step 5 the sample should have a flat even matte finish. At step 7 the samples were polished with 3 µm diamond solution on white low nap trident polishing cloths. The cloth used for polishing was found to be very important as the low nap allowed for the diamonds to ride on top of the cloth and helped to maintain a flat sample. At this step the brown high nap cloth was used but was found to not achieve as good of a polish at this micron level. After 10-15 minutes at the 3 µm stage the sample should appear as a hazy mirror as if it has a layer of steam that you can remove. Step 8 utilized the high nap microcloth in which 1 µm diamond rides in the fibers of the cloth. After this step the samples should appear to have a high mirror finish with extremely minimal scratches only visible in an optical as the sample is tilted to catch light in the scratch. The final step 9 is the most important and tends to the limiting factor when it
comes to final surface quality for EBSD. A 1:1 water to colloidal silica suspension (Buehler MasterMet2) mixture was used in a VibroMet™ 2 on a 50-70% setting with a high nap microcloth. Due to the ~10pH of the colloidal silica suspension if the concentration was any higher than 1:1 pitting would occur quickly in the aluminum material. Time was also found to be a key factor requiring samples to be polished for no more than two hours. If samples were left too long in many cases significant pitting would occur so for some samples shorter vibro polishing times were required ranging from 1:40 to 2 hours. After vibro polishing samples were immediately rinsed with copious amounts of water and swabbed with a wet cotton swab to assure removal of colloidal silica contamination. Sonication was also implemented to assure minimal contamination of larger polishing particles throughout the steps. As a final note automatic polishing was used interchangeably via an EcoMet™ 300 Pro with a polishing force of 20 newtons and a head speed of 60RPM in the counter direction but was sometimes found to lack the control and feel found with polishing by hand.

3.2.3 Cold rolling and Thermomechanical processing procedure

3.2.3.1 Cold rolling for in situ TEM experiments

In order to understand the impact of dislocation density on secondary β phase precipitation samples of varying cold rolling reductions were made from 5456-H116 material. Rectangular coupons of dimension 0.5cm x 0.25cm x 0.635cm were cut from the bulk 0.25” plate and cold rolled to values of 30% and 50% reduction. This was completed in addition to the H116 treatment in the same direction as the original cold rolling. 3mm disks were then taken according to the procedure in the TEM sample preparation section above.
3.2.3.2 Bulk SEM Thermomechanical processing

3.2.3.2.1 Through thickness bulk thermomechanical processing

Bulk 1/2” 5083-H116 plate (Plate A) was prepared for observation of through thickness bulk thermomechanical processing in an attempt to further improve the H116 treatment. Multiple samples were cut from the plate and processed according to the flow chart below.

Sample Processing Procedure

1. **As Received**
   AA5083-H116

2. **Annealed**
   345°C/1 hr/air cooled

3. **Cold rolled**
   10, 20, 30, or 50% reduction

4. **Heat treated**
   400 or 500°C/1 hr/water quenched

5. **Sensitized**
   150°C/100 hrs/air cooled

6. **ASTM G67 Nitric Acid Mass Loss Test**
   30L/m² of 70 wt% HNO₃
   30°C/24 hours

   *All samples were corroded in the G67 test*

**Figure 16: Annealing process flow chart for thermomechanical treatment approach of AA5083-H116**

Control samples were set aside and were not thermomechanically treated but were sensitized for comparison. All samples except for the control were annealed at 345°C for
1 hour and air cooled. A set of two 0% reduced samples were then heat treated at either 
400 or 500°C for 1 hour and then water quenched. Samples which were to be cold rolled 
were ground to a thickness which when cold rolled would achieve a final thickness equal 
to all other samples of ~6mm. So for instance if the 10% sample was not ground to the 
final thickness of the 50% reduced sample it would ultimately be 40% thicker and skew 
the nitric acid mass loss tests which can vary with thickness. The rolled samples were 
then annealed at 400 or 500°C for 1 hour and water quenched. Two samples of each 
treatment (in Figure 16 each box represents 2 samples) were cut and final sample 
dimensions of 6mm x 50mm x 50mm were achieved by bulk grinding with SiC paper. 
After this all samples were marked with Letter/number punches to assure post NAMLT 
identification and then sensitized at 150°C for 100 hours and air cooled. G67 NAMLT 
testing was conducted on all samples according to ASTM g67[55] and section of this 
document.

3.2.3.2.2 Surface vs. Center comparison of thermomechanical processing

A plate of 12”x12” 3/8 inch thick AA5083-H116 material was acquired from 
McMaster-Carr in order to compare the surface and center corrosion resistance after 
thermomechanical processing was completed. The sample flow chart for 
thermomechanical processing of plate B is shown in the Figure 17.
In a similar flow chart to plate A above plate B was annealed, cold rolled, solution treated, and sensitized. Plate B was cut with a band saw into six pieces with dimensions 4” (transverse) x6” (longitudinal) in area. Samples were then milled to achieve uniform final thicknesses after cold rolling at percentages of 0, 5, 10, 15, and 20% reductions. Some material was set aside to act as the control and the rest of the material was solution annealed at 400°C for 1 hour and water quenched. This process was used to normalize the material removing any damage from the band saw and also acted to return any Mg which had precipitated back into solution. After the anneal the plates were cold rolled parallel to

Figure 17: Flow Chart of Applied Thermo-Mechanical Processing of plate B
the H116 treatment. An additional 400°C anneal for 1 hour with a subsequent water quench was completed to aid in recovery. Six ASTM G67[55] samples were then cut from the bulk, 3 samples were cut from the area towards the top and 3 from the center of the bulk processed piece as shown in Figure 18.

![Surface and Center](image)

**Figure 18:** Example showing location of G67 samples taken from the surface and center of processed plate B.

The samples were then sensitized at 100°C for 100 hours and air cooled. Samples which did not receive sensitization did not receive any other treatment. Final ASTM G67[55] dimensions of 50mm x 50mm x 6mm were achieved using an end mill. The samples which the surface microstructure was of interest retained the entire cross section while the samples observing the center microstructure had an extra 0.07” milled from both rolled surfaces. The reason for this is that the rolled microstructures from the surface were found to extend deep into the center of the material in the 10% cold rolled plate.
Due to this, all “center” samples were milled in order to avoid surface microstructure contributions and to assure consistent results.

**3.2.5 Bulk ASTM G67 corrosion testing**

All nitric acid mass loss corrosion testing (NAMLT) was completed in accordance with the procedure found within ASTM G67[55] standard. All samples were machined to final dimensions of 50mm x 6mm by thickness of material and multiple test specimens for each condition were tested. Samples were all measured with calipers, and labeled using letter and number punches and each given a specific code. Samples were then cleaned to remove any oil or contamination from processing via a desmutting procedure as shown here:

1. In a chemical fume hood, dissolve 15 g NaOH into 300 mL H_2O and heat to 80°C
2. Place aluminum sample into NaOH solution for 1 min. – turning the sample over after 30 sec.
3. Rinse the sample with water
4. Place the sample in nitric acid for 30 sec. – turning the sample over after 15 sec.
5. Rinse the sample with water and place onto a paper towel to dry overnight

All samples were then sent to Naval Surface Warfare Center, Carderock where the samples were weighed, emerged in a nitric acid bath for 24 hours at a constantly maintained temperature of 30°C. After the nitric acid emersion samples were rinsed and sonicated to release any material which had not fallen off of the samples and then final weights were taken. Finally, the degree of sensitization or mass loss was calculated and described in terms of mg/cm^2 representing the amount of weight loss over unit area.
3.2.6 Ex situ heating experiments

Ex situ heating experiments were completed to complement in situ results and act as a check for common pitfalls of in situ TEM such as thin film effects and thermal variations. All in situ study heat treatments were applied to the same sample material in bulk form and used as a “in situ control”. Samples were cut from the same bulk starting material processed either by cold rolling or thermal treatment and then processed as all other TEM samples as detailed above.

3.3 In situ TEM heating procedure

The TEM used for all studies except EELs segregation studies was a JEOL 2100 LaB$_6$ TEM at Drexel University’s Centralized Research Facility. In situ heating experiments were carried out using a Gatan heating holder model 628 and the included digital temperature controller to record time and temperature. Experiments were recorded in situ at 10 frames per second via Debut digital screen capture software using a Gatan Orius 832 fiber optic 10.7 megapixel ccd detector. A typical heating experiment heat treatment is shown below (unless otherwise noted):

1: An area was found containing multiple grains preferably near pre-existing β’ precipitate or triple points and a high contrast objective aperture to maximize visibility of GBs and precipitates
2: Bright field TEM images were taken to act as a “before” image for later comparison
3: Next the temperature ramping at 0.5°C/sec and start video acquisition was begun
4: The area of interest was kept centralized using the TEM trackball and focus was maintained using defocus and z height when possible
5: When the maximum temperature was reached (typically 300°C) the sample was held for 5 minutes and any changes were observed.
6: The temperature was ramped back down to room temperature
7: Post heat bright field TEM images were taken and any post precipitate analysis was completed
While the procedure is fairly straightforward there were many difficulties when attempting the heating experiments. One of the most difficult aspects of this work is trying to find a location where precipitation would occur. In most cases unless the sample was heavily deformed the majority of precipitation happened in other areas of the sample. The only real solution for this is to repeat the experiments until something occurs which can take many trials. Also, once samples were heated they were deemed “destroyed” and were not used again except for post heat precipitate analysis. Another note to keep in mind is that in order to avoid any potential thin film effects areas directly near the center of the TEM disk hole were avoided and focus was applied to thicker areas of the TEM foil. Also as a check all treatments were repeated ex situ to apply a more “real life” condition as it is known that some strange phenomenon can potentially occur in the TEM.

3.3.1 Post heat treatment analysis

3.3.1.2 Misorientation analysis via Nanomegas

Post-annealing precession diffraction analysis in regions of interest (GBs, dislocation networks) was performed using Nanomegas ASTAR™ orientation imaging. The Nanomegas ASTAR™ system works by generating orientation image maps similar to electron back scatter diffraction (EBSD) by using electron diffraction patterns rather than Kikuchi bands. This tool takes control of the TEM scan coils (B) via the control unit (NanoMegas DigiSTAR precession unit (D)) and rasters the beam over the sample area. Each spot in which the beam dwells a nanobeam diffraction pattern is generated on the inclined phosphorescent screen and acquired by an externally attached high speed CCD camera (A). Finally the patterns were collected and stored by the software for further analysis (E).
Figure 19: Nanomegas ASTAR system installed on JEOL-2100 TEM at Drexel University[101]

A similar operating procedure has been described in other students works at Drexel University[101] but will be rehashed within this work with a few updates. The operation begins by observing an area of interest in which a good nanobeam diffraction pattern can be acquired easily. Once this is found in bright field TEM mode the smallest condenser aperture is inserted into the microscope and aligned. Centering of the aperture and knowing when it is best centered can be tricky. The best approach for this is to bring the aperture to the center of the phosphor screen with the adjustment knobs then turning the brightness knob back and forth through the crossover the aperture should appear to pivot around its self. If the aperture appears to move from side to side then it needs to be
adjusted. Continuing, the TEM is then switched to nanobeam diffraction mode (NBD) and hysteresis is removed by switching back between TEM mode and NBD mode until beam is stable. The spot size was adjusted until the desired beam intensity was achieved. While there is a range of spot sizes available 15nm and 25nm were used primarily in this work. It should also be noted that the actual spot size was larger than reported by the TEM. The focus and voltage center was then rechecked to assure that there was minimal movement of the beam. The beam was then processed at an angle 0.61° at 100Hz to increase the intensity of diffraction spots. Due to the usage of procession the beam was aligned to form a single spot rather than a ring using the adjustment controller (C). Beam adjustments were also made in diffraction mode to minimize movement of the diffraction pattern by using the diff focus knob on the TEM. The descan and nanobeam were also adjusted to assure proper alignment of the system. Once all alignments were complete scans were then setup using the included software on the computer (E) with input parameters of step size and area (usually step size of 5nm was used and the scan size changed depending on magnification).

Once the scans were acquired orientation maps were generated by cross correlating the collected diffraction patterns with the “known” or theoretical patterns. All orientation image maps within this work were generated by using an aluminum bank file created from a .cif file (Crystallographic Information File) with the included Nanomegas software. Since each pattern was matched values for the quality of the matching was giving in a measure known as “index”. In general higher index represents a closer match and the higher the “reliability” the greater the confidence index. Images with very low values were discarded but this was most attributed to samples which were too thick. On
the other hand samples can have a low reliability when the sample is on zone so best judgment should be used when analyzing these results. The primary use of this technique was to gain the misorientation angle of grain boundaries in which precipitation had occurred. Within the analysis software the dropdown menu over the orientation map has the option “disorientations” or misorientations. When this dropdown is selected a line can be drawn across the grain boundary or area of interest and the misorientations are given between each acquired diffraction pattern as shown below.

Figure 20: Example of misorientation data output from Nanomegas mapviewer software.

3.3.3 Precipitate measurements

In an attempt to correlate misorientation angle and/or rolling reduction with precipitate size the precipitates grown during in situ heating experiments needed to be
measured. Areas of interest were scanned with Nanomegas ASTAR™ as shown above and the misorientation angles were found using the accompanied software. Typically misorientation was measured multiple times across the grain boundaries in which precipitation had occurred to assure no changes along the length of the boundary as shown in Figure 21 (a).

![Figure 21: Pictorial steps of precipitate analysis: (a) The misorientation information is generated using the Nanomegas ASTAR™ software. Lines are drawn across grain boundaries where precipitation has occurred and the angle between the grains is recorded. The precipitate analysis (images b and c) is conducted by using AdobePS™ (Adobe Photoshop) to fill the precipitates and remove all other features of the image. The original image b’s scale bar is used to calibrate the ImageJ software and the precipitates in image c were measured for their area using the “Analyze particles” function. The results are returned in nm².](image)

Bright field TEM images were taken in the same area and the images were imported into AdobePS™. All other features within the image were removed and the area of the image containing the precipitates was filled with a solid color so that easy differentiation was possible. The background was also made to be white to aid in contrast. These images were then saved and the original image then loaded into ImageJ where the scale bar was used to globally calibrate the software. Next the white image with blacked out precipitates (Figure 21c) was loaded into imageJ and the threshold was
adjusted for by using Image \( \rightarrow \) Adjust \( \rightarrow \) threshold. This procedure was done to assure that the entire precipitate was being observed by the software. Next the procedure of Analyze \( \rightarrow \) Analyze particles was used and the results were returned in units of nm\(^2\). This procedure was repeated multiple times across many grain boundaries and samples to assure a reasonable level of statistical significance.

### 3.3.4 In situ video analysis

In order to gain some kinetics information about the precipitates grown during the in situ TEM heating experiments in situ video analysis was completed. The videos acquired from the experiments were cut using Adobe Premiere and final videos focusing around the time precipitation occurred were generated. Next still images were extracted at 10 second intervals starting from 10 seconds before precipitation occurred and throughout the entirety of the experiment. This typically involved about 10-13 minutes of total growth and coarsening time. Precipitate sizes were them measured according to the above procedure. Since the time and temperatures were recorded along with the video the exact starting and ending temperatures and times were extracted for each image. The results were then plotted in terms of Precipitate size (nm\(^2\)) vs. time (s).

### 3.3.5 Activation energy calculations

Activation energy calculations were completed to obtain quantitative data from the in situ heating experiments. The values of time (seconds) area (meters\(^2\)) and temperature (kelvin) were all known from the in situ heating trials allowing for usage of the Arrhenius equation[27]:
Equation 3: $k = A e^{-\frac{Q}{RT}}$

In order to simplify the calculations the area of the particles had to be simplified to the area of a circular particle and assume equal growth in all directions. While particles may grow more quickly in the grain vs. along the grain boundary or vice versa the selection of equal growth in all directions at early stages of precipitation, like ones in question here, seems acceptable. Once this was done the radius of the particles were back calculated from the area of a circle giving radius $r$ in meters. The rate of precipitation was calculated by dividing the radius by time in seconds giving $\text{Rate} = (m/s)$. The natural log of the rate was taken and a plot of $\ln(\text{Rate})$ vs. $1/\text{Temperature (kelvin)}$ was generated in excel. The slope of this curve is then equal to $-\frac{Q}{R}$ with $R$ being the constant or 8.314 (J/mol) but converted for units to be 0.008314 (KJ/mol). Finally the slope was multiplied by $-0.008314$ giving $Q$ in terms of (KJ/mol).

3.4 Atom probe tomography

In an attempt to better understand the precipitation mechanism of $\beta$ phase in 5456-H116 alloys atom probe tomography experiments were conducted. Bulk 5456-H116 was cold rolled to 15% reduction and sensitized at 225°C for 1 hour in a box furnace. The sample was prepared to EBSD standards according to the EBSD procedure above. Inverse pole figure maps were utilized to locate grain boundaries of interest and were chosen for liftout using a FEI Strata DB-235 FIB-SEM equipped with a Model 100.7 Omniprobe and a FEI Helios NanoLab. Once a grain boundary was extracted the liftout coupons were welded to tungsten wires which had been sharpened by electropolishing. Annular milling was then carried out at 30KeV to form the final needle dimensions for proper
evaporation in the Cameca 4000X-HR LEAP. All samples were imaged in a JEOL 2100 LaB6 at Drexel University with a Nanomegas precession diffraction system to confirm grain boundary misorientation angle. An example of a final milled needle is shown in Figure 22.

![Example of final 5456-H115 atom probe needle with measurements](image)

**Figure 22:** Example of final 5456-H115 atom probe needle with measurements

### 3.5 In situ heating EELs experiments

Electron energy loss spectroscopy experiments were completed during in situ heating experiments using a JEOL 2100F TEM located in Drexel University CRF which is equipped with the following:

- a) Schottky source and high-resolution pole piece with Cs = 1.0mm
- b) IS1000XP CCE camera
- c) K2 Summit direct detection camera
- d) EDS by Oxford via X-MAX 80mm^2 SDD detector

Samples for these experiments were prepared in a similar manner as the previous in situ heating experiments explained above. The key difference was that at various stages
of heating the sample was held at the given temperature and eels spectra was taken over the area. With the given setup the scan time was around 5 minutes. In order to observe the entire life cycle of precipitation especially the local changes in Mg concentration the samples underwent the following heat cycle:

As shown in above the sample was heated from room temperature to 200°C held at that temperature until an area scan was complete the temperature was then ramped again until the next temperature of interest and so on. The only stage in the experiment which did not allow for at temperature EELs was at 400°C due to excessive amounts of drift. Due to this the sample was ramped back down to room temperature and scanned. One difficulty
with trying to merge these two techniques together STEM EELs and in situ heating is the balance of sample thickness. The in situ heating can be completed on very thin samples but to avoid any thin film effects thicker samples are preferable. In some early experiment in this work precipitation occurred more readily in the thicker areas. In contrast using thick samples with the STEM EELs technique did lead to some difficulty due to the excessing mean free path. One of the artifacts that were found to occur was that the aluminum plasmon would grow very large and was out other elements if the sample was too thick. If the samples were too thin Cu was found to diffuse into the very thin areas of the sample and cause contamination. In general for this type of experiment the sample thickness can effect results rather drastically and it was found that a sample of ~200-300nm in thickness which with ion milling is very difficult to control.
Chapter 4: Grain Boundary Misorientation Dependence of β Phase Precipitation in an Al-Mg Alloy

4.1 Abstract

Precipitation of β phase (Al3Mg2) in an Al-Mg alloy is investigated by in situ heating and precession diffraction-based orientation imaging in a transmission electron microscope. Initial β formation occurs more readily at low angle grain boundaries rather than at high angle boundaries, however larger precipitates are found at high angle boundaries. We propose a mechanism for β formation based on boundary energy and grain boundary free volume. These results advance the understanding of β phase formation, aiding future corrosion prevention.

4.2 Background/Motivation

The Al-Mg 5xxx series aluminum alloy is a material commonly used in marine environments, such as naval ships and commercial vessels[2, 6, 19], and gains its strength from additions of >3% Mg and cold work, yielding medium strength and high ductility[2]. The use of Al5xxx instead of steel alloys allows for lighter ships with greater maneuverability and fuel efficiency; the use of aluminum can reduce ship weight by up to 22% [6]. A drawback of the use of the Al5xxx series alloy series, however, is its susceptibility to corrosion and cracking due to low temperature sensitization [4, 7].

Corrosion in Al5xxx results from sensitization, a process where the material is exposed to elevated temperatures from 50°C to 400°C for extended periods of time[14, 46]. This phenomenon is characterized by the nucleation and growth of Al3Mg2 (β)
precipitates, which can form along grain boundaries[10, 102], and ultimately lead to stress corrosion cracking [10, 103-105]. While the nucleation and growth mechanisms of the β phase are still not fully understood, it has been suggested that equilibrium β forms by the following reaction (equation (1)) [4]:

\[
\text{Solid solution } \alpha \rightarrow \text{GP zones} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta
\]

*Note: GP zones and β” have only been known to form in materials with >13%Mg

The β’ precipitates are a metastable phase with a hexagonal crystal structure, semi coherent to the matrix, typically forming between 50°C-200°C [7]. The equilibrium β phase is cubic and incoherent with respect to the grain boundary nucleation sites. Due to the complexity of formation the focus of this study will be on the formation of the final β phase at equilibrium.

While a wealth of evidence exists that β phase precipitation is a thermally-activated process [33, 34] occurring after long periods of exposure to temperature, little information exists on the early stages of its formation. Most observations of β phase growth concentrate on long term precipitation studies over many hours of exposure to elevated temperatures (~50°C to 150°C) [5, 9, 106], originally performed to mimic ship exposure times ([18] . Accelerated sensitization studies, which allow for the examination of earlier stages of β phase growth, are performed within temperature ranges of 150-175°C, for 1 to 10s of hours[7, 107]. Within this time and temperature regime, β phase precipitates have been observed to grow heterogeneously on grain boundaries and intermetallic precipitates [29, 108]. Studies by Goswami et al. [4, 109] suggested that initial β phase formation is facilitated by pipe diffusion of Mg via dislocations to the grain boundaries and that initial β phase growth appeared as isolated precipitates but after
long heat treatments, took on a ribbon like morphology along grain boundaries. While these observations of pipe diffusion are valid [33] and assist in our understanding of how beta phase forms in Al5xxx alloys, they do not explain the anisotropy with respect to grain boundary type.

There exists a limited amount of information about the dependence of $\beta$ precipitation on grain boundary character in 5xxx alloys [38, 64]. TEM-based studies by Carroll et al. [10] characterized the effect of Zn additions on grain boundary precipitation in AA5083 after sensitization at 200°C for 24 hours. The results revealed that $\beta$ phase preferred both high angle and sub grain boundaries, however misorientation angle dependence was not examined. Unwin and Nicholson [15] compared Al-6 Zn-3 Mg and Al-7Mg aged for 3 hours at 180°C, and found that the Zn addition promoted nucleation at subgrains, and precipitation was more difficult on low angle rather than random high angle grain boundaries [15]. A recent study by Tan and Allen [13] observed the relationship between thermomechanical processing and the corrosion of AA5083 and revealed that samples with larger dislocation networks and low angle grain boundaries exhibited superior corrosion resistance, which was consistent with a study by Davenport et al. [12], in which an examination AA5182 sensitized at 150°C for 10 hours using atomic force microscopy (AFM), electron back scattered diffraction (EBSD) and TEM showed that there was no sign of $\beta$ phase on low angle grain boundaries and that those with less than 20° misorientation are resistant to corrosive attack.

The general trend among these previous studies is that low angle boundaries (<20° misorientation) in 5xxx alloys are resistant to corrosive attack due to precipitation occurring primarily on high angle grain boundaries, free dislocations, and intermetallic
precipitates. The eventual formation of $\beta$ on the above mentioned microstructural features is clearly documented, however there is still little evidence of their primary formation. A more predictive understanding of the initial nucleation mechanisms and growth of $\beta$ phase in Al5xxx alloys is necessary. Using a coupled approach of in situ annealing and orientation imaging (Nanomegas ASTAR™) in the TEM [110, 111], the nucleation and growth of the $\beta$ precipitates during sensitization is studied as a function of grain boundary misorientation.

Aluminum alloy 5456 (5.5%Mg), in the H116 temper condition, was prepared for in situ TEM from bulk as-received material using traditional metallographic polishing, and TEM preparation using a Fishione ion mill for final electron transparency. In situ sensitization was conducted using a Gatan heating holder; the temperature was ramped from room temperature to 300°C at a rate of 0.3°C/s, held at 300°C temperature for 5 minutes, then ramped back down to room temperature. The temperature of 300°C was chosen to accelerate $\beta$ phase growth which normally forms comparable precipitate sizes over 100 hours of sensitization at 150°C [7, 12, 112]. This temperature regime has been shown in previous studies [28, 113] to yield $\beta$ phase precipitates after 10 minutes, in which is a reasonable timeframe for TEM studies. Post-heating analysis was conducted using Nanomegas ASTAR™ system, which utilizes precession diffraction to match acquired TEM diffraction images to known diffraction patterns, with a precession angle of 0.60° at 100 Hz. Orientation maps were generated from nanobeam diffraction patterns acquired by the Nanomegas system via beam rastering Manual nanobeam diffraction and EDS analysis were coupled with this technique to reduce any ambiguity (see
supplementary material). The experiments were repeated several times and yielded a total of 42 analyzed grain boundaries.

Bright field TEM images of the unsensitized state of the material (before in situ sensitization) and revealed an extensive subgrain structure and a high dislocation density, most likely due to the cold work from the H116 treatment. The H116 naming convention explains the material is in the strain hardened condition (strain is between 1/8 and ¼ hard of the fully hardened condition, in this case 12% rolling reduction) without a subsequent heat treatment [24]. The as-received condition also contained scarce amounts of preexisting β’ precipitates, found on low angle grain boundaries, which can also be attributed the final heat treatment of the H116 temper (Figure 24 (A) and Figure 25 (A)).

Areas containing previously existing β’ precipitates in the as received material were chosen as the first sites for in situ observation due to a previous understanding that Mg-enriched, β’-containing areas lead to the formation of β in equilibrium [28, 38]. Thus, before an extensive grain boundary dependency study could be performed, the dependence on previously existing β’ had to be examined as a baseline. In situ accelerated sensitization revealed that β’ precipitates began to dissolve at ~200°C and were fully dissolved at ~275°C, shown in Fig. (1). Equilibrium β first appears to nucleate at 275°C, and was accompanied by a sharp change in contrast during in situ capture (Fig.1 C-D). During the experiments, new β’ precipitates did not form under these conditions, which could be attributed to the accelerated time of the annealing/sensitization.
Figure 24: (A-D) Images taken in situ during ramp from 200°C to 300°C. (A) Sample at 200°C with preexisting β’ precipitate. (B) Sample at 252°C with β’ partially dissolved. (C) Sample at 275°C with β’ dissolving and formation of β on left adjacent boundary. (D) Sample at 300°C with some remaining β’ and β formation.

The in situ heating experiments showed that preexisting location of the β’ did not necessarily yield β phase, as shown in Fig 2 B (below). The β’ dissolves before β forms, however the location of the β nucleation was not observed to be correlated with the previous location of β’. The β’ does not transform into the cubic β and they do not share a common nucleation site. This agrees with previous findings during non-isothermal aging where β’ and β dissolve and form independently of one another [21, 30]. Extensive post heating TEM analysis confirmed this observation (Figure 25).

Figure 25:(A) Preexisting β’ precipitate at grain boundary pre in situ heat treatment (B) Dissolved β’ precipitate after 300°C in situ heat treatment with no β formation (C) Examples of β at locations close to but not at dissolved β’ precipitate.
While the presence of $\beta'$ precipitates was determined to be a less significant factor in the nucleation and growth of $\beta$ precipitates, a clear trend based on grain boundary type emerged: while higher angle grain boundaries allowed for larger precipitate growth during in situ studies, precipitate nucleation on low angle grain boundaries as well, yet accompanied by stagnated growth. To analyze this developing trend more quantitatively, post-sensitization analysis of the grown $\beta$ precipitates was conducted using Nanomegas ASTAR™ orientation imaging in TEM to obtain orientation image maps (OIM) of the annealed/sensitized microstructures. Specifically, TEM-based orientation imaging was used in conjunction with in situ and ex situ TEM analysis of $\beta$ precipitation (see Figure 26 and supplemental material S1 and S2). Such analysis was performed on various heat treated samples to yield misorientation and precipitate size for 42 grain precipitate/grain boundary pairs (Figure 26). The results suggest that more $\beta$ phase was found at low angle grain boundaries.

Figure 26: Plot of precipitate size vs. misorientation angle (A). Precipitate size analysis (B-F) TEM bright-field area of interest (B) Nanomegas ASTAR™ orientation map (C) Diffraction pattern from top precipitate (D) Pseudo dark field image from Nanomegas software (E) Precipitate size analysis with imageJ software and area where misorientation data was taken (red line) from Nanomegas ASTAR™ software (F) Example of precipitate size analysis (F).
The plot shows a comparison of grain boundary misorientation angle measured by vs. precipitate size. The orientation scans were taken from various locations across a group of samples (with the same heat-treatment) to achieve more informed statistical information. Grain boundaries with misorientation from 15° to 40° appear to have no precipitates but this can be attributed to the amount of boundaries surveyed. It is believed that the precipitates occurred on all types of angles but the random selection of areas observed did not contain those angles; however, the orientation maps show that the majority of precipitates during the in situ experiments are on low angle (<15°) grain boundaries and dislocations (omitted in the plot). It should be noted that the precipitates on the low and high angle boundaries were observed over the entirety of the sample in thicker areas away from the center, or thinnest region, of the foil. Since precipitates of similar morphology, size, and grain boundary angle (low and high) are observed away from the center it can be concluded that the surface effect is not the primary precipitation mechanism [114, 115]. Relatively few precipitates were seen to form on high angle boundaries, but they were larger than those found on low angle grain boundaries (indicating uninhibited growth).
The precipitate size increased with misorientation angle. Figure 27 (a) and (d) shows a comparison between precipitates on a 5° low angle boundary and a 40° high angle boundary. Nucleation beading on very low angles (<3°) suggests that initial formation may occur on low angle sub structure via dislocations (Figure 27D), but is halted, while uninhibited precipitate growth occurs on higher energy boundaries. Grain boundaries <15° are considered to be of low energy and thus less attractive sites for nucleation when compared to higher angle boundaries. In this system the largest area observed on low angle grain boundaries was around 4000nm² but the majority of precipitates analyzed were closer to 2000nm². Precipitates on high angle grain boundaries, while more scarce, were triple the size of those on low angles. This suggests that there is a size limitation of the β phase on the lower energy low
angle grain boundaries. In some cases precipitates grew preferentially on the low angle boundary despite being located only a few nm away from a high angle grain boundary, in direct contrast to previous findings of high angle grain boundary preference [110]. Heat treatments [19] have been implemented previously, however, to improve corrosion resistance in 5xxx alloys by increasing β precipitation at low angle boundaries and within grains rather than at high angles.

The grain boundary plane may also play a role in the formation and morphology of the precipitates. This was found to be the case in the Davenport study [12], in which the susceptibility of higher angle <20° grain boundary was found to be more dependent on grain boundary plane than misorientation between grains. It has been alluded to that for long term sensitization β phase grows preferentially on <111> matrix with <112> as a secondary plane which has an impact on how continuous the precipitate is along the grain boundaries [13, 38]. Understanding the grain boundary plane and misorientation will lead to a better understanding of the nucleation and formation of the β precipitates as a function of grain boundary free volume, which has been known to vary with grain boundary type [116]. Attaining information about the effect of grain boundary plane will provide new insight into the initial β phase growth. Other factors, such as percent of Mg, have also been known to play a role, as some studies have shown that higher levels of Mg would lead to faster formation [38, 112] which may explain the lack of growth at low angle grain boundaries, and could be studied more extensively.

4.3 Conclusions

We have shown that initial β phase formation occurs at low angle grain boundaries, which conflicts with previous observations of β phase growth only occurring
on high angle grain boundaries. Low angle boundaries are susceptible to sensitization. Also, it has been shown that the $\beta'$ phase does not transform into $\beta$; rather, the $\beta$ forms on its own after the $\beta'$ has begun to dissolve which agrees with what has previously been suggested. The primary nucleation sites observed during in situ experiments are intergranular defects and low angle subgrain boundaries. In many instances, the $\beta$ phase formation preferred low angle rather than high angle grain boundaries. Although formation on low angle boundaries was more prevalent, precipitate growth on low angle boundaries was halted at a maximum size, most likely dependent on boundary energy, whereas precipitates on high angle boundaries shows signs of uninhibited growth. Moreover, as the misorientation angle increased, the precipitate area increased. Studies to better connect the dependence of $\beta$ phase precipitation on both boundary structure and energy are underway.
Chapter 5: Direct Measurement of the effect of cold rolling on β phase precipitation kinetics in 5xxx series aluminum alloys

5.1 Abstract

The aluminum magnesium alloy system has notable attributes, such as a high strength to weight ratio and weldability, but it can become susceptible to sensitization at relatively low temperatures, which can lead to stress corrosion cracking. It is well established that growth of the secondary β phase is temperature driven, however there is little understanding about the role of prior strain in the β phase nucleation and growth process. Understanding the effect of cold rolling will also bring new insight into better themomechanical treatments leading to a more appropriate temper to improve sensitization resistance. In this study cold rolled AA5456-H116 is observed during in situ transmission electron microscopy heating experiments. The results of this study show the impact of an increased dislocation density, due to cold rolling, on β phase precipitation as well as the effect of misorientation on growth and kinetics. The effect of additional dislocations is also observed to show an increase in precipitate density and a lowering of nucleation temperature attributed to Mg pipe diffusion.

5.2 Introduction

The 5xxx series Al-Mg alloy system has received considerable attention as an alternative to steel to decrease structural weights and increase overall fuel efficiency due to their high strength to weight ratio and weldability[2]. These materials are generally
used as structural materials in marine, automotive, and aircraft industries as well as food handling and chemical industries [2, 117-119]. As global warming plays a larger part in material selection, further development on Al-Mg usage has been conducted to improve fuel consumption and emissions, as well as increase recycling potential of final automotive components [2, 117-119]. Use of this material in service, however, has been undermined by stress corrosion cracking [4] resulting from sensitization at moderate and even low temperatures [40]. Growth of a deleterious secondary phase, known as the β phase (Al₃Mg₂), during sensitization of Al-Mg alloys has been a problem for in-service naval vessels for many years [6]. Specifically, while exposed to harsh in-service environments, such as sea water, a galvanic couple is formed between the aluminum matrix and the β phase precipitates[43]. This ultimately leads to a preferential dissolving of these precipitates that result in intergranular cracking[14, 15, 43, 119] But it is possible for crack propagation to occur from non-continuous beta precipitates as well[10].

It is well known that the formation of β phase is temperature driven[28, 29, 31] but the nucleation and growth mechanisms are not fully understood. It is generally agreed upon that during exposure to elevated temperatures (50-300°C) the Mg segregation begins from the supersaturated solution (>3%Mg or higher[2]), resulting in the formation of a final, stable β equilibrium phase[4, 28, 29]. Hamana et al.[30] observed β equilibrium to form independently during non-isothermal differential calorimetric analysis, indicating that a direct transformation from its metastable precipitate form, β’, was not required. The majority of studies[5, 9, 106] have shown β phase precipitation during long term growth periods at elevated temperatures and have observed the formation of this secondary phase occurs at the grain boundaries (GBs), sub-grains, and
defects in the material[120]. Some shorter term accelerated studies have also been used at higher temperature ranges and shorter time periods, and were successful at growing β at GBs and intermetallic precipitates[10, 11]. Despite the heat treatment approach, the precipitate formation of this secondary phase occurred at the GBs, sub-grains, and defects in the material[10, 120].

There exists a lack of information about the location of precipitation, such as dislocations or subgrains and GB character, in relation to precipitate size and speed of formation. Carroll et al. [10] observed the effect of Zn additions in AA5083 after short term sensitization and found β precipitate growth on both high and low angle boundaries but misorientation angle dependence was not examined. In a study of AA5182 sensitization by Davenport et al. [12], however, low-angle boundaries were found to be devoid of β phase precipitation. Our recent work [121] utilized TEM and Astar/Nanomegas orientation imaging to examine GBs misorientation dependence in AA5456-H116 during accelerated in situ heating experiments, and found that β precipitates were present on both high angle and low angle GBs, which was consistent with later studies [63]. Those precipitates found at low angle boundaries indicated inhibited growth (all precipitates were small primarily ranging from 250nm$^2$ to 1000nm$^2$) while those found on higher angle GBs had grown to much larger sizes >5000nm$^2$. Initial studies[16] on 5xxx series Al-Mg system suggested that precipitation on the subgrain structure is actually preferred over high angle boundaries in relation to corrosion performance but there is still a lack of information connecting sub-GB density and its effect on precipitate size and density at high angle GBs. The addition of prior strain will
affect the GBs character distribution as discussed in previous studies[87, 122, 123] by changing the texture and recrystallization behavior and in turn increase the overall density of subgrains.

While various aforementioned studies [4, 5, 9, 28-30, 106] discuss β phase formation from a supersaturated solution, little information exists to explain the specific mechanism of formation. There is a clear lack of information between the supersaturation and the stable presence of β in an equilibrium state. The most common formation mechanism suggested by the literature is that Mg precipitates form from super saturated solution, a process which is facilitated by pipe diffusion via dislocations. Goswami et al.[7] observed that a sample of 5083-H131 showed enhanced β phase growth due to a large dislocation density and, consistent with this finding, observed β phase formation in severely plastically deformed material [8]. Specifically, it was found that during ball milling, GBs were enriched with Mg and thus lead to higher levels of sensitization. On the contrary, a study by Tan and Allen[13] used thermomechanical processing to improve corrosion resistance and found that larger dislocation networks and low angle boundaries lead to better sensitization resistance. Early work by Dix et al [16] expressed the effects of cold work on sensitization, showing a thin line between strength maximization and corrosion resistance during material development. It was discussed that despite lower Mg content, with additional cold rolling, a material could sensitize in the same amount of time as a material with higher Mg content. Gronsky and Furrer [72] also suggested that GB precipitation could be encouraged by additions of extrinsic defects. The amount of prior deformation needs to be observed in more detail to better understand its full effect on β phase precipitation. Besides increasing the dislocation density and thus the
nucleation sites and pathways for precipitation, the impact of pre strain on β phase precipitation is still not well known in relation to growth kinetics. The addition of the pre strain in the form of cold rolling should not alter the growth rate but it should produce higher densities of precipitates due to the increased diffusion paths.

While heterogeneous nucleation of the β phase is known to occur at dislocations, intermetallics, and GBs[10, 11, 120], and is most likely linked with density of dislocations, what remains a challenge is connecting the nucleation and growth behavior to alloy history and processing. In particular, induced strain from cold rolling and resulting GBs character distribution and dislocation density have a distinctive role in defining the nucleation, growth, and distribution of β phase in 5xxx series Al-Mg alloys. A fully predictive understanding of β phase precipitation is not possible without a clear picture of the role of GBs character in the nucleation and growth mechanism. Using a combined approach of in situ TEM and precession electron diffraction [121] new insight into the effect of prior strain on the onset of β phase nucleation and its subsequent growth is presented. The acquisition of real time video reveals the time, temperature, location and kinetic growth rates of the precipitates and highlights the role of various dislocation densities at the initial onset of β phase nucleation. The results of this work help paint a more complete picture of the nucleation and growth behavior of β phase growth during strain-producing, in-service conditions.

5.3 Experimental

5.3.1 Sample Preparation
Aluminum alloy 5456-H116 (5% Mg) was supplied by Alcoa (Alcoa Center, Pa) for this study. Rectangular strips (0.5cm x 0.25cm x 0.635cm) were cut from the bulk (1/4 inch plate) and cold-rolled to 30% and 50% reduction parallel to the rolling direction of the H116 treatment. Rectangular cross-section coupons (2.5cm x 1.2cm x 0.635cm) looking into the rolling direction were cut from the bulk 5456- H116 material (H116) and rolled samples. The coupons were thinned to final dimension of 25mm x 12mm x 0.1mm by mechanical polishing and 3 mm diameter disks were punched. The disks were then polished to 50 microns thickness and ion milled to electron transparency using a Fischione ion mill. Samples were heat treated in a JEOL 2100 Lab6 TEM using a Gatan heating holder at a ramp rate of 0.5° per second up to 300°C and held there for 5 minutes. All experiments were recorded in situ at 10 frames per second using Debut digital screen capture software using a Gatan Orius 832 fiber optic 10.7 megapixel ccd detector. Post-annealing precession diffraction analysis in regions of interest (GBs, dislocation networks) was performed using Nanomegas ASTAR™ orientation imaging as described in section 2.2.

5.3.2 Precipitate Characterization and GBs Analysis

The Nanomegas ASTAR™ system was used to acquire the misorientation of GBs with β phase precipitates. The system controls the scan coils of the TEM and allows for nanobeam diffraction patterns to be taken across the desired viewing area, similar to electron back scatter diffraction in a scanning electron microscope [110, 111, 121]. Traditional orientation imaging in a scanning electron microscope is usually conducted using Kikuchi lines while orientation via the Nanomegas ASTAR™ system uses
nanobeam diffraction patterns. These observed diffraction patterns are matched to the theoretical diffraction patterns generated from a crystal file indexing the crystal orientation. The Nanomegas ASTAR™ software than yields an inverse pole figure map with the corresponding indexed diffraction patterns at each pixel of the scanned area. An example of this process can be viewed in the supplementary section of this manuscript. While this technique is useful for gaining misorientation data it does lack the ability for finding the boundary plane.

5.3.3 Precipitate Growth Kinetics Analysis

As described previously, video was collected using Debut digital screen capture software at a frame rate of 10/second using a Gatan Orius 832 fiber optic 10.7 megapixel CCD detector. Images were taken every 10 seconds from the video data starting from 10 seconds prior to the first noticeable signs of nucleation until the 5 minute hold at 300°C was complete. Precipitate analysis was conducted using the ImageJ software package to measure the size of the precipitate at each respective time. These results were then compiled and plotted with all data points normalized with respect to starting nucleation time. The activation energy required for precipitation before and after 300°C were also calculated using the Arrhenius equation. The radius of the particles were calculated from the measured area, and the slope of Ln(Rate) vs. 1/T was used to find the activation energy.
5.4 Results

5.4.1 Effect of rolling reduction on β phase precipitate density and size

The addition of extra strain from cold rolling had a large impact on the number density of beta precipitates both within grain matrices and at GBs. This is evident in Figure 28, which shows images of annealed, 0% reduced sample at 20Kx magnification and an annealed, 30% reduced sample at 30Kx magnification. It is clear that there is a large difference in the overall density of precipitation. The 0% reduced samples tended to have more sporadic coverage over the entire area of the sample, whereas the 30% reduced samples had more uniform coverage at GBs and within grain matrices. Finally, the connectivity of the β phase along the GBs was much more uniform in the pre-strained samples than the H116 samples, having smaller distances between precipitates in the rolled samples (Figure 28b).

Figure 28: TEM bright field image of H116 after in situ heating experiment at 20kx magnification (b) TEM bright field of 30% reduced sample after in situ heating at 30kx magnification
5.4.2 Precipitate nucleation and growth

Direct visualization of precipitate growth was observed during in situ TEM heating experiments. Bright field images were taken during in situ annealing showed precipitate evolution at various rolling reductions in Figure 29. Due to the high difficulty of predicting where the precipitation would take place the area of observation was chosen on criteria of general sample quality and number of visible boundaries. Also once the heating experiments were carried out the samples were deemed useless and retrials were not possible due to microstructural evolution upon dissolution. Videos can be found in the supplemental section.

Figure 29: Example of precipitate growth during in-situ heating experiment of 30% reduced sample (a-f). Initial appearance of GB at Time: 208s and Temperature: 141°C (a). First appearance of precipitation at Time: 216s Temperature: 207°C (b). Continued growth at Time: 241s Temperature: 228°C (c), at Time: 281s Temperature: 264°C (d) and at Time: 310s Temperature: 288°C (e). Precipitate growth near completion of experiment Time: 600s and 300°C (f).
Precipitate growth rates were plotted and compared in Figure 30. In both the H116 and 30% reduced samples only one precipitate grew within view, both of which occurred on high angle (HA) boundaries. The 50% reduced sample had two HA (labeled 1 and 2) as well as one low angle (LA) boundary precipitate. Precipitate growth rates increased with additional rolling reduction; nuclei in samples with greater rolling reduction were observed to grow faster than those observed in the H116 samples. Growth rates were also found to vary depending on the misorientation of the GBs on which the precipitate grew. While it is difficult to directly compare growth rates across precipitates grown in different samples, Figure 30 was used with the x axis normalized with respect to the starting time of the precipitates with point (0,0) being 10 seconds before initial nucleation occurred for any precipitate. This offset allowed for closer comparison of the rates between samples as though the precipitates were all grown in the same sample. The 300°C bar in Figure 30 represents a general range using the fastest and slowest time required to achieve the temperature.
Figure 30: Plot of precipitation rates (Precipitate size (nm²) vs. Time (s)) for all samples.

Figure 30 demonstrates the large variation between the rates of nucleation and the precipitation growth rate as a function of prior strain and GBs misorientation. It should be noted that noise present in the growth rate data can be attributed to slight changes in image contrast during in situ annealing, which led to, in some cases, precipitate size measurement deviations of +/- 5%. Immediately noticeable was the stagnation that occurred in cold rolled samples once they reached the 300°C hold temperature, denoting a nucleation and growth transition around 300°C, which will be discussed later. It was also evident that the nucleation stage for the H116 sample did not occur until 120 seconds after the cold rolled samples began to nucleate. With respect to differences in the amount of rolling reduction or prior strain, the 30% and 50% reduced samples showed signs of nucleation within 30 seconds of one another, with the 30% reduced sample starting
earlier, or at a lower temperature, than the 50% reduced sample. The data shown in Figure 30 was normalized and the nucleation occurs before the heat treatment reaches the 300°C isothermal hold. A dramatic difference is observed in the nucleation temperature between the H116 samples, in which nucleation was first observed at 265°C, and the 30% and 50% reduced samples, in which nucleation was first observed at 191° and 225°C, respectively.

With respect to misorientation, the growth rate of the precipitates on the low angle boundary began before the high angle but had a slower growth rate in comparison as seen in Table 1. Figure 30 also details the size vs. time of precipitates with respect to misorientation angle. For a precipitate grown on a 45° boundary in an H116 sample, nucleation begins at ~265°C and remains sluggish until the 300°C hold temperature is met. Once at 300°C the precipitate growth rate increases and remains steady, reaching a size of ~6000nm². In comparison, initial nucleation of a precipitate on a 20° boundary in the 30% reduced sample is much faster than that of the H116 sample before the 300°C hold is reached, and continues to grow up to a size of 8800nm². Two precipitates measured on two different 60° boundaries, and one precipitate on a low angle boundary (misorientation angle of 5°), were measured in the 50% reduced sample. The first precipitate to nucleate was that found on the low angle boundary, followed by one on a high angle boundary at a triple point, and finally precipitation occurred on the second high angle boundary, also close to a triple point. In the case of these three boundaries, each of the nucleation events began within 10 seconds of the previous one; within 30 seconds, all precipitates had nucleated.
A transition between the nucleation and the growth was observed between the samples; the effect of boundary misorientation and prior strain/rolling reduction on this transition is summarized in Table 1. An immediate observation made was that an increase in rolling reduction did increase the rate of β phase growth. It was also noted that not only did the samples that were cold-rolled nucleate faster, but also, they reached the growth stage first. The rolled samples nucleated during the ramp up to 300°C and once the sample reached 300°C the growth mechanism took over and the precipitate growth slowed and stabilized. The H116 sample grows at a similar rate as the rolled samples did during the ramp up to 300°C. During the nucleation regime the rolled samples have increased slopes for the precipitates grown on high angle boundaries vs low angle. The rates for the two high angle precipitates in the 50% reduced sample are similar while the 30% reduced sample is slightly faster. The precipitate found on a low angle boundary in the cold rolled sample, however, grew very slowly (~75% slower). Additionally, the precipitate in the H116 showed signs of both later/delayed nucleation as well as a slower growth rate. When the rolled samples are observed during the 300°C isothermal hold for 5 minutes the overall observation is that the rate of growth decreases or comes to a halt for the rolled samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nucleation temp</th>
<th>Final size (nm2)</th>
<th>Nucleation rate (nm2/s)</th>
<th>Growth rate (nm2/s)</th>
<th>Max rate before or after 300°C</th>
<th>Activation energy before 300°C (KJ/Mol)</th>
<th>Activation energy after 300°C (KJ/Mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H116 45°</td>
<td>265°C</td>
<td>6310</td>
<td>6.5 (±0.9)</td>
<td>15.7 (±0.97)</td>
<td>After</td>
<td>61.08</td>
<td>68.10</td>
</tr>
<tr>
<td>30% reduced 20°</td>
<td>191°C</td>
<td>8819</td>
<td>29.7 (±3.5)</td>
<td>11.2 (±0.33)</td>
<td>Before</td>
<td>22.70</td>
<td>136.21</td>
</tr>
<tr>
<td>50% reduced 60° (1)</td>
<td>233°C</td>
<td>2547</td>
<td>25.0 (±1.5)</td>
<td>3.6 (±0.34)</td>
<td>Before</td>
<td>26.29</td>
<td>136.21</td>
</tr>
<tr>
<td>50% reduced 60°</td>
<td>242°C</td>
<td>3145</td>
<td></td>
<td></td>
<td>Before</td>
<td>39.33</td>
<td>113.51</td>
</tr>
</tbody>
</table>
Table 5: Summary of rates for H116 and rolled samples

<table>
<thead>
<tr>
<th>Reduction</th>
<th>Temperature</th>
<th>Activation Energy</th>
<th>Misorientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>50% reduced 5°</td>
<td>225°C</td>
<td>22.8 (±2.8)</td>
<td>0.27 (±0.09)</td>
</tr>
<tr>
<td>5%</td>
<td>515</td>
<td>5.9 (±0.8)</td>
<td>0.24 (±0.015)</td>
</tr>
</tbody>
</table>

The resulting activation energies are shown in the final two columns of the table. The activation energy for the H116 sample did not change significantly before or after the 300°C hold and only increased slightly afterwards coinciding with the steady continued growth after 300°C. The rolled samples, on the other hand, had a significantly lower activation energy before 300°C and a much higher activation energy after 300°C. This agrees well with the rolled samples showing faster growth at lower temperatures while having halted growth at 300°C. As the process continues over time, more Mg diffuses to the growing Mg rich precipitates, leading to higher levels of Mg saturation at the boundary and ultimately a slowed growth. A higher activation energy was calculated in this regime.

5.4.3 Precipitate distribution with respect to GBs misorientation

Precipitates grown during in situ experiments were measured after annealing to compare size (nm²) and misorientation angle (degrees) for the three different rolling reductions: 0% (H116), 30%, and 50%. Size, as mentioned above, was measured using Image J, while GBs misorientation was calculated via automated crystal orientation mapping using the Nanomegas ASTARTM system using a method we described previously [121]. An example of this suite of data and images is shown in Figure 31, below.
Figure 31: Before and after images of in situ heating experiments with Nanomegas scans of H116 (a -c) 30% reduction (d-f) and 50% reduction (g-i).

A distribution of precipitate size as a function of misorientation angle for all three rolling reductions is shown in Figure 32. Each data point in the plot represents a measured value for a single precipitate; 42 GBs were analyzed in the H116 condition, while only 20 boundaries were analyzed in the 30% and 50% reduced samples to achieve the same number of precipitates measured. In the plot, the H116 and 50% reduced samples appear to have fewer precipitates between 20 and 35° misorientation compared to the 30% reduced but this can be attributed to the random selection of boundaries. The majority of precipitates found during the accelerated heating experiments were located on low angle
boundaries. A trend similar to previous work[121] was found in that the precipitates grown on low angle boundaries are smaller than those grown on high angle boundaries, which largely exhibited uninhibited growth. The key observation taken from the data shown in Figure 32 is the lack of an impact of rolling reduction on the overall precipitate size. The rolled precipitates show the same trend as the H116 samples in that low angle boundary precipitates remain small while high angle precipitates can grow larger. What is also noticeable is that the rolled samples show a larger range of sizes per misorientation. At 45° misorientation for instance sizes range from a few 100nm² up to 4000nm² and everywhere in between. It is evident from the plot that increasing misorientation angle did not always lead to larger precipitates illustrated in Figure 32b. Figure 32c shows the average precipitate size for the low angle (<15°) and high angle boundaries (>15°) vs. cold rolling reduction. The 30% reduction shows much smaller average size with the H116 and 50% reduced samples at about the same.

Figure 32: Plot of size (nm²) vs. misorientation angle (degrees) of precipitates (a). Bar graph of average precipitate size (nm²) vs. misorientation angle (degrees) (b). Average precipitate size (High and low angle) vs. rolling reduction (c).
5.5 Discussion

Precipitate growth rates increased with rolling reduction; nuclei in samples with greater rolling reduction were observed to grow faster than those in the H116 samples. Growth rates were also found to vary depending on the misorientation of the grain boundary on which the precipitate grew. According to previous results [121] it would be expected that as the misorientation angle increases the size of precipitates would increase as well. While it is true that larger misorientation angles have the ability to accommodate larger precipitates, a high number (in comparison to the H116) of smaller sized precipitates were also found in the cold rolled samples at high angles. This can be attributed to the available amount of Mg in the grain. The increase in precipitation sites within the grain and at the GBs takes away from the total available Mg, thus leaving fewer available solute atoms leading to smaller sized precipitates. The comparison between rolling reduction and precipitate size shows that the increased dislocation density does not always yield larger precipitates. The cold rolled boundaries do however follow the same observations seen in the H116 samples, which are that the low angle precipitates have inhibited growth and the high angle boundaries can accommodate larger precipitates agreeing with the previous study[121]. While the average size of the precipitates did not increase, there was a noticeable increase in the number density of precipitates and thus coverage along the grain boundary indicating a higher degree of sensitization also seen in previous literature[124]. For similar reasons as above deformation from cold rolling yielded more available nucleation sites for β to form and thus the larger number density commonly seen in other systems[125]. These dislocations can also lower the activation energy of precipitation at the grain boundaries which most
likely attributes to the increase in more continuous precipitation found at the grain
boundaries in the rolled samples.

As a result of the increase in diffusion paths and nucleation sites caused by the
higher dislocation density, the precipitates were found to be small in size, but higher in
density. The finite number of free Mg atoms within the grain is thought to have
diminished faster due the increased nucleation sites yielding smaller precipitates but
overall more Mg segregation. As seen in previous studies [8, 126, 127] increasing the
dislocation density increased the overall degree of sensitization in materials, perhaps due
to the larger number of nucleated secondary phases. This finding is similar to other
studies which show precipitate refinement and increased number density [128] as well as
smaller precipitates with smaller precipitate spacing [129] in pre strained samples. While
it has been suggested that a concept of hard impingement and extended volume can occur
in this alloy system [130], β phase growth as monitored in the experiments presented
herein did not follow that mechanism at this temperature regime and accelerated
timescale. The β phase particles remained discrete, taking on a saw tooth pattern along
the GB (Figure 28 b).

It stands to be noted that a majority of the precipitation found in this study
occurred at low angle GBs. It is generally discussed that low angle GBs possess low
energies and degrees of segregation which allow them to be highly resistant to
intergranular fracture. [131]. On the other hand, it has been reported that segregated
atoms can have an effect on GB energy [132] and thus increase the energy of the low
angle GB, but this does not necessarily lower the cohesive strength of the boundary[133].
This idea can be seen in current tempers (H116, H321, and H128), which have been developed to allow precipitation at intergranular locations rather than at the GBs [17]. Zhang et al. [66] discussed that HAGBs increase overall DOS while low angle GBs hinder DOS; moreover they discuss that misorientation has a significant impact on sensitization. In comparison, the results of the precipitation studies presented herein show that the low angle GBs do indeed act as nucleation sites, but as the heating process continues, high angle GBs accommodate larger precipitates. This is most likely caused by the low angle GBs only accommodating a precipitate up to a finite size whereas the high angle boundary precipitation is uninhibited as shown in this and previous work [121].

β phase formation is temperature driven [28, 29, 31] and this phenomena is altered by the presence of prior strain. Specifically, the temperature for nucleation to begin was drastically lowered in the cold rolled samples. The main contribution of the increased dislocation density appears to be a lowering of the overall nucleation temperature and thus more Mg diffusion at lower temperatures. This is shown by the results with the rolled samples having a 30-70°C drop in initial nucleation temperature as well as a lower initial activation energy. These results follow previous studies which show increased dislocation density can lead to lower temperature diffusion [134] brought on by pipe diffusion. As the theory of pipe diffusion via dislocations describes [58] at higher temperatures pipe diffusion has a negligible effect on segregation but at lower temperatures the activation energy for diffusion to begin is greatly lowered. This is directly shown in the precipitation of the reduced samples and their lower activation energies at lower temperatures. While pipe diffusion accounts for the decrease in nucleation temperature as well as increase of nucleation sites the increased precipitation
at lower temperatures may be attributed to another factor as well. Due to the higher level of deformation on top of the H116 temper it may be possible for the GBs to be at non-equilibrium states increasing their energy and free volume [116] but on the other hand a severe level of deformation is not likely at these rolling reductions and the changes should be primarily attributed to pipe diffusion.

The comparison between the H116 and the rolled samples showed that the precipitate growth rate was sped up due to the cold rolling. A comparison between the high angle precipitates in the rolled conditions showed very similar growth rates overall despite the additional rolling reduction suggesting diminishing returns above 30% reduction for this alloy. The precipitates at the low angle boundaries were the first to nucleate and grow but did have the slowest growth rate. The key difference between samples is when in which the majority of the growth occurred in the samples. The nucleation and growth of the rolled samples was well completed before the H116 samples precipitate nucleation began. Once the higher temperature of 300°C is reached and held the precipitate growth in the rolled samples begins to slow compared to the H116 sample which tends to have a more steady growth rate. This observation is consistent with the higher calculated value of activation energy after 300°C, consistent with a notion of saturation, with little growth occurring after this temperature. Along with an increased growth rate the rolled samples had many more precipitates form in the same time as the H116, owing to the high density of dislocation nucleation sites. This is in agreement with the idea that pipe diffusion can enhance diffusivity at lower temperatures as well as follows previous assumptions [7, 135] that the growth rate is enhanced which is discussed below.
According to the kinetic growth rates of the precipitates the speed of growth is changed by the amount of dislocations. The nucleation regime in the rolled samples is initiated earlier due to a lowering of the activation energy from pipe diffusion. The alloy system precipitation appears to follow classical nucleation growth theories well. The nucleation regime in the rolled samples was where the primary mass of the precipitate accumulated while in the H116 samples the nucleation was slow but the growth rate increased once higher temperatures were achieved. This difference can be observed by the strong plateau shown in the rolled samples distinguishing the nucleation regime from particle coarsening regime. Conversely in the H116 samples the particle growth regime yields most precipitation. So the increased dislocation density helped to lower the energy for nucleation to begin as well as increased the speed at which the precipitates grew. The difficulty lies in the fact that the rolled samples are not at isothermal conditions compared to that of the H116 samples. The nucleation and growth rates of precipitates at isothermal vs non-isothermal conditions can be very different [24] which may be adding to the rate discrepancy. Finally there is difficulty in directly comparing the above results as they all start nucleating at different times and temperatures as well as in different samples.

It is apparent that the two regimes of precipitation, nucleation and particle coarsening, can be altered by cold rolling [136, 137]. Similarly as to what is shown by Mei et al.[136] lower degrees of cold rolling can increase nucleation sites aiding in precipitate growth but at very high levels precipitation can be stifled due to lack of solute atoms as well as recrystallization. Another study by Fare et al [137] discussed that recovery of heavily deformed structure and precipitation from super saturated solution
can occur at the same time. It was also observed that due to high levels of deformation that the aging process occurred rapidly while hardness levels dropped due to recrystallization. The precipitation of the beta phase in the 5xxx series Al-Mg alloy appears to follow these guidelines. At rolling reductions from H116 to 30% (on top of the H116 treatment) the increase in dislocation density allows for more nucleation sites and faster growth rate but overall smaller precipitates similar to work by Dutta et al [135]. This idea breaks down though once higher levels of reduction are added and the precipitation becomes similar to the H116 condition only with a slightly higher rate. This can be explained by the fact that the above experiments were conducted on thin TEM foils in which the increase in dislocation density at the given temperatures could easily lead to some recrystallization, which is similar to results presented by Drits et al. [138], in which faster recrystallization rates were found in thin films compared to bulk. It has been shown even in bulk Al-Mg alloys with high levels of deformation can undergo quick recovery at high temperatures (345°C) and short times <5min[139]. This agrees well with the rates shown in Figure 30. Both the H116 and 30% reduced samples continue to grow steadily after the 300°C hold is reached but the 50% reduced sample has very stagnated growth at that temperature. The difference found in the 50% reduced sample can be explained by the idea that the material with higher reduction levels complete the precipitation process faster, and when exposed to higher temperatures recovery of the deformed structure takes over, behavior which is consistent with the aforementioned studies[74, 136-140]. Again while the 50% reduction plus the H116 treatment used in this work may not be at a deformation level equivalent to severely plastic deformed material
the extent of the H116 reduction is not fully known due to manufacturer proprietary information and may place the actual reduction closer to 60-70% or even higher.

5.6 Conclusions

5.6.1 Impact of pre strain on precipitate size and density

The results show that an increase in dislocation density via cold rolling has an impact on the overall sensitization of the 5xxx series Al-Mg alloy. The size of the precipitates found samples with elevated degrees of cold rolling were very similar to those found in the H116 samples. While the size of the precipitates did not change dramatically between the rolled and H116 conditions the density of β phase precipitates did increase, which is attributed to the increased dislocation density (heterogeneous sites). The coverage on the grain boundary was found to be drastically different in the pre-strained samples, with the rolled samples having much less space between nucleation sites compared to the H116 which showed large spans between precipitates.

5.6.2 Growth rate differences caused by pre strain

An increased rolling reduction did increase the rate of growth of β phase. There was a difference observed in rates due to misorientation angle with high angle boundaries showing faster precipitate growth than found on lower angles. The largest impact due to the cold rolling on β phase growth was that on the lowering of the nucleation temperature. The rolled samples saw a much faster nucleation regime rate which occurred at lower temperatures than the H116 sample. The H116 sample took a longer time to nucleate and grew at a slower rate than rolled samples even when higher temperatures
were achieved. Initial activation energies of the rolled samples were lowered due to increased dislocation density coinciding with the pipe diffusion mechanism. When higher levels of rolling reduction were used the rate did drop and the material mimicked the H116 sample. This was attributed to some material recovery during the heating process.
Chapter 6: The Effect of Thermo-Mechanical Processing on the Microstructure and Corrosion Resistance of Aluminum Alloy 5083-H116

6.1 Abstract

Many industries employ 5xxx series aluminum alloys in ship hulls and superstructures due to their favorable strength to weight ratio and weldability. However, exposure to elevated temperatures for extended times causes sensitization, and subsequent intergranular corrosion and stress corrosion cracking, leading to premature failure. Understanding how thermomechanical processing could benefit the corrosion resistance of AA5083 is of great importance with respect to extending its lifetime. In this study, two different plates of AA5083-H116 were subjected to a rolling and annealing schedule in an effort to understand how these treatments effect the microstructure and ultimately improve the corrosion resistance of the alloy. Electron Backscatter Diffraction was employed to characterize the material microstructure and quantify the grain size along the cross sectional thickness. The first 5083-H116 material was treated with a 5% cold rolling reduction and a 500°C anneal which drastically improved corrosion resistance, while a second plate of 5083-H116 from a different supplier required a 15% reduction and 400°C anneal to show similar corrosion resistance. Both treatments ultimately performed better than the as received H116 condition. However, it was found that variability in starting material, due to large range of H116 parameters, required different rolling percentages to positively alter corrosion resistance in a uniform fashion. The processing constraints of the H116 temper starting material would need a narrower parameter space before any repeatable thermomechanical
treatments can be applied. The thermomechanical treatment also induced recrystallization at both the surface and center of the plate, which is inconsistent with previous studies. These results indicate that the processing and characterization of AA5083 is further complicated by the inherent variability in the H116 temper and the resultant microstructures.

6.2 Introduction and Background

Many industries, from the automotive to the marine sector, consider weight as a primary design criterion [1]. Aluminum 5xxx series aluminum alloys offer improved corrosion resistance, good weldability, and easier formability compared to steel, in addition to its lighter weight. Certain alloys are approaching the strength levels of steel, making them a serious contender for new mobile platforms. The strength of non-heat treatable [22, 141] 5xxx aluminum alloys is derived from solid solution hardening from magnesium additions of 3% or higher, and in the case of the H116 temper considered herein, 12% strain through cold working [24]. Unfortunately, alloys with greater than 3.5 wt.% Mg are prone to intergranular corrosion (IGC) and stress corrosion cracking (SCC) under operating temperatures exceeding 65°C and in corrosive environments [5, 14, 15, 43, 119], specifically, AA5083 (~4.45 wt.% Mg) exist in a thermodynamically unstable supersaturated state α’. Given enough thermal energy, Al3Mg2, known as the β phase, nucleates on triple junctions, grain boundaries, intermetallic particle interfaces, and other defects [32, 106, 107, 120]; this precipitation reaction, known as sensitization, ultimately causes IGC and SCC. Sensitization is a well-documented mechanism causes the β phase being anodic relative to the Al matrix [7, 13, 14, 21, 46, 48], thus forming a galvanic couple between the β and α phases, in which the β phase preferentially dissolves
first. Environments such as humid air or seawater when combined with sufficient tensile stress, can attack the $\beta$ phase and initiate an intergranular crack that propagates through SCC. Improving the IGC resistance of AA5xxx alloys is directly dependent upon controlling and mitigating the precipitation of $\beta$ phase on grain boundaries and other microstructural defects.

Control of the distribution of grain boundaries and related defects in an alloy microstructure can be achieved by thermomechanical processing [142, 143] Previous studies of steel and nickel-based alloys have shown that stress corrosion cracking and intergranular corrosion can be successfully mitigated using thermomechanical processing [144-148]. Shimada el al.[147] applied a 5% pre-strain and a long low temperature anneal treatment to 304L stainless steel, resulting in an improved resistance to intergranular corrosion. Similarly, Xia el al.[148] used a minimal pre-strain and a short annealing time to manipulate the grain boundary network of Alloy 690 tube which led to a lower weight loss or grain dropout during corrosion testing. While these types of approaches have been successful in steel and nickel based alloys, they have not been fully adapted or readily studied in aluminum alloys, mostly due to the reliance of the success of the processing in forming twins. In aluminum alloys, while twinning is not the mechanism responsible for improved corrosion resistance in thermomechanically processed alloys, changes in the microstructure through processing have been successful. In the 6xxx aluminum system, Esmaeili et al. [149] used thermomechanical processing for grain refinement allowing for more equiaxed grains with a weak texture. Tan, Allen et al.[18] showed a successful thermomechanical processing of 5xxx aluminum system, which exhibited better corrosion performance mostly attributed the improved grain shape and increased low
angle boundary density. Thus, it is possible that thermomechanical processing is an effective and viable way to alter the grain boundary structure of the material and influence the precipitation of $\beta$ phase [13, 21, 113, 150].

It is known that both dislocation density [8, 151] and grain boundary character [63, 66, 121] play key roles in the sensitization process. Cold work in the form of rolling reduction introduces a high density of dislocations that upon recovery, form low angle subgrain structures within existing grains. These features provide energetically favorable heterogeneous nucleation sites for the $\beta$ phase upon sensitization. Multiple subgrains can form within a grain, and a continuous grain boundary film of $\beta$ phase can be avoided by providing a large number of nucleation sites within short diffusion distances. If the nucleation sites are inside the grain, the anodic $\beta$ phase is not subjected to a corrosive environment and the material’s IGC and SCC resistance is improved [21]. As previously mentioned, the H116 temper induces a sizeable dislocation density due to the added percent strain from cold working [24]. These features provide favorable heterogeneous nucleation sites for the $\beta$ phase upon sensitization. Multiple subgrains can form within a grain, and a continuous grain boundary film of $\beta$ phase can be avoided by providing a large number of nucleation sites within short diffusion distances [16]. Scotto D’Antuono et. al. demonstrated that $\beta$ phase initially precipitates preferentially on low angle grain boundaries, meaning subgrains of this nature are a promising way to control $\beta$ nucleation [121]. Precipitates on these boundaries exhibited limited growth, which can be beneficial by not weakening the matrix through solid solution depletion. The majority of studies have shown that $\beta$ precipitation mainly occurs on high angle grain boundaries due to their reduced nucleation energy and are not growth limited [21]. More recent studies have
agreed that precipitate within the grain and at low angle boundaries does occur[65]
following that breaking up of the GB network via subgrains can improve DOS[66].

In addition to grain boundary character, corrosion resistance can be controlled
through grain boundary area, which is inversely proportional to grain size in some cases
[152] but effect of grain size on corrosion resistance can be highly contradictory within
the literature[69]. Thermomechanical treatment can be employed to induce
recrystallization at the surface of the plate where interactions with a corrosive
environment occur. A surface consisting of large grains reduces the amount of grain
boundary area susceptible to sensitization and IGC, therefore increasing corrosion
resistance by decreasing mass loss via grain exfoliation.

In an attempt to better understand the effects of thermomechanical processing,
and the inherent role of associated microstructural, in corrosion resistance of 5xxx
aluminum alloys, a systematic study of varying deformation and annealing parameters
was performed. The study clarifies the role of surface as well as through-thickness
microstructural modifications to achieve a material with high corrosion resistance in the
absence of diminished mechanical properties. The results reveal an improvement in the
overall corrosion resistance, outperforming the widely used H116 heat treatment. The
presented thermomechanical process also proved to be successful in achieving
microstructural, and thus performance uniformity by controlling/processing the entire
sample thickness. Implementation of such treatments for 5xxx aluminum alloys in their
various applications will ultimately help extend vessel lifetimes and mitigate the effects
of corrosion damage that these alloys experience.
6.3 Experimental Methods

6.3.1 Thermomechanical Processing

Two studies were conducted to compare the difference of starting material and thermomechanical treatment and its impact on corrosion resistance. The first study tested the resulting through thickness of the starting material in its entirety, while the second study directly compared the resulting thermomechanical processed top and center sections.

The first study used bulk ½ inch plate of type 5083-H116 aluminum (Al-4.4Mg-0.7Mn-0.15Cr) which was supplied by Carderock Naval Surface Warfare Center (referred to “plate A” in this work). The control samples were not thermomechanically treated and were cut to size and sensitized later for comparison. All other samples were annealed at 345°C for 1 hour and air cooled to normalize the material. Samples of the annealed plate were cut and set aside for later comparison and the remaining material was cut for samples to be cold rolled. All samples undergoing cold rolling were ground to a thickness larger than their respective reduction ratio to assure equal final thickness of all samples. Samples were the cold rolled to 0%, 10, 20, 30, and 50% reductions as shown in Figure 33(3) 5083-H116 plate A process flow chart with error of ± 2%. Note while it is not shown in the figure reductions of 5% and 15% were later added to plate A processing as well. After cold rolling, sample dimensions were adjusted by grinding to be 6mm by 50mm. Half of the treated samples were heat treated at 500°C and the other half at 400°C. A minimum of two samples from each category was made to assure reliable results. The entire annealing process flow chart for plate A is shown below in Figure 33.
Figure 33: Annealing process flow chart for thermomechanical treatment approach of AA5083-H116 plate A (left) and plate B (right)

The AA5083-H116 material used in the second study was obtained from McMaster-Carr as a plate 12 inch by 12 inch in area and 3/8 inch thick (referred to as “plate B” in this work). The as-received plate B was subsequently cut into six equal pieces; for uniform thickness across all pieces after rolling, a mill was used to reduce each thickness inversely proportional to the percent rolling reduction. Samples were then processed similarly to plate A in the first study but only for the 400°C post cold rolling anneal. All pieces, except one control, were thermally annealed at 400°C for 1 hour followed by a water quench to normalize the samples. Following the anneal, plates were cold rolled parallel to the longitudinal direction to approximately 0%, 5%, 10%, 15%, and 20% reduction in thickness. The rolling reductions are reported in Table 6. Another 400 °C anneal for 1 hour with water quench was employed as the final thermomechanical step.
<table>
<thead>
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<th>Target Reduction (%)</th>
<th>Reduction (%) Study 1 Plate A</th>
<th>Reduction (%) Study 2 Plate B</th>
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<td>14.5</td>
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<tr>
<td>20</td>
<td>19.73</td>
<td>19.1</td>
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Table 6: Rolling Reductions for study 1 (plate A) and 2 (plate B)

6.3.2 Sensitization, Corrosion Testing, and Microstructural Analysis

After thermomechanical processing, plate A samples were sensitized for 100hrs at 150°C and plate B samples were sensitized at 100°C for 100hrs. Some as received samples were not sensitized to provide a control pool. Specimens were analyzed using Nitric Acid Mass Loss Testing (NAMLT) at the Naval Surface Warfare Center, following ASTM G67 procedures [55].

Specific to plate B specimens in study 2: Samples for which the surface microstructure was tested retained their full cross sectional thickness of approximately 0.3 inch while samples which were tested for the performance of the center microstructure had approximately 0.07 inch milled from both of their rolled surfaces. This was done to assure the center part of the sample was not “contaminated” by the surface microstructures. Continuing for both plate A and B, Scanning Electron
Microscopy (SEM) and Electron Backscatter Diffraction (EBSD) were used to characterize the material’s grain structure and orientation distribution. This data was first used to characterize the transverse cross section of each rolling reduction to differentiate between the surface and center microstructures. Longitudinal cross section samples from the surface and center were then examined.

6.4 Results and Discussion

6.4.1 Mass Loss as a Function of Thermomechanical Processing

Nitric acid mass loss testing, in accordance with ASTM G67[55], was performed on all sensitized samples. The resulting G67 mass loss data for plate A is shown in Figure 34a for the various applied thermomechanical treatments. The data shows that the addition of any of the proposed treatments to plate A (already having the H116 treatment) aided in overall corrosion resistance, and the best performing treatment being the 5% 500°C annealed sample. As the rolling reduction was increased, the effect was diminished approaching the performance of the as received sample. Using this as a foundation, a similar approach was taken in the second study this time comparing the surface to the center and using a different starting material (plate B). Mass loss as a function of rolling reduction % is presented in Figure 34b while mass loss as a function of grain size is shown in Figure 34c showing results for both the center and surface of the material.
The center microstructure displayed a better corrosion resistance across all rolling reductions with the exception of the 10% condition. This is because the corrosion resistance of the material is strongly related to the grain size at the surface of the material. Larger grained materials have less grain boundary area that is susceptible to sensitization. As a consequence, the number of pathways for intergranular corrosion to take place is significantly reduced, having the effect of decreasing mass loss via grain fallout. In Figure 34c the 10% surface sample is shown to not follow the trend for having a lower degree of mass loss for its relatively larger grain size. This is because the surface of this sample contained a shallow layer of small grains while the average grain size remains high due to the underlying layer of large grains shown later in Figure 37.

The resultant sample surfaces (of plate B only) were examined in an SEM to qualitatively assess the material’s response to the mass loss testing shown in Figure 35. The general character of the corrosion can be seen by the extent of grain exfoliation or fallout. Specifically, the 0% and 5% reductions exhibit small grains and significant mass loss (c-f) while the 10% condition (g-h) shows a mixture of both small and large grain fallout at the both the surface and center of the plate. Lastly, the 15% (i-j) and 20% (k-l)
reduction samples exhibit clear intergranular corrosion, but are not subjected to the same extent of mass loss. The faces of the 15% reduction corrosion samples qualitatively demonstrate the best corrosion resistance and least amount of grain fallout of all samples tested.

![Image](image_url)

**Figure 35:** Scanning Electron Micrographs of ASTM G 67 Tested Sample Surfaces. (a) Control Surface, (b) Control Center, (c) 0% Surface, (d) 0% Center, (e) 5% Surface, (f) 5% Center, (g) 10% Surface, (h) 10% Center, (i) 15% Surface, (j) 15% Center, (k) 20% Surface, (l) 20% center.

### 6.4.2 Microstructural Analysis

The as-received H116 condition of both plates was characterized by EBSD to determine the initial microstructure of the material. EBSD maps of as-received plate A (Figure 36a) as well as the as-received plate B (Figure 36c-f) are shown in Figure 36. In the case of plate B, and keeping with the theme of comparing the center to surface treatments, the transverse and longitudinal directions at both the surface and center
(Figure 36c-f) of the plate are shown. The microstructure of the best performing 5% and 500°C heat treated sample from plate A is also added to show the change from the plate A as received condition. The comparison between images a and b in Figure 36 show the stark difference between plate A microstructures which lead to a DOS improvement of ~25mg/cm² less mass loss due to the additional 5% rolling reduction and 500°C annealing treatment.

Figure 36:(a) EBSD scan of the cross-section of the As Received sample. (b) 5% cold rolled and 500°C heat treated sample under the EBSD. (c-f) As-received EBSD maps of the Transverse and longitudinal cross sections
It is clear that comparing the starting microstructures of plate A and B (Figure 36 a and c) that there is a major difference between the two as-received conditions. In plate B’s surface/center comparison (Figure 36c-f) it can be seen that the as-received H116 condition exhibited a strong anisotropy with elongated grains in the rolling direction. Additionally, grain size at the center of the plate was marginally larger than at the surface. However, there was no dominant texture present.

Plate B was further analyzed, post thermomechanical treatment, via EBSD maps in the transverse direction exhibiting how the material microstructure responded to the applied thermomechanical treatment along the cross section, as shown in Figure 37. A total of six (6) segmented regions were scanned and stitched together to create a continuous map approximately 0.2 inch in the transverse direction and 350μm in the longitudinal direction. The microstructure primarily consisted of equiaxed and fully recrystallized grains.

![Figure 37: (a-d) Transverse Cross Sectional EBSD Maps of Processed Samples](image)
Continuing with plat B, EBSD data showed that with the exception of the 10% rolling reduction sample, all other conditions displayed a fairly homogenous microstructure along the plate’s cross section. The 10% sample exhibited a shallow area of small grains before transitioning to a large grain microstructure extending approximately 1.5 mm. There was a sharp transition to a smaller grain size that appears to be the dominant microstructure beneath the surface. A mix of large and small grains was observed at the geometric center of the plate. The remaining rolling reduction samples exhibited a general trend where the grain size at the center of the plate is marginally larger than the surface, which is consistent with the observed microstructure of plate A’s condition. The grain size at the surface and center of the plates were calculated in the transverse direction for plate B and are presented in Figure 38a.

Figure 38: Plot of rolling reduction vs grain size in transverse direction and the resulting CSL boundary distribution comparing the as received Plate B to the well performing 15% reduced, and poorly performing 5% reduced samples.
Changes to special grain boundary number fractions were also considered. Figure 38b shows the comparison between the as received plate B samples with the best and worst performing G67 values 15% and 5% respectively (again is should be noted that in plate A the 5% condition performed the best). The best performing sample, 15%, showed slight lowering of sigma fractions of type 3, 9, and 11 but increases in type 5, 15, 21b, 23 and 29 Σ values. The worst performing sample, 5%, showed similar fraction increases and decreases. In general the as received plate B contained a comparable fraction of CSL type boundaries to all processed samples and also contained the highest fraction of low order Σ boundaries (Σ 3-11). Similarly to previous studies [13] the number fractions of CSL type boundaries are so low that any increase/decrease in corrosion resistance is coincidental. Also changes in number fractions of low (<15°) and high (>15°) angle boundaries types were minimal clarifying grain size as the primary variable.

EBSD maps of plate B were also collected in the longitudinal direction to confirm the equiaxed nature of the microstructure observed in the transverse direction, and are shown in Figure 39. The microstructure consisted of equiaxed and fully recrystallized grains. Again, grain size at the center of the plate was marginally larger than at the surface. It was observed that grain size in the longitudinal direction was larger than in the transverse direction for all samples and that this difference increased with increasing rolling reduction, likely due to the residual effects of cold rolling.
Figure 39: Longitudinal EBSD scans of plate B for all processed samples.

Our initial findings showed that the proposed thermomechanical treatment could retain the H116 microstructure at the center of a plate. However, these results indicate that complete recrystallization occurred along the entire cross section and no significant anisotropy remained. A recent study demonstrated that the H116 temper can produce a wide range of microstructures leading to significant variability between suppliers and individual lots [47]. As discussed, the as-received plate B material used in this study displayed no significant texture, which is inconsistent with material plate A. Following the same thermomechanical treatment, the two plates exhibited vastly different microstructures at the center of the plate. Plate A with strong initial texture retained that microstructure while plate B without strong initial texture was fully recrystallized post thermomechanical treatment. Again to reiterate if the best performing treatment of plate A, 5% reduction ratio with 500°C anneal, was applied to plate B the corrosion rate would increase significantly in plate B. These inconsistent results indicate that due to the high variability of the H116 temper, attempting to achieve a specific microstructure across
different lots or manufacturers of material by a pre-prescribed thermomechanical treatment is next to impossible.

In general, the data shows that mass loss is greatly impacted by changes in grain size a common theme when discussing corrosion\[69\]. Larger sized grains tended to exhibit better corrosion resistance despite the negative implications on mechanical properties. This may be a downfall of NAMLT G67 testing as discussed in other studies in which recrystallized grains and flat pressed grains tend to fall away from the bulk of the material at different rates\[153\], but the impact of subgrains and dislocations may also play a contributing role. The higher levels of deformation promote more recrystallization at the surface of the plates leading to the higher mass loss. Conversely, moderate levels of dislocations and subgrains have been shown to improve corrosion resistance by promoting precipitation within the grain\[66\], effectively the purpose of the H116 treatment\[17\]. This concept is observed in the V shaped pattern in the plots of rolling reduction vs. mass loss (figure 2 a and b) where corrosion rates can be improved with some added rolling reductions and thermal treatment but the opposite occurs at higher cold rolling percentages. This is where the variability and difficulty of the H116 treatment comes into play, in maintaining a fine balance between mechanical properties and corrosion resistance. Needless to say, tighter specification and higher quality control around the H116 treatment should be implemented as there is much room for improvement.
6.5 Conclusions

Two studies were compiled within this work using two different plates of 5083-H116 focusing around comparing the effect of thermomechanical processing on corrosion resistance. This work showed that thermomechanical treatment in addition to the H116 temper of AA5083 can result in a material with improved corrosion resistance. A key downside observed is that due to the wide specification of the H116 treatment a singular thermomechanical treatment that may improve one lot/manufacture of material may actually lead to more corrosion in another. For instance in this work a 5% reduction with 500°C anneal in plate A performed best but in a secondary study plate B required a treatment of a 15% reduction with a 400°C anneal to achieve comparable corrosion resistance.

A general reduction of mass loss was shown as a result of having a larger grain size which in turns reduces the grain boundary area susceptible to β phase precipitation and sensitization. However, the treatment induced recrystallization throughout the entire cross section resulting in a homogenous microstructure consisting of equiaxed grains in plate B. Initial trials using this treatment with a different AA5083-H116 (plate A) did not experience recrystallization at the center of the plate. Ultimately, the variability in the H116 temper was shown to produce inconsistent results across different plates under the same material designation. Finally the majority of the corrosion resistance was attributed to larger grain size which while extending service life would regrettably lower mechanical properties.
Chapter 7: Metastable Precipitates in 5xxx Aluminum Alloys as Predominant Failure Mechanism in Aluminum 5xxx Alloys

7.1 Abstract

The 5xxx series aluminum magnesium alloy system is used for light weight structural components, such as naval vessels and automotive components. Exposure to elevated temperatures gives rise to sensitization, causing Mg segregation and Al$_3$Mg$_2$ precipitate formation, which can preferentially corrode in harsh environments, ultimately leading to intergranular corrosion and stress corrosion cracking. During sensitization, it is known that the precipitation of both $\beta'$ and $\beta$ (equilibrium) phases are possible, however it is unclear what precipitate is more prevalent in typical exposure environments (e.g., marine or high temperature automotive). Using a combination of in situ and ex situ transmission electron microscopy, samples taken directly from in-service naval vessels as well as samples sensitized in laboratory conditions are examined. The study highlights the discrepancies found when comparing laboratory sensitization treatments to in-service materials and draws a clear delineation between the $\beta'$ and $\beta$ (equilibrium) phases with respect to the phase predominantly found in material exposed to in-service conditions. More broadly, our findings allow for a more refined understanding of Al-Mg precipitate evolution as well as more accurate precipitate stability parameters within the Al-Mg alloy system.
7.2 Background

Lightweight structural alloys, such as the 5xxx aluminum magnesium system, have been implemented into designing, structures, vehicles and vessels with improved maneuverability, speed, and fuel efficiency [2, 3, 6]. Despite these advances, 5xxx still suffer from sensitization (and eventual corrosion) after exposure to elevated temperatures. During this process, Al$_3$Mg$_2$, or β phase, can form on existing intermetallic phases and dislocations [7], as well as most importantly along the grain boundaries [10, 12, 14, 16, 68], which are anodic to the matrix material [16, 43]. A galvanic couple is created during exposure to harsh environments, such as salt water, ultimately leading to stress corrosion cracking [14, 15, 124, 154].

A wealth of information is available regarding the thermally activated precipitation processes in 5xxx series [28, 29, 31, 40, 155, 156], however key questions related to critical aspects of the Al$_3$Mg$_2$ and related phases, such as composition, structure, formation mechanism, and growth kinetics, remain unanswered. It is known that the Mg in the matrix begins as a super saturated solution at 3% or greater, segregates to the grain boundary, intermetallics, and defects at 50°C or higher and ultimately forms β equilibrium phase with its solvus at ~280°C for materials with 5% Mg content [18, 89]. The β’ phase is a metastable precursor to the β equilibrium phase, and forms at temperatures around 50-200°C [4, 29-31] and takes on a pseudo hexagonal structure with lattice parameters a=1.002 nm and c=1.636 nm [35, 39]. This phase typically forms at the GBs and is semi-coherent with the matrix, taking on the shape of rods or plates.
depending on the plane direction [38]. Its exact composition of β’ is also up for debate, but is said to be close to Al₃Mg₂, the same as β equilibrium.

Despite the generally accepted understanding of (1) the evolution of Al₃Mg₂ phases begins with the metastable β’ phase, ultimately forming into the β equilibrium phase above 200°C [28, 36, 157], and (2) the sensitization processes occurring in common applications at temperatures below 150°C, the β equilibrium phase is most commonly reported as the “culprit” of sensitization independent of heat treatment [5, 7, 12, 13, 17, 107, 158], with the metastable phase often being ignored.

In fact, there is little information regarding the metastable β’ phase in general. Structural characterization of the β equilibrium phase from previous works [39] describes a face cubic centered (FCC) structure with a very large lattice parameter of 28.2 angstroms. This phase growth is incoherent [5, 21] with respect to the grain boundaries and occurs at temperatures of 200-300°C, with dissolution at ~400°C [21, 28, 30], depending on Mg%. Despite having a different crystal structure, β phase is believed to have a composition very close to β’ [28, 29], commonly simplified to Al₃Mg₂.

Interestingly, Al₈Mg₅ was often used to describe the composition for both β’ and β equilibrium in earlier works [41, 42]. Another delineation is that the β precipitation occurs heterogeneously like that of β’ but is said to occur at later stages of aging [7, 21]. Some recent works have attempted to further describe the evolution of β phase precipitation as well as characterize the metastable phase. Yi et al. [32] observed β” and β’ within GBs of 5456 H116 naval ship material. Yan et al. [70] studied precipitate evolution along dispersoids within Al 5083 which were shown to connect via dislocation bands possibly leading to faster precipitate growth. While these studies have aimed to
understand early β evolution there are still questions regarding the exact temperature regimes for the various types of β phase.

Pinpointing a temperature window for both precipitate formation and stability seems to be the ultimate challenge, given the wide range of conflicting results reported. It has been published, for example, that the formation of β equilibrium phase occurs at 200-300°C, but some have found β equilibrium phase precipitates appearing at ageing conditions below 200°C [5, 7, 107]. Specifically, Goswami et al. [109] examined β precipitates in a 5083-H131 alloy which was homogenized at 250°C for 10hrs and aged at 100C for 3,7,14,30,45,60, and 90 days. Despite these relatively short aging times, β equilibrium precipitates were observed along the GBs for all ageing times but no β” or β’ precipitates were found. Zhu et al. [5] observed β equilibrium phase in 5083-H131, after long term aging at 70°C for 1 year and 175°C for 15 days, based on STEM EDS quantification and comparison of FFT patterns to simulated Al₃Mg₂ d-spacings. It should be noted, however, that the authors agreed that theoretically long aging times at low temperatures could have allowed for the β phase precipitation but more work would be required to confirm that it was indeed the β equilibrium phase that actually formed.

Conversely, some examples of β equilibrium precipitation occurring at higher temperatures and shorter ageing times exist. Nebti et al. [28] have presented results explaining the formation and growth life cycle of β phase with β equilibrium phase existing well above 250°C, although in a higher Mg containing alloy. Carroll et al. [8] showed β phase growth which was observed at both grain boundaries and subgrain boundaries in AA-5083 after 24 hours at 200°C. Fuller et al. [11] aged samples of 5754 modified with small additions of Sc and Zr at 288°C and 300°C for 72 hours which
resulted in formation of β precipitates which formed at the GBs. Finally, in situ experiments from Scotto D’Antuono et al. show precipitation of β at temperatures closer to 300°C during accelerated in situ TEM heating experiments [121, 151].

It is clear from these studies that both low and high temperature heat treatments give rise to some form of β phase precipitates (either metastable or equilibrium) but it is not always clear what type of precipitate, β’ or β, is being observed. Despite the heat treatment, the commonly accepted term used to describe these phases is “β phase” with very little mention of the metastable form β’. Adding to the confusion is the similarity of composition (Al₃Mg₂) which makes distinguishing between β’ and β difficult, solely with EDS [32]. While the general consensus is that the precipitates in question are the equilibrium form of the β phase [29, 30, 35], many have argued that the β’ phase are the main precipitates formed, especially at lower temperatures. Distinguishing between the two phases is a challenge. Starink and Zahara [29] used DSC to characterize β’ and β precipitation in an Al-16 at.% Mg alloy. It was found that the β’ was formed between 180-290°C and dissolution occurring at ~200-300°C with a ~280-330°C range where β’ transitioned to a state with β above ~330 no β’ was observed. It was also found that this transition between β’ and β is dependent on the heating rate. Samples heated at 40°C/min did not show this transition and β formation was complete at the end of the treatment. Lower heating rates of 5°C/min allowed for this transformation to be observed. In a DSC study by Hamana et al. [30] an Al-12wt.%Mg alloy exposed to long isothermal ageing (>1500hrs) at 150°C showed stable β’ precipitates which later transformed to β equilibrium phase agreeing with the phase diagram. It was also shown that there was no direct transformation at non-isothermal conditions and β’ and β dissolved and formed
independently from one another. This is further confirmed by the DSC study by Nebti et al. [28] on an 8 and 12wt%Mg Al-Mg alloy where the β’ to β transition did not occur below 200°C at short times and direct formation of equilibrium β phase occurred from supersaturated solution above 250°C with β precipitation after 10min at 300°C. From these works it appears that the transition between β’ to β can only occur over very long periods of time (>1000’s of hours) at lower temperatures below 200°C under isothermal conditions otherwise the only other way to get β equilibrium is directly from SSS which requires temperatures 200°C or higher depending on the weight percentage of Mg.

While these two forms, β’ and β, may be very similar and thus difficult to distinguish using many characterization techniques, it is critical to have an understanding of what precipitate contributes most to failed in-service material. As such, this paper presents observations of thermal stability windows of these precipitates via in situ heating and high resolution techniques, which are required to fully understand which phase is occurring within the samples as well as information such as sensitization treatment. Understanding the temperature regimes of the β’ or β phase helps shed light on the stability of the precipitates, thus improving opportunities for corrosion resistance in all future applications of the 5xxx series alloy.

7.3 Methods

Samples of failed in-service ship material alloy 5456-H116 were acquired from the Naval Surface Warfare Center- Carderock (West Bethesda, MD). The material had cracked due to years of exposure to sea water and elevated temperatures. Samples of new
unused 5456-H116 from Alcoa were also acquired to serve as a comparison ((1) sensitized at 175°C for 1 hour, (2) 300°C for 1 hour, and (3) sensitized at 325°C for 15 minutes). Samples for transmission electron microscopy (TEM) were prepared using conventional metallographic procedures to view the transverse section of the material. Final thinning was carried out using a Fishione ion mill to electron transparency. All specimens were examined using a JEOL 2100 LaB₆ at an operating voltage of 200 kV. A Gatan in situ heating holder model 628 was used to perform the experiments. Both β’ and β secondary phases were analyzed using a combination of nano-beam diffraction and energy dispersive X-ray spectroscopy (EDS). Finally, bulk samples of in service material and of new 5456-H116 (bulk sensitized at 150°C for 72 hours and 300°C for 72 hours) were prepared for nitric acid mass loss testing according to ASTM G67 [43] sample dimensions. Optical light microscope images were also taken of corroded G67 samples.

In situ TEM microscopy was utilized to observe any possible phase transformation in the in-service material upon heating to help confirm stability of present phase type (β’ or β equilibrium) and morphology. This approach allowed for initial characterization of the precipitates within the in-service material, as well as a way to see any changes when exposed to higher temperatures. Concurrent bulk heat treatments in a box furnace were also conducted to assure accuracy of in situ TEM results in relation to precipitate temperature ranges. Bulk ASTM G67[55] was conducted on lab sensitized material as well as the in-service material to compare corrosion mass loss of high temperature and low temperature treatments.
7.4 Results and Discussion

Full characterization of the precipitates within the failed in-service and bulk lab sensitized 5456-H116 material was conducted. Images from the failed in-service material are shown in figure 40 (a) and (b). The precipitates are fairly large and typically form as long narrow semicoherent plates along the GB. Precipitates also exhibited a striated appearance similar to those found in other works[32]. A lower than expected number density of precipitates was observed as compared with previous results [121, 151] with coverage of the GBs limited to single precipitates in most cases as shown in Figure 40a. The particles were typically located far away from one another and no signs of ribbon type precipitates were observed, contradicting previous understanding of β equilibrium precipitate formation [130, 159]. The unique morphology of the precipitates resembles a striated band structure within the precipitate itself, easily viewed in Figure 40b.
Figure 40: (a) Bright field TEM images of β in in-service ship material with hexagonal diffraction pattern inset, (b) Image of in-service material β phase exhibiting striated morphology, (c) Bulk 5456-H116 furnace sensitized at 175°C for 1 hour showing striated morphology, (d) Bulk 5456-H116 furnace sensitized at 325°C for 15 minutes showing dense homogenous morphology.

Ex situ bulk TEM bright field images of a sample grown at 175°C for 1 hour are shown in Figure 40 (c). The precipitate in the image shows an identical morphology to the ones found in the in-service material from Figure 40 (a) and (b). Ex situ high temperature treatment at 325°C for 15min was also completed with resulting precipitates in Figure 40 (d). These high temperature precipitates show a more uniform dense morphology and do not exhibit the striated pattern morphology. Also, as was observed over many samples, exposure to higher temperatures yields a larger number density of smaller precipitates along the GBs as exhibited in Figure 40(d).

The ex situ annealing results show that the approach that best mimics in-service conditions is that of a lower temperature sensitization over longer periods of time. Specifically, the TEM images in Figure 40(c) show that a treatment of 175°C for 1 hour can yield comparable Mg rich precipitates to that of the in-service material, appearing to be the same type of precipitation based on morphology and hexagonal diffraction pattern. Both precipitates exhibit a striated pattern within them. The sample heated at 175°C for 1 hour also had sparsely placed precipitates with most of the GB area void of precipitation. While the 175°C for 1 hour did appear to have more precipitates in no cases were fully continuous precipitation observed at the GBs.
The results of the in-situ heating experiment, starting with a pre-existing precipitate within the in-service material, can be viewed in Figure 41. The sample was exposed in situ to 150°C and held at that temperature for 1 hour. Despite being exposed to the aforementioned growth enhancing temperature of 150°C[28] the precipitate did not change size after an hour of exposure. The sample was then heated to 300°C and during heating the precipitate at the boundary began to dissolve at 275°C (Figure 41b). Complete dissolution occurred within the sample at 295-300°C (figure 2 (c)). Upon further heating at 300°C which was held for 5 minutes before quenching, new precipitates, characterized as β equilibrium phase, grew in the matrix (Figure 41 (c)) and at the GBs (Figure 41 (d)), forming in accordance to previous in situ studies[121, 151]. The newly grown Mg rich phase (Figure 41(d)) at a different boundary in the same sample shows a different morphology with no signs of the striated structure and a more uniform dense appearance and are identical to those found in the high temperature bulk ex situ samples (Figure 40 (d)), also characterized as β.

The stability of the “β” phase in the in-service material does not follow the phase diagram accurately. As shown in Figure 41 (b) the precipitate begins to dissolve around
275°C and the GB is desensitized more as it approached 300°C. After the 300°C temperature was reached in the material, another Mg rich precipitate phase grew at the GB shown in Figure 41 (c) and (d). It was concluded that these precipitates were the β equilibrium phase showing a cubic diffraction pattern. Therefore, the precipitation within the in-service material, and that of which was responsible for the material failure, is the metastable β prime or (β’). The β equilibrium precipitates began to grow at 300°C and continued to coarsen during the 5 minute hold. These results were consistent with previous accelerated heating experiments [121, 151] as well as previous DSC studies [30]. It should also be noted that despite prolonged periods (~10 years) of exposure to elevated temperatures there were no observed β equilibrium precipitates in the material. While it may be possible a few were present it was still not enough sensitization to transform all precipitates from metastable to the equilibrium phase. This suggests that when low sensitization temperatures <150°C are used that most likely the majority if not all of the precipitates are the metastable β’ form.

To assure that the in situ heating was not being controlled by thin film effects or temperature gradients, an ex-situ examination was completed in Figure 40d. The sample in figure 1(d) was heated at 325°C for 15 minutes yielded the same precipitates as those during the high temperature in situ study. Comparing the heated in-service precipitates (Figure 41(d)) to the ex situ (Figure 40(d)) show similar morphology and coherence. The high temperature precipitates are coherent on one side of the boundary and take on a saw tooth pattern. The contrast across the precipitates is also uniform and the striated appearance is lost within the higher temperature form.
It is to be noted that both the in situ and bulk ex situ heating exhibited the exact same evolution which in turn contradicts the previous understanding of the precipitate evolution in Al-Mg alloys [8, 14, 21, 25].

The 5xxx series aluminum alloys contain manganese, chromium, copper, and iron [16, 42], which their concentrations may have an effect on precipitation temperature ranges. A final point is that while both types of precipitation may be deleterious due to their anodic nature and removal of Mg from the matrix the β prime precipitate is the one which lead to the in service failure. According to earlier studies by Bernole [35] the β prime precipitate was suggested as the primary precipitate leading to corrosion in 5xxx series Al alloys, and that assumption appears to be correct. Also susceptibility to IGC was found to be greater at 150-200°C [46]. It has also been shown that β’ growth begins at 100°C and is accelerated at 150°C [28]. This signifies that the low temperature precipitate (β’) may lead to more deleterious effects.

In order to compare the corrosion response between the low and high temperature regimes ASTM G67 [55] testing was completed. The low temperature samples sensitized at 150°C for 72 hours had an average mass loss of 47.2mg/cm² while the high temperature samples showed mass loss values of 1.7mg/cm². Optical microscopy images were taken of the post G67 samples as shown in Figure 42 below.
The low temperature sensitized samples (Figure 42 a and b) exhibit a significant amount of material loss along the grain boundaries in some cases penetrating up to 50µm into the sample. Comparing this to the high temperature treatment (Figure 42 c and d) there is minimal penetration along the boundaries at ~10µm. In the high temperature sample it appears that 10-20µm pieces of material began to fall away highlighted by arrows in image d. This may signify a different corrosion mechanism in the higher temperature treatment but regardless, the damage is much less significant despite still containing Mg rich precipitates (shown in Figure 43b). The average in service G67 mass loss values were found to be an extremely high 68.36mg/cm² signifying a strong agreement with the low temperature treatment. These results show that the lower temperature precipitate β’, the only precipitate phase found within the cracked ship material, causes more sensitization to occur and thus is the more detrimental precipitate
form. This result coincides with previous theories stating that the $\beta'$ is the most deleterious version [35].

A new more accurate description of $\beta$ precipitate formation has been compiled, from observations of accelerated in situ and bulk ex situ growth of $\beta$ precipitates, into a precipitate regime timeline shown in figure 43. It begins by formation of the $\beta'$ phase which forms from long term exposer at temperatures from room temperature up to 275°C with dissolution occurring around 275°C. In the range between 275 and 300°C the $\beta'$ dissolves and the $\beta$ equilibrium phase can form concurrently or after the $\beta'$ phase fully dissolves above 300°C. The $\beta$ equilibrium phase then grows at 300°C and continues to coarsen after a hold at that temperature as seen in both in situ and ex situ experiments. The $\beta$ equilibrium phase is quite stable and was shown to exist at 325°C and possibly higher temperatures as well. These results agree with previous studies[28] showing a possible direct growth of $\beta$ equilibrium phase at high temperatures. Considering the application of the in service material, the ship would experience constant day to day changes in temperatures which would likely never reach temperatures $>100^\circ\text{C}$ and not being at isothermal temperatures consistently for 1000s of hours it is more likely that the precipitates in question are $\beta'$ metastable phase which is what has been shown.
Figure 43: Schematic displaying β' and β precipitate temperature regimes. (a) Image of an in service sample containing β' precipitates at a GB. (b) Ex situ sample heated to 300°C for 1 hour showing β' phase still dissolving at the grain boundary. (c) Ex situ bulk sample with β equilibrium precipitates which was heated to 325°C for 15 minutes.

One of the difficulties in understanding β phase precipitation in 5xxx series Al alloys is that there is a lack of delineation between the β prime phase and β equilibrium phase within the literature. Typically a blanketed “β phase” is used no matter what type of heat treatment is applied. Many of the inconsistencies within the literature are most likely due to a lack of high resolution techniques and precipitate identification via temperature regimes based off of the binary phase diagram. Given the results in this work it is clear that many of the current studies relying on low temperature sensitization treatments are observing the metastable β’ rather than β equilibrium. This shows the need for more high resolution TEM based studies as well as an observance of wider range of temperature regimes to better understand the precipitation process in these alloy systems. It is also clear that moving forward, future works must form a better delineation between the two phase types β’ and β as it appears that there is a stronger corrosion potential of one phase over the other.
7.5 Conclusions

The type of precipitate within the failed in service material is that of the β’ phase, as determined using in situ TEM coupled with high resolution analysis and bulk ex situ heating. It is clear from our work that low resolution, bulk SEM, EDS or use of the phase diagram alone, is not enough to delineate between β’ or β unless perhaps a purely binary material is used.

A new precipitate evolution of β equilibrium in AA5456-H116 has been defined. Here, the metastable β’ exists from room temperature to ~275°C where it begins to dissolve. The β’ phase continues to dissolve and eventually the stable β equilibrium phase forms around 300°C. The high temperature β equilibrium phase remains stable well above the binary phase solvus in this alloy.

ASTM G67 testing has confirmed that the low temperature treatment yielded the highest level of mass loss. The in service material follows the same trend as the low temperature treated samples which shows that the β’ precipitate is the more corrosive form and a need for a clear delineation between β’ and β in future works is crucial.
Chapter 8: Atom Probe Tomography analysis of pipe diffusion in 5456 aluminum alloy

8.1 Abstract

Atom probe tomography analysis has shown that the primary mechanism for beta phase precipitation in 5xxx series alloy is pipe diffusion. The principle of gallium embrittlement was used to trace the pathways of the magnesium within the alloy. Low angle grain boundaries exhibited gallium diffusion within the discrete dislocations while the high angle grain boundaries exhibit a more generalized grain boundary diffusion path. Both types of grain boundaries showed a general depletion of magnesium. Elevated gallium concentrations were also found inside magnesium rich beta precipitates adjacent to the grain boundaries. Understanding the mechanism for beta phase precipitation will lead to better temper design and a more corrosion resistant material.

8.2 Introduction

The 5xxx series aluminum (Al) alloys contain 5% magnesium and gain the majority of their strength from cold rolling and magnesium (Mg) solute additions. The alloys possess a high strength to weight ratio and weldability, making them a popular choice for marine vessel construction to increase fuel efficiencies [2]. While the Mg increases these properties these alloys are vulnerable to sensitization, a process where Mg segregates toward the grain boundaries (GBs) and precipitates as β phase (Al₃Mg₂), when exposed to moderate temperatures for extended periods of time [5, 6]. When these alloys are exposed to a harsh in-service environments, such as sea water, a galvanic couple is
formed between the β phase particles and the aluminum matrix, leading to preferential
corrosion of the β phase and ultimately stress corrosion cracking[4, 14].

The process of sensitization is strongly temperature driven [28] but the
mechanism of formation is not fully understood. The mechanism of sensitization has
primarily been studied by TEM imaging, with relatively little data available on the grain
boundary chemistry of sensitized material and no data available correlating grain
boundary chemistry with misorientation. Searles et al.[14] observed depletion of
magnesium from 4.4 wt% to 3.5 wt% at a grain boundary segment not containing a
precipitate using STEM-EDS, but the grain boundary type was not reported. This result
supports the collector plate mechanism proposed by Aaron and Aaronson [73], where at
relatively low temperatures solute slowly diffuses to the grain boundary, then is rapidly
transported to the precipitates. Conversely, Goswami and Holtz [109] also report a EDS
line scan across a grain boundary of unidentified type but did not observe any depletion
of magnesium. The growth rate of these precipitates, both the initial nucleation and
growth of discrete particles and the thickness of continuous films of β phase at grain
boundaries after extended periods of time, is higher than is expected from the bulk
diffusion of Mg to the grain boundaries, which has suggested that pipe diffusion is
enhancing the bulk diffusivity of Mg [7, 109].

Pipe diffusion as a precipitation mechanism has been proposed for many years but
with very scarce physical evidence[79]. Pipe diffusion is effectively modeled around the
idea of a narrow high diffusivity path located within a matrix of lower diffusivity acting
as a pathway for diffusion[58, 79, 80]. An atomistic simulation study by Picu and
Zhang[78] showed that in a Al-Mg alloy the activation energy for diffusion along a
dislocation core was 75% lower than the bulk diffusion value. Legros et al.[33] observed
diffusion of Si in an Al film during in situ TEM studies showing that dislocations can
transport atoms at rates orders of magnitude faster than bulk diffusion. While the
literature shows segregation via pipe diffusion is possible and more energetically
favorable it does not explain the dependence of the dislocation network with respect to
the grain boundary precipitation especially in relation to boundary misorientation.

While it is difficult to view the process of pipe diffusion occurring in situ it may
be possible to confirm after the Mg has segregated. In an attempt to better visualize the
pathways of the Mg and confirm if pipe diffusion has an impact on precipitation a tracer
element which would follow a similar path of the Mg is needed. Liquid metal
embrittlement using gallium has been exploited to enhance contrast in the past, with grain
boundaries below 1° having been observed in SEM through utilizing LME[160]. The
penetration of Ga along Al grain boundaries has been studied in the past by placing a
small amount of liquid gallium onto the sample, then scratching the surface to break the
oxide layer and allow embrittlement of the aluminum specimen. The thickness of the
resulting Ga layer on grain boundaries has been directly measured using synchrotron x-
ray microradiography[161, 162], and In situ TEM has been utilized to observe the
velocity of the Ga penetration front[163-165]. These experiments demonstrated the
sensitivity of LME to grain boundary character, with low energy boundaries such as twin
[20] and low angle grain boundaries[165] absorbing gallium more slowly than random
high angle grain boundaries. Simulations have suggested that this dependence may be
due to the structure and free volume of the grain boundaries in question [165, 166],
however these studies have focused on the special low energy high angle boundaries such as twins.

The liquid metal embrittlement phenomena provides an opportunity to study the diffusion pathways in 5xxx aluminum. This is accomplished by dosing the outside with the small amount of Ga implanted from the liquid metal ion source, characterization of the grain boundary in TEM, then observing the penetration into the sample using the LEAP (local electrode atom-probe). This allows the behavior of relatively small amounts of gallium and its interaction with grain boundaries, dislocations and precipitates to be characterized. Most importantly this method will highlight the diffusion paths which the magnesium used during the sensitization process and show if pipe diffusion is the key mechanism of precipitation in 5xxx series aluminum alloy.

8.3 Experimental Procedure

The material analyzed is a 5456 H116 aluminum alloy supplied by Alcoa (Alcoa Center, Pa), which was given a 15% cold rolling reduction followed by a 1 hour sensitization treatment at 225 °C. The sample was then prepared for EBSD using conventional grinding and polishing to 1μm diamond, followed by a vibratory polish using 0.02μm colloidal silica. Samples were analyzed with EBSD to locate grain boundaries of interest, which were then targeted for liftout using a FEI Strata DB-235 FIB-SEM equipped with a Model 100.7 Omniprobe and a FEI Helios NanoLab. Liftout specimens containing grain boundaries were transferred to tungsten wires sharpened by electropolishing. The specimens then underwent annular milling at 30KeV to form the needle geometry required for evaporation in the Cameca 4000X-HR LEAP. The
specimens were imaged in a JEOL 2100 LaB$_6$ instrument at Drexel University equipped with a NanoMEGAS precession diffraction orientation mapping system.

8.4 Results and Discussion

A single atom probe specimen was found to contain a triple junction of low angle grain boundaries, as well as multiple Mg rich $\beta$ phase particles. Figure 44 shows this specimen with the largest section of grain boundary edge on in brightfield TEM, along with an orientation map from the NanoMEGAS orientation mapping software and the pseudo-brightfield image generated from the central spot of the diffraction pattern.

Figure 44: (a) Brightfield TEM of grain boundary edge-on. (b) Corresponding NanoMEGAs pseudo-brightfield image. (c) Nanomegas orientation map.
The calculated disorientation between these two grains in the orientation map is 2.8°. Figure 45 (a) shows the Mg atoms, which clearly illustrates that Mg is depleted in the grain boundary in the center and concentrated into a number of precipitates. These precipitates are highlighted in (b) by a 15% isoconcentration surface. Figure 45 (c) shows Ga ions, which are clearly concentrated along the grain boundary. Upon closer inspection, the lower third of the reconstruction shows parallel lines of Ga atoms. Figure 45 (d) illustrates the clustering of these Ga ions with 3% isoconcentration surfaces. Figure 45 (e) and (f) show the same 3% isoconcentration surfaces in two orientations rotated about the vertical axis of the image, first filtered to exclude surfaces with less than 200 polygons, then further filtered manually to highlight the banded structure.

Figure 45: a) Mg atoms  b) 15% Mg Isoconcentration surface  c) Ga atoms d) 3% Ga isoconcentration surfaces e) Filtered 3% Ga isoconcentration surfaces f) Filtered 3% isoconcentration surfaces 90° from (e).
2D concentration maps based on a section of the dislocations adjacent to the low angle grain boundary are shown in Figure 46a for Ga and Figure 46c for Mg. It is clearly illustrated that an elevated Ga concentration is located within the dislocations while there is a depletion of Mg around the dislocation with some Mg still located within the dislocations. This shows strong evidence that Mg is leaving the matrix, segregating toward the dislocations, and able to travel in the dislocation. Adding to this, areas which have lower levels of Ga along the dislocation tend to contain a high level of Mg and vice versa thus filling the free space within dislocation. When the combination of both the Ga and Mg concentrations are viewed together within the dislocation network a full visualization of the dislocation is revealed Figure 46b.
The spacing of these dislocation bands (highlighted by Ga atom concentrations) was measured to be 10 nm based on a 2D distribution of the Ga in the grain boundary, as shown in Figure 46a. However, this distance from the top to the bottom precipitates in the APT reconstruction was measured to be 765 nm, while it was measured to be only 361 nm in the TEM image. This gives a ratio of 0.47, which when applied to the bands yields a spacing of approximately 5 nm. The expected slip system in aluminum at low temperatures is (111) plane with a ½[110] burgers vector. Using this burgers vector and the 5 nm dislocation spacing as measured with the combination of TEM and LEAP inputs into the dislocation model of low angle grain boundaries [167],

\[ \sin \left( \frac{\theta}{2} \right) = \frac{b}{2d} \]

where \( \theta \) is the disorientation angle, \( d \) is the dislocation spacing and \( b \) is the burgers vector of the dislocations, gives a misorientation of 3.0 degrees. This is 0.2 degrees off of the angle measured with NanoMEGAS, which is well within the 0.5 degree accuracy of that method.

The concentration of Ga in the low angle grain boundary shown edge-on in Figure 44 is approximately 3%, calculated with a concentration profile across the boundary. For...
comparison, a 25° high angle grain boundary, shown in Figure 47, has approximately a 5% Ga concentration in the grain boundary as shown in Figure 48b.

Figure 47: a) Ga atoms segregated to dislocations, grain boundary and a precipitate. B) Mg atoms depleted in grain boundary and enriched in precipitate. C) 0.5% Ga isosurfaces (blue) showing dislocations, grain boundary and 15% Mg precipitate on grain boundary.
This boundary, however, does not exhibit the variations in Ga concentration within the grain boundary observed in the low angle grain boundary, which may also account for the overall increased Ga concentration in this grain boundary, as the concentration profile across the low angle grain boundary averages the higher gallium concentration in the dislocations and the lower concentration between them. Figure 4 also contains a second feature of interest, in that Ga is concentrated in three one-dimensional clusters. This shows that Ga will diffuse down individual dislocations, not just dislocations in a low angle grain boundary.
The precipitates shown in Figures Figure 45, Figure 47 and Figure 49 are all Mg rich, however all precipitates in Figure 45 and Figure 47 contain Ga while the precipitate in Figure 49 does not. The precipitates in the Figure 45 and Figure 47 range from 10% to 25% Mg, 30 to 60% Ga and the balance is aluminum with no Cu admixture. Figure 46d, e show a proximity histogram and a concentration profile across the precipitate indicated in Figure 45b, revealing that the Mg concentration begins to drop before Ga concentration, which suggests that a layer of Ga has formed at the matrix-precipitate interface. This observation is strengthened by Figure 48a, which shows concentration profiles across the precipitate shown in Figure 47. This concentration profile shows far more distinct extension in the Ga concentration beyond the edges of the Mg rich precipitate. The precipitate in Figure 49 contains approximately 70 at% Mg and 23 at% Si in its center, with the balance 5.5 at% Al and 1.5 at% Cu, as shown in Figure 50. This chemistry is consistent with the expected Mg$_2$Si precipitates, which have been reported to contain Cu when it is present in the alloy[168-170].
TRIM calculations reveal that 30 KeV ions from the FIB-SEM can penetrate to approximately 24 nm (skewness = 0.4480, straggle = 9 nm, kurtosis = 3.0495) in Al [171], however to reach some of the precipitates the Ga ions would have had to travel over 600 nm from tip of the specimen during the annular milling, approximately 70 nm laterally from the closest free surface, or the Ga diffused to the precipitates. The high Ga content of the precipitates indicates that diffusion is involved, although that by itself does not mean that either of the first two mechanisms are not active. Figure 45c and d, however, show that below approximately 150 nm from the tip in reconstruction, or approximately 75 nm from the tip in the TEM image, the specimen contains little Ga in the regions away from the grain boundary and edge, which indicates that the Ga is diffusing into the sample along the grain boundary in this region.
The remaining question is whether the Ga was implanted and diffused to the boundaries and precipitates, or instead diffused from the surface layer of Ga along the boundaries to the precipitates. The specimens in Figure 51a, b were prepared from the same liftout, using the same milling procedure and aged for different amounts of time at the ambient temperature of 22°C of the microscopy facility. The specimen in Figure 51a, aged for 20 hours, clearly shows that little Ga has diffused into the specimen, concentrated at a Mg rich precipitate in the upper right edge of the field of view. Figure 51b, aged 89 hours, clearly shows gallium diffusing along dislocations from the edge of the dataset. Similarly, specimen depicted in Figure 49 was prepared in parallel with the samples depicted in Figure 45 and Figure 47 and contains both Ga contamination along the grain boundary and no Ga contamination in the Mg rich precipitate. While it is possible that the Si content of this precipitate makes it resistant to absorbing Ga, the interphase with the aluminum matrix should still be a Ga sink, forming a Ga layer such as those shown in Figure 46e and Figure 48a, as Ga is known to diffuse along aluminum-
aluminum grain boundaries which likely have a lower energy than an aluminum-precipitate interphase. This confirms that diffusion paths such as dislocation are required to transport the Ga to the precipitates, rather than it being implanted throughout the sample and diffusing to the precipitates. Figure 52 depicts a schematic of the proposed mechanism for precipitation at a low angle boundary. The first stage illustrates the general low angle boundary before heating. As heat is applied (stages 2-5) the Mg atoms begin to migrate toward the dislocations (stage 2) and eventually the centers of the dislocations (stage 3) constructing the LAGB. At stage 4 we have Mg flowing through the pathways of the dislocations toward the free space between dislocations where finally at stage 5 the precipitate begins to form.

Figure 52: Cartoon depiction of proposed LAGB precipitation mechanism. (1) Sample in the as received condition. (2) Upon heating migration of Mg atoms toward the LAGB. (3) Migration of Mg toward the cores of the dislocations. (4) Segregation along the dislocation via pipe diffusion towards either end of the dislocations. (5) Agglomeration of Mg at free space at either end of dislocations constructing LAGB eventually forming precipitates.
The logical conclusion of the band structure in the grain boundaries in Figure 45 and Figure 49 and the one-dimensional Ga concentrations in Figure 45 and Figure 47 is that these are Ga concentrations at dislocations, which offer diffusion paths to the precipitates. This conclusion is based upon the spacing of the bands, which matches well with the expected dislocation spacing in the specimen in which the disorientation is known, the high Ga content of the precipitates connected to grain boundaries and the Ga free nature of the precipitate which is not connected to a grain boundary or one dimensional Ga concentration. These precipitates act as Ga sinks when located on a grain boundary or dislocation, absorbing large amounts of Ga which was deposited near the surface during the annular milling and cleaning steps.

The Ga content can be used as a tracer to identify grain boundaries and dislocations which are thought to serve as conduits for Mg during sensitization. Both the high and low angle grain boundaries in the sample have a concentration of 1.5 at% Mg, which is substantially depleted compared to the 5 at% bulk content of the alloy, however unlike the Ga content, the Mg is concentrated uniformly in the dislocations; this is expected, as much of the Mg already diffused to the precipitates during sensitization. The importance of this is that the Ga segregation is not driven by Mg rich areas, rather the Ga is following the high diffusion pathways as the Mg did during sensitization, clustering at the same sink locations. Therefore, areas where precipitation occurred prior to straining and sensitization, such as the Mg$_2$Si particle in Figure 49, do not contain Ga. Expanding on this Ga is strongly located in the dislocations and grain boundaries and because of this it is most likely the path which the Mg traveled to form the β phase.
As a note for future aluminum APT studies it is clear that the high gallium content of these precipitates also possess a significant challenge to efforts to clean FIB Ga from Al samples using ion milling [21], as the Ga is clearly entering into the precipitates and not merely forming a film at the precipitate-matrix interface, significantly changing the precipitate chemistry and, presumably, its structure as well. The Ga may react with the Mg rich β phase to form other phases such as Mg$_2$Ga, Mg$_2$Ga$_2$ or Mg$_2$Ga$_5$, all of which are reportedly stable at room temperature [172], which may chemically bind it in the precipitate, and will have catastrophic consequences to any attempt to study the crystal structure of a β phase precipitate on a grain boundary or in a dislocation network that has been prepared using a Ga ion beam.

8.5 Conclusions

In summary, both low angle and high angle grain boundaries showed depletion of Mg to 1.5 at% in sensitized 5456. The LEAP experiments conducted clearly show that in sufficiently low angle boundaries the Ga concentrates around individual dislocations. Dislocations, both in the low angle grain boundary and separate from it, provided pathways for accelerated transport of solute atoms to the sinks into the specimen from the surface. This pipe diffusion was visualized using the penetration of the Ga into the sample, the areas around which are depleted of Mg in the low angle grain boundary, which diffused from the implanted region at the surface of the sample to precipitates at least 70 nm below the nearest free surface, highlighting these structures for analysis in the APT reconstruction. Precipitates connected by a GB or dislocation network contained Ga while precipitates formed from the melt, despite high levels of Mg, did not, thus
showing that a high diffusivity path is required to allow pipe diffusion or grain boundary diffusion of the Ga through the Al matrix.

These properties pose issues in use of Ga FIB-SEM instruments in the preparation of TEM and LEAP specimens of aluminum; while they present an opportunity to study the diffusion paths available to Mg during sensitization, the amount of Ga present in the precipitates both distorts the chemical analysis and likely changes the precipitates crystal structure as well.
Chapter 9: Observation of β phase remediation during in situ TEM heating experiments and its bulk scale impact on corrosion resistance.

9.1 Abstract

It is well known that the 5xxx series alloys have been plagued by the deleterious effects of secondary β phase precipitation due to elevated temperatures. When exposed to harsh environments in many cases material failure due to cracking is inevitable. Some attempts have been made to reverse the localized precipitation by heating close to the solvus temperature and thus, dissolving the precipitation back into solution. This has proven to lower the overall degree of sensitization but there is a major lack of information regarding, confirmation of dissolution of precipitation as well as the direct effect of elevated temperatures on the microstructure of the material in terms of dislocation recovery. In an attempt to better understand the stability ranges of sensitization AA5456-H116 was examined to directly visualize the remediation process during in situ TEM experiments. Bulk ex-situ remediation was also conducted to understand the changes to dislocation density at various stages of remediation. As a result the stability of the beta phase precipitation has been shown to be higher than previously thought and even at moderate temperatures recovery of the dislocations can occur.

9.2 Introduction

It is generally agreed upon that stress corrosion cracking has plagued the 5xxx series aluminum magnesium alloy system for a number of years. When these materials are subjected to mildly elevated temperatures a process known as sensitization can occur[4, 7, 28]. Here Mg within the alloy segregates toward the grain boundaries and
precipitates at the grain boundaries as $\text{Al}_3\text{Mg}_2$ or $\beta$ phase. The amount of Mg and dislocations can both increase the rate at which the Mg reaches the boundaries. The downside to this process is that once exposed to harsh environments, preferential corrosion of the $\beta$ precipitates can occur, as they are anodic to the matrix. Typically these materials are used in structural components[47] which are under high levels of stress which in turn leads to stress corrosion cracking[38, 53, 154, 173]. Here, corrosion of the $\beta$ phase occurs leaving small pits along the grain boundary network, as the material is stressed these pits connect and lead to larger crack formation. In an attempt to combat this process from occurring post sensitization treatments have been completed to reverse the localized corrosion from the grain boundaries. According to the phase diagram the solvus of Mg at 5wt %, an approximate concentration in the widely used 5083 and 5456[20], is $\sim 280^\circ\text{C}$. By heating the material to this temperature it, in theory, is possible to dissolve the secondary $\beta$ phase precipitates and redistribute the Mg back into solution.

Although it has been shown that remediation can lower the overall DoS[18], it does appear that the mechanical properties can diminish due to exposure to the required remediation temperature which could be caused by dislocation recovery[89]. The dislocations play a significant role in the 5xxx series alloy system along with the Mg additions. While the solute solution hardening benefits from the Mg are helpful the major benefit of Mg is the ability to increase aluminum’s potential to work harden[23]. Significant strength increases are accomplished by use of the H116 treatment which entails a cold rolling reduction of 1/8 to 1/4 of the maximum possible hardness[20, 24]. As shown in previous work these strength increases come at a cost with increased levels of dislocations potentially leading to a higher density of $\beta$ phase precipitates[151].
While the concept is still new some attempts in the literature have been made to combat sensitization by remediation. In most cases the samples which have undergone sensitization are heated to a temperature above the solidus of Mg in Al (~280°C) thus allowing Mg to go back into solution. Chen and Lai[89] found that annealing AA5456-H116 at 250°C resulted in material which was comparable to un-sensitized material with only a slight decrease in material hardness. Kramer et al.[18] developed a thermal process to locally reverse sensitization using a heated steel plate. The process exposed sensitized material to temperatures ranging from 240-280°C for up to 10min which reversed the sensitization but did not adversely affect mechanical properties. It should be noted that after de-sensitization the material did re-sensitize when exposed to elevated temperatures showing the results were not permanent. Macke exposed AA5456-H116 to a wide range of sensitization treatments (80°C-175°C) for extended periods of time (250-1000hrs) and found that longer sensitization treatments lead to lower strength and ductility. A thermal stabilization treatment of 280°C allowed for improved mechanical properties as well as resolution of Mg from the GBs. It was concluded that the higher the degree of sensitization led to increased cracking supporting the idea that beta phase precipitates are the primary cause of environmental assisted cracking in 5xxx aluminum.

While these studies do show the potential for reversing the localized corrosion there is no direct evidence showing if removal of β phase has actually occurred or what time/temperature regime is necessary. While lowering of the mass loss values is a positive it does not mean that the material is back at its original condition and remediation may only delay the inevitable. Also it has been shown in other works[151, 174] that varying dislocation densities can have a dramatic effect on sensitization, and
since the H116 treatment has been shown to vary wildly a catch all remediation treatment appears challenging. In an attempt to better understand the remediation process in situ cyclic annealing experiments will be conducted to see what effect the given treatments have on precipitation. Cyclic annealing treatments will be applied to bulk 5456-H116 material to see the NAMLT response to remediation. Finally, the remediation regime temperatures of fully recrystallized 5456-H116 gathered though in situ heating TEM experiments will be compared to the initial 5456-H116 material to observe if a singular thermal treatment is possible.

9.3 Experimental Techniques

9.3.1 In situ remediation treatments

Aluminum alloy 5456-H116 material was acquired from Alcoa (Alcoa Center, Pa) for this study. The 1/4inch plate was cut in the transverse plane looking down the longitudinal direction yielding rectangular coupons with dimensions of 1.25 cm x 0.15 cm x 0.635 cm. The coupon was then evenly ground on both sides with, 400, 600, and 800 SiC grinding papers. When a final thickness of ~50µm was achieved TEM samples were cut out of the foil using a Gatan 3mm disk punch. Samples were then ion milled to final electron transparency, via a Fischione 1010 ion mill with a milling angle of 12° and 5kV energy. In situ TEM heating experiments were conducted on a JEOL 2100 LaB₆ with a Gatan heating stage. Samples were heated from room temperature to 300°C and held for 5 minutes at a ramp rate of 0.5°C per second. After the 5 minute hold the holder temperature was increased to 400°C held for 1 minute and brought back to room temperature. Finally the sample was reheated from room temperature to 300°C to repeat
the sensitization process. Video and images of the experiments were recorded in situ using a Gatan Orius 832 fiber optic 10.7 megapixel ccd detector.

9.3.2 Corrosion Testing

Thermally treated G67 samples from the as received 5456-H116 plate were prepared for corrosion testing. The approach highlighted here was implemented to test the corrosion response of the material at different stages of the sensitization process, particularly after remediation. Samples were cut into 6mm x 50mm x 6.35mm bars and were thermally processed to understand the degree of sensitization (DOS) throughout the entire precipitation life cycle. A minimum of 2 two samples was made for each planned thermal treatment to assure accuracy of results. A complete processing schedule is located in the appendix of this work, but a typical heating cycle for the 5456-H116 material is shown in the table below:

<table>
<thead>
<tr>
<th>Sample id</th>
<th>Treatment Step</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Treatment Step</td>
</tr>
<tr>
<td>21</td>
<td>3 days 150°C</td>
</tr>
<tr>
<td>5-1</td>
<td>3 days 150°C 425°C 1 hr</td>
</tr>
<tr>
<td>EF1</td>
<td>3 days 150°C 425°C 1 hr 3 days 150°C</td>
</tr>
</tbody>
</table>

Table 1: Example of thermal treatment applied to G67 samples

Depending on the treatment schedule samples would undergo one, or a combination of the following thermal treatments: 1) sensitization treatment at either high
or low temperatures or both, 2) remediation at high temperatures to remove any precipitation and, 3) re-sensitization treatment to attempt to re-grow precipitates. For example, sample 21 from the above table was only treated with the sensitization treatment of 3 days at 150°C but sample EF1 was treated with the sensitization treatment of 150°C for 3 days, plus remediation at 425°C for 1hr and then an additional re-sensitization treatment of 150°C for 3 days. This approach yielded samples from each stage of precipitate life cycle. All samples which received the same given thermal treatment were annealed at the same time to assure consistent temperatures. Samples not requiring any further treatments were stored for later G67 testing. After all heat treatments were applied nitric acid mass loss testing (NAMLT) was conducted according to the ASTM G67 standard. As a comparison failed in service 5456-H116 material was also processed with a remediation procedure and G67 testing was completed. Finally, in order to better visualize the resulting remediation, TEM samples were made from the G67 samples to observe any β phase precipitation at the Grain boundaries.

9.4 Results

9.4.1 Cyclic annealing

In situ cyclic annealing TEM experiments were conducted on 5456-H116 material to establish temperature regimes required for remediation and the results of which are shown in Figure 53. Figure 53 exhibits the progression of an in situ experiment where AA5456-H116 was heated from room temperature to 300°C to form β precipitates (a), quenched to room temperature, heated to dissolved newly formed precipitates at 400°C (b), quenched again, and re-heated to attempt to grow new precipitates at the same GB(c).
The resulting precipitation is highlighted by white arrows and was taken from the exact same location along the grain boundary. The initial image, Figure 53 a, shows three precipitates which were grown due to the initial sensitization treatment. The sample was quenched after the initial precipitates were grown and reheated to 400°C to see the temperature required to dissolve the β phase, shown in Figure 53 b. The precipitate was stable until ~395°C when it began to dissolve and was completely dissolved at 400°C. The sample was then quench again and reheated to 300°C to regrow precipitates at the same boundary. This time upon sensitization only a singular precipitate was found along the boundary depicted in Figure 53 c.

Concurrent ex situ bulk remediation was also completed on the same material as well as failed in service material to observe the corrosion response to remediation treatment. Bulk ASTM NAMLT tests were completed on samples of various compounding heat treatments and the key results are given and discussed in the tables below.
Table 7: NAML T of 5456-H116 material sensitized at 150°C for 3 days and remediated

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Mass loss (mg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>150°C 3 days</td>
<td></td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>5</td>
<td>150°C 3 days</td>
<td>425°C 1hr</td>
<td></td>
<td>1.33</td>
</tr>
<tr>
<td>EF1</td>
<td>150°C 3 days</td>
<td>425°C 1hr</td>
<td>150°C 3 days</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>150°C 3 days</td>
<td></td>
<td>300°C 1hr</td>
<td>1.36</td>
</tr>
<tr>
<td>6</td>
<td>150°C 3 days</td>
<td></td>
<td>300°C 3 days</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 1 shows the results of 5456-H116 material sensitized at 150°C for 3 days and remediated at 425°C for 1 hour, 300°C for 1 hour, and 300°C for 3 days. Both the 300°C and 400°C for 1 hour remediation treatments were able to reduce the mass loss of the 150°C for 3 day treatment from 37 mg/cm² to a low 1.3 mg/cm². However, when the sample was held at the remediation temperature of 300°C for a longer period of time, in this case 3 days, the mass loss was found to be 20 mg/cm² a value which would deem the material unusable according to ASTM B928[20]. Remediation of a higher temperature sensitization was attempted with results found in Table 8. The alloy was sensitized at 250°C for 3 days yielding a moderate NAML T value of 44 mg/cm². Again as in the 150°C example the remediation treatment of 425°C was successful at lowering the NAML T to 1.3 mg/cm². When the material was re sensitized after the remediation for an additional 3 days at 250°C (sample id 9 in Table 8) the sample did not achieve the
same level of sensitization as it did prior. When an additional treatment of 150°C for 3 days was applied the resulting NAMLT value dropped slightly from 11.4 to 8mg/cm². This value can be considered null change as it fits well within the deviation of the mass lost testing according to ASTM 67[55]. What is significant on the other hand is when the material is sensitized at 300° for 3 days (as in sample DD1) rather than 250°C and then the 150°C for 3 days treatment is applied as well. Here, the resulting NAMLT value is 47.96 signifying that the 300°C treatment aided in a significant increase compared to the 250° in sample ID# 10.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>mg/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>250°C 3 days</td>
<td></td>
<td></td>
<td></td>
<td>44</td>
</tr>
<tr>
<td>8</td>
<td>250°C 3 days</td>
<td>425°C 1hr</td>
<td></td>
<td></td>
<td>1.3</td>
</tr>
<tr>
<td>9</td>
<td>250°C 3 days</td>
<td>425°C 1hr</td>
<td>250°C 3 days</td>
<td></td>
<td>11.4</td>
</tr>
<tr>
<td>10</td>
<td>250°C 3 days</td>
<td>425°C 1hr</td>
<td>250°C 3 days</td>
<td>150°C 3 days</td>
<td>8</td>
</tr>
<tr>
<td>DD1</td>
<td>300°C 3 days</td>
<td>425°C 1hr</td>
<td>300°C 3 Days</td>
<td>150°C 3 Days</td>
<td>47.96</td>
</tr>
<tr>
<td>BC</td>
<td>300°C 3 days</td>
<td>425°C 1hr</td>
<td>300°C 3 Days</td>
<td></td>
<td>1.75</td>
</tr>
</tbody>
</table>

Table 8: NAMLT of 5456-H116 material sensitized at 250°C for 3 days and remediated

The most accurate form of sensitization is found in samples which have experienced in service conditions and failed due to cracking. In order to see if remediation would work on this type of material, exhibiting an extreme level of
sensitization, samples of failed in service material were made and remediated at 425°C for 1 hour and re-sensitized at 300°C for 3 days. The resulting mass loss for each stage of the process are shown below.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sample ID</th>
<th>NAMALT value (mg/cm²)</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>In service</td>
<td>AA</td>
<td>67.65</td>
<td>As received</td>
</tr>
<tr>
<td>In service</td>
<td>AB</td>
<td>1.17</td>
<td>1 hr, 425°C</td>
</tr>
<tr>
<td>In service</td>
<td>AC</td>
<td>1.61</td>
<td>1 hr, 425°C; 3 days 300C</td>
</tr>
</tbody>
</table>

*Table 9: NAMLT of in service remediated material*

In order to assure that the remediation had removed the sensitization from the grain boundaries post G67 TEM samples were examined and shown in Figure 54. The material in the images is the sample labeled AC in Table 9 which had been sensitized naturally in service, remediated at 425°C for 1 hour, and re sensitized at 300°C for 3 days. From the images a-d in Figure 54 it is clear that precipitation still exist despite the high temperature treatments and low NAMALT values. The EDS located on the right side of Figure 54 show that the predicates are Mg rich and take on the same morphology as those found in our previous work[121, 151, 175].
Figure 54: (a-d) Post G67 Precipitate stability showing sensitized in service material after remediation treatment of 425°C for 1 hour and additional sensitization of 300°C for 3 days (sample name AC1) and (Right) Spot EDS scans of the resulting β precipitates at the boundaries with elevated Mg compared to the matrix.

The effect of remediation on dislocation density post G67 EBSD was completed in figure.

Figure 55: (Left) Plot of kernel average misorientation versus degree of sensitization. (a and b) KAM of 3-1 which was sensitized for 3 days at 250°C. A) IPF showing elongated grains B) KAM shows high strain present in the sample. Degree of sensitization is 44.11. c) IPF and d) KAM of 8-1 which was sensitized for 3 days at 250°C and remediated for 1 hour at 425°C. c) IPF show equiaxed grains while d) KAM show low to moderate strain present in the sample. Degree of sensitization is 1.38.
As a final comparison fully recrystallized 5456-H116 material was used to compare the precipitate stability regimes to the original 5456-H116 used in the above cyclic annealing in situ and bulk experiments. The results are shown in figure below. As shown in figure a some preexisting β’ phase was found and used as a starting location as done in previous studies[121, 151]. In figure the sample has already been heated to 275°C and the β’ has begun to dissolve pointed out by the red arrow. The white arrows in image a show the start of the β equilibrium phase which has started to grow at 275°C. As the temperature was increased to 300°C the new β equilibrium precipitates continue to grow and coarsen (Figure 56 b and c). During the standard 5 minute hold the β equilibrium phases began to dissolve and an additional 2 minutes was added until the dissolution stopped. As a result the precipitate at the lower section dissolved away leaving only the top precipitate pointed out by the white arrow(Figure 56 d). Once the dissolution appeared to stop the temperature was increased towards 325°C. Here the precipitate continued to dissolve away until complete dissolution occurred (Figure 56 e and f).
That fully recrystallized material is just as bad as adding too many dislocations. Some materials may undergo remediation and dislocation recovery may cause sensitization to occur faster than it did previously. But more work need to go into comparing this.

<table>
<thead>
<tr>
<th>In situ TEM temperature regimes</th>
<th>Partial recrystallized (DSD studies 1 and 2)</th>
<th>Fully recrystallized</th>
<th>In service material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolution of β'</td>
<td>275°C</td>
<td>240°C-275°C</td>
<td>275°C-300°C</td>
</tr>
<tr>
<td>Growth of β eq</td>
<td>295-305°C</td>
<td>250-260°C</td>
<td>300°C</td>
</tr>
<tr>
<td>Dissolution of β eq</td>
<td>400°C</td>
<td>325°C</td>
<td>375°C</td>
</tr>
</tbody>
</table>

Table 10: Comparison between previous in situ temperature regimes and fully recrystallized sample.

9.5 Discussion

The in situ TEM cyclic heating experiments were successful at finding the stability and temperature ranges required to remove precipitation from the grain boundaries. The high temperature grown β equilibrium phase was stable during the in situ
experiments from 300°C to 395°C with very little if any change in size during the
temperature ramping to 400°C. Once the sample reached 400°C the precipitates at the
grain boundary dissolved almost instantly. The interesting observation is that once the
material was reheated to 300°C precipitation grew back on the same boundary but with a
much lower number density. One factor that may control this is that the temperature
required to remove the initial precipitation was higher than half the melting temperature
of the material. At these high temperatures recovery is most certainly possible which has
been shown by other works using similar material[89]. If recovery of the dislocation can
occur does happen then it would lead to less nucleation sites and less pathways for Mg to
segregate back to the grain boundary as suggested previously[8, 151].

In order to observe the response of remediation and its impact on corrosion
resistance, cyclic annealing experiments were completed and tested according to ASTM
G67 standards. The results show some strange swings in mass loss value depending on
the type of remediation treatment used. Samples sensitized at 150°C for 3 days had a
moderately high mass loss of 37mg/cm² which is over the 15 mg/cm² necessary to be
considered sensitized according to ASTM B928 [20]. Both remediation treatments of
300°C for 1hr and 425°C for 1 hr were able to lower the mass loss to 1.36 and 1.33
mg/cm² respectfully. A strange result occurred when the samples were held at 300°C for
an extended period of time shown by sample 6 in table 7. When the sample was exposed
to the successful remediation temperature of 300°C for 3 days rather than 1hr, the mass
loss actually increased from 1.36mg/cm² to 20 mg/cm². What appears to be happening
here is that there is a transition occurring between the resulting precipitation of the 150°C
for 3 day sensitization and the 300°C for 3 days. According to previous in situ work[121,
a transition between $\beta'$ and $\beta$ equilibrium was found to occur around 300°C. What is most likely occurring is that the 300°C for 1 hour is high enough to remove the $\beta'$ precipitation from the boundaries, but if left too long at that temperature the $\beta$ equilibrium begins to grow. This assumption is reasonable given that the process will occur much faster in situ due to the thin sample versus a bulk furnace annealed sample. A similar phenomenon is shown in the results of Table 8 where a higher initial sensitization of 250°C for 3 days is attempted. Here the 250°C for 3 days yielded a very high 44 mg/cm² which is a remediation temperature suggested by other studies[89] to remove precipitation from the boundaries. When the 425°C for 1hr is applied to the 250°C sensitization treatment it does lower the mass loss value as shown in table 8. When the material is resensitized as in sample 9 in table 8 there is a clear drop in mass loss compared to the initial sensitization. This again is most likely attributed to recovery occurring within the material at the 425°C treatment. Similarly to the findings at 150°C the 250°C treatments also exhibited some strange occurrences at the 300°C mark specifically in sample DD1 in table 8. Sample DD1 was sensitized at 300°C for 3 days, remediated at 425°C, and resensitized at 300°C for 3 days, and again at 150°C for 3 days yielding a high mass loss of 47.96 mg/cm². Sample 10 was given a similar treatment but replacing the 300°C with 250°C and only yielded a mass loss of 8 mg/cm². When looking at sample BC in table 8 the treatment of 300°C for 3 days, remediation at 425°C and re-sensitization at 300°C gave a value of only 1.75 which is much lower than expected. Again 150°C treatment alone yielded a mass loss of 37 mg/cm² but when the treatment was accompanied by the 300°C for 3 days the resulting mass loss was much higher. So what this suggests is that if a material is remediated at 300°C it may potentially lead to
higher mass loss upon re-exposure to elevated temperatures. These results show the choice of remediation temperature is not as straightforward as originally thought. In the case of this material the lower range remediation temperature of 250°C is not enough to lower the mass loss value and while the 300°C remediation does lower the mass loss value it can lead to higher sensitization levels that possible prior to remediation.

The next section of this work focused on failed in service material to see if remediation was possible on the most accurate form of sensitization possible. Mass loss tests were completed on the in service material which gave an incredibly high value of 67.65 mg/cm². A remediation of 425°C was completed and lowered the mass loss value back to 1.17 mg/cm². A treatment of 1 hour at 425°C and a re-sensitization at 300°C for 3 days was also applied but yielded 1.61 mg/cm² suggesting that no new sensitization occurred. Taking this one step further sample AC was observed in the TEM which showed major signs of sensitization despite the low mass loss value. As shown in figure 54 sample AC exhibited precipitation along the boundaries consistent with previous studies [121, 151] as well as precipitation near intermetallics. Spot EDS was completed on these precipitates showing an enrichment of Mg in comparison to the matrix. What this shows is that despite having a low mass loss value it is possible to still have a large amount of Mg at the boundaries. Due to the high temperatures used to sensitize this sample it follows that this precipitate is the equilibrium β phase as shown in our previous work on this same material[175].

EBSD was taken of all ASTM g67 samples and kernel average misorientation (KAM) measurements were compared for all samples shown in the plot in figure 55. Overall samples exhibiting a higher KAM exhibit a higher mass loss value. Effectively
as shown by other work[151] increases in the amount of strain aids in the sensitization process, which again is seen in the figure 55 plot for most samples. Now comparing the effect of remediation on the amount of strain present is exhibited by the EBSD scans on the right of figure 55. The top scan shows sample 3-1 which has a very high mass loss (DoS) or 40 mg/cm² and also has a high KAM value. When this sample is remediated shown by sample 8-1 the mass loss drops but so does the KAM value. The KAM value drops to a more moderate level and the grains also become more equiaxed in the process signifying a lowering of mechanical properties. Sample 1-2 was sensitized for 3 days at 100°C and even with a remediation treatment of 300°C for 1 hour the KAM value fell. Generally speaking since this material gains the majority of its strength though strain hardening[23] any time strain values drop, the strength benefits will degrade as well. For this material at least, lower remediation treatments of 250°C only lead to more sensitization so it is clear that there is a small window for both remediation to occur and retention of the mechanical properties.

An example of how small this window is can be shown in figure 56 exhibiting a cyclic annealing experiment conducted on fully recrystallized 5456-H116. As the sample is heated preexisting β’ precipitation is present shown by the red arrow in figure 56a. At 275°C new β equilibrium precipitates begin to grow shown by the white arrows. As the temperature progresses the β’ (red arrow) dissolves and the β equilibrium continues to grow once the heat treatment achieves the hold at 300°C some of the newly formed β equilibrium phase begins to dissolve (d). Upon continued heating to 315°C the β equilibrium phase is completely gone. A comparison between the temperature regimes observed in this experiment and previous in situ experiments are shown in table 10. The
stark difference between the stability ranges of the recrystallized material and the previously used partially recrystallized and in service material is evident. Due to the fully recrystallized nature of the material, the lack of dislocations and subgrains can be attributed to the speed at which this materials sensitizes. Effectively there is nothing to stop the Mg from reaching the grain boundaries and thus the precipitation at lower temperatures. The comparison between these samples signifies the extreme difficulty of remediation. There does not appear to be a solitary remediation temperature and that depending on the material a given temperature may remove sensitization or actually lead to further sensitize the material. The only way remediation could be feasible is if the particular application uses material with the same levels of strain, and microstructure, which given the nature of the H116 treatment is highly unlikely.

9.6 Conclusions

In situ cyclic heating has confirmed that remediation can remove sensitization from the grain boundaries but it can also grow back after re exposure to elevated temperatures. The temperature regimes found during the in situ treatments however, are much higher than previously reported. Bulk ex situ remediation trials show that the NAMALT values do decrease with temperatures over 300°C. The remediation time has been shown to be a key factor as well as when held at the remediation temperature of 300°C for 3 days the material NAMLT value increased to 20mg/cm². The reason for this was described to be the crossover between the β’ and β equilibrium phase. This was confirmed by two cases were extended exposure at 300°C lead to increased sensitization levels.
It was found that despite a lowering of the NAMLT values that Mg rich precipitates were still stable at the GB despite temperature remediation treatments above the solvus of 280°C. These results suggest that even aggressive remediation treatments by not be able to full heal the material after extreme sensitization levels have been achieved. Also while a very high temperature remediation can act as a “catch-all” the reduction of dislocation density is a major drawback, signifying a necessary compromise between mechanical properties or reduction of potential crack formation.

Finally, it has been suggested by this work that even moderate sensitization treatments may fail as well depending on the particular starting material. As exhibited by the fully recrystallized sample which still fits within the H116 classification sensitized at much lower temperatures than the in service or 5456-H116 material. A comparison was made expressing that if a low temperature remediation of 280°C was applied to the fully recrystallized material the NAMLT may actually increase. What this shows is that every piece of material used in the application would have to be characterized as there is a thin line between remediation and sensitization.
Chapter 10: Mg Segregation in 5xxx Series Aluminum

10.1 Abstract

Aluminum magnesium alloys have been of recent interest due to the secondary β phase precipitation of Al₃Mg₂ at the grain boundaries which can potentially lead to material failure from stress corrosion cracking. Within the literature treatment to combat the deleterious effects of the β phase have attempted to remediate or “heal” the material. Overall some of these treatments have shown promise but there is a major lack of information regarding what occurs to the localized Mg concentrations during remediation. Accelerated in situ heating during STEM EELs experiments have been utilized to trace the Mg during the entire life cycle of the β phase precipitation process. Failed in service aluminum alloy 5456-H116 material which had cracked due to sensitization was used to act as the most accurate representation of sensitized material. The localized change in Mg was examined at various stages including: the dissolution of β’, formation of β equilibrium, remediation, and re-sensitization to see what thermal treatments were required to redistribute the solute atoms to the original intended condition. It was shown that much higher temperatures than previously reported are required to fully remediate and redistribute Mg back into solution. Bulk ex situ of high temperature treated 5456-H116 is also examined, and exhibited Mg rich precipitates at the grain boundaries after treatment of 325°C for 20 minutes which contradicts the binary phase diagram.

10.2 Background

The concept of β phase precipitation within Al-Mg alloys is well known as a negative side effect of added Mg solute[2, 6]. While the Mg supports significant
increases in the ability for the material to work harden\cite{19, 23}, when exposed to elevated temperatures the material can undergo sensitization or Mg segregation\cite{2, 4, 7, 28-30}. Due to this, the local distribution of Mg within the material is changed as Mg segregates to grain boundaries, intermetallics, and dislocations. When exposed to harsh environments the secondary precipitates can preferentially dissolve leaving pits along the grain boundary network, which when under stress can lead to stress corrosion cracking\cite{5, 14, 15, 43}. In order to combat secondary precipitation at the grain boundaries, attempts have been made to counteract the process of sensitization by increasing the temperature of the material above or around the solvus (280°C for 5% Mg\cite{25}) in order to alleviate excess Mg at the boundary. While this has been shown to reduce the overall degree of sensitization\cite{18, 89}, exposure to temperature over 225°C can have a negative impact on mechanical properties even if completed at short periods of time\cite{113}.

It has been shown extensively throughout the literature that sensitization is a thermally driven process\cite{28-30}. As the phase diagram suggests there is a positive slope of the solvus line as Mg and temperature is increased, indicating that precipitation events can occur\cite{21}. The resulting effect of thermal exposure has been studied previously in terms of measuring Mg segregation post sensitization but there is a significant lack of evidence during each stage of the process especially during remediation. Goswami et al\cite{7} observed Mg rich precipitates located on Al-Mn intermetallics using EDS line scans in samples of AA5083 which were sensitized for 10 days at 175°C. The ratio of the scan area of Al to Mg was found to be ~3:2, later concluded to be the β equilibrium phase. Work by Yi et al\cite{159} observed β phase aged at 70°C over various stages within a 30 month time period. As the time proceeded the β precipitation was found to begin as
plates and then develop into a more continuous film along the GBs. EDS line scans were taken of the long term sensitized sample (30 month) exhibiting a 150nm region containing depleted levels of Mg on either side of the GB. This diffusion distance was reported to be 50 percent of the average grain size. Unocic et al.[21] found that 5083 material sensitized for 553h at 150°C also exhibited a continuous Mg rich film along the grain boundaries. A line scan was taken across the boundary showing Mg enrichment and Al depletion at the boundary in which the Al counts were below the Mg level but the exact ratio was not reported. Despite the ratio the NAMLT of the resulting treatment was reported as 39.3 mg/cm². While the exact ratios of Al to Mg at the GB appear to vary slightly due to sample chemistry or sensitization treatment, a clear trend of Mg enrichment and Aluminum depletion is observed for the resulting β phase.

In an attempt to counteract the Mg segregation to the grain boundaries a procedure known as remediation has been used to dissolve the β phase back into solution. This process is usually completed by heating the sensitized material up to or around its solvus which for 4-5 wt% Mg is ~280°C. This process in theory desensitizes the grain boundaries and lowers the threat of further corrosion. Chen and Lai[89] attempted to reverse the sensitization of 5456-H116 alloy via a short term annealing treatment of 250°C. NAMLT testing, electrochemical measurements, and SEM were used to confirm the success of the sensitization reversal. It was found that an exposure time of 10-30 minutes at 250°C lowered the corrosion potential and did not have a negative effect on the mechanical properties. Work by Kramer et al. developed a method of heating the sensitized aluminum using a steel plate and found that specimens heated within the range of 240-280°C for as times as short as 10 minutes reverted the sensitization process. These
results were confirmed comparing a sample sensitized at 150°C for 24 hours with NAMLT ~30mg/mm² to below 5 mg/mm² after treatment of 280°C for 10 minutes. It was also shown though that upon reheating to 150°C the mass loss values did in fact revert back to the original values signifying reversal is not a permanent solution.

It is also not known if remediation actually removes the precipitation and if the local solute actually goes back into solution after the given treatments. The majority of studies attempting to apply remediation treatments tend to utilize low resolution techniques such as optical and scanning electron microscopy and rely primarily on NAMLT G67 values. While these values show the increase/decrease of corrosion it does not show if there is still localized precipitation at the GB. While remediation does lower the degree of sensitization, it does not indicate if Mg has been removed from the GBs and is fully redistributed back into solution. Another down side to these studies is that all of these observations were completed after the precipitation had occurred. There is a clear lack of information during and after the precipitation process. Due to this, the unique approach of combining in situ heating and STEM EELs was implemented to better understand the Mg segregation at the GB. By doing this it was possible to track the Mg and understand the temperatures which were required to remove the Mg from the boundary and back into solution. Ex situ bulk samples were also observed as a comparison to the in situ observations. Using this approach has helped shed light on the localized Mg changes throughout the precipitation and remediation process. The results of this study show the discrepancies of the remediation process and that removal of the Mg from the GB is more difficult than previously thought. It is vital that remediation be
understood in terms of localized Mg concentration in relation to the grain boundary if there is any hope of improving the corrosion resistance of this material system.

10.3 Methods

10.3.1 In situ cyclic annealing experiments

Aluminum alloy 5456-H116 in the form of \( \frac{1}{4} \) inch plate, from Alcoa (Alcoa center, Pa) was used for this study. Rectangular coupons were cut in the transverse direction with dimensions 1.5cm x 0.15cm x 0.635cm looking down the longitudinal (rolling) direction. Samples were ground using SiC papers to 800 grit to a final thickness of ~50µm. A Gatan disk punch was used to make 3mm TEM samples and final electron transparency was achieved via a Fishione 1010 ion mill with a milling angle of 12° and 5kV energy. In situ TEM heating experiments were conducted in a JEOL 2100 LaB\(_6\) using a Gatan heating holder. The samples were heated in a cyclic manner to first sensitize the material, dissolve it away, and attempt to regrow any precipitation. In between each stage the sample was quenched by turning off the power to the control unit to assure instantaneous heat dissipation. As a result of this approach the direct observation of the onset of precipitate dissolution was observed.

10.3.2 In situ STEM EELs treatments

Failed in service 5456-H116 material was acquired from the Naval Surface Warfare Center, Carderock division. This material was taken from an intake area of a naval ship which had cracked due to sensitization from years of exposure to heat and ocean water. TEM sample preparation was carried out in a similar manner as described above. In situ heating STEM EELs experiments were completed on a JEOL 2100F
equipped with the following: Schottky source and high-resolution pole piece with Cs = 1.0mm, IS1000XP CCE camera, and K2 Summit direct detection camera. Heating experiments were conducted using a Gatan heating stage and temperature controller. Samples were heated and held at temperature while STEM EELs maps were taken (~5 minutes), upon completion the heater current was increased to the next heating stage until the entire heating cycle was complete. Samples were examined consecutively at 200, 250, 275, 300, 325, 400, after quenching to room temperature, and upon re-heating to 300°C. Due to excessive sample drift samples were quenched after the 400°C treatment was reached and maps completed at room temperature.

10.3.3 Ex situ bulk analysis

As a comparison the same unused 5456-H116 material from the cyclic annealing experiments was used for bulk ex situ analysis. Bulk pieces were cut from the main plate with dimensions of 2.54cm x 1.27cm x 0.635cm to be annealed in a box furnace which was heated and allowed to stabilize for a minimum of 1 hour. Once the furnace temperature was stable, the sample was sensitized for 325°C for 20 minutes and quenched in water immediately after removal. TEM samples were then made following the steps above. STEM EELs maps were completed as above using a double tilt holder at room temperature. In order to observe stability of the high temperature precipitates remediation treatments were applied in addition to the 325°C sensitization which included; 375°C for 15 minutes, and 400°C for 15 minutes. Resulting samples were then examined in the TEM for any signs of GB precipitation.
The above approach was utilized to follow and understand Mg segregation throughout the entire remediation cycle. Key temperature regimes were observed such as β’ dissolution temperature (275-300°C), β equilibrium growth (300 -325°C), β dissolution temperature (400°C), which have been adapted from previous studies for this alloy. The techniques implemented in this work have allowed for in real time, highly localized solute information which has previously only been seen post sensitization. The ability to follow Mg throughout the remediation heat treatment has allowed for a much greater understanding of Mg segregation in the 5xxx series alloy system.

10.4 Results and Discussion

An example of a cyclic annealing experiment is shown in figure 1. Here the material was heated from room temperature to 300°C and held for 5 minutes. The resulting precipitation from the heat treatment is shown in figure 1 a. After the 5 minute hold the sample was then quench to room temperature and heated to 400°C to remove the precipitates from the boundary. As shown in figure 1 b this process was successful at remediating the sensitization. In an attempt to re-sensitize the material the sample was quenched again and reheated to 300°C to see if precipitation would regrow on the same boundary. As shown in figure 1 c regrowth of precipitation did occur (red bottom arrow) but not on the same boundary. There are a few key points which can be taken from this experiment in regards to Mg segregation and β phase sensitization. This first is that the precipitation is much more stable than previously thought. The precipitation dissolution did not begin until temperatures very close to 400°C were achieved and once at temperature the dissolution was rapid. Secondly when attempts were made to re-sensitize the material, no new precipitation had occurred on the boundary, but rather on a boundary
in different parts of the sample. It is clear from this work and others[18] that even after remediation sensitization can occur. This experiment shows that the sensitization does not always come back to the same location. In other words despite have the ability for the GB to sensitize it does not always do so which may be a factor of localized Mg concentration. The results of which will be shown next.

Figure 57: In situ remediation treatment showing the removal of sensitization at the GB at 400°C and the growth of precipitation at a different grain boundary.

At the beginning of the in situ STEM EELs experiments a starting location with preexisting β’ precipitation (previously confirmed in Scotto D’Antuono et al. [175]) was chosen. Out of convenience the β’ precipitation was located near a Al-Cr-Fe-Mn intermetallic which served as a good visual anchor point. The sample was first scanned at room temperature to assure Mg rich β’ precipitation and upon confirmation the material was heated to temperatures of 200, 300, 325, and 400C and stem eels scans were completed at each stage of the process. On average the temperature was held for about 2
minutes while the microscope was setup for a scan which scan times ranging from 4-5 minutes. The results of the in situ STEM EELs heating experiments are displayed in figure 1.

![Figure 58: HAADF images of in situ heated in service 5456-H116 at temperatures of 200, 300, 325 and 400°C with STEM EELs (Scan location marked with red box in HAADF image), exhibiting the aluminum (green) and magnesium (red), concentration profiles.](image)

At 200°C there was observed to be no change to Mg concentration in comparison to the initial room temperature scan. It is clear from the scan that there is a slight decrease in Al concentration at the grain boundary with a definitive increase of Mg compared to the matrix. The current of the heating controller was then increased to allow for the
temperature to increase to 300°C and another scan in the same spot was taken. It was found that the Mg had depleted in this area so a second scan closer to the intermetallic was taken. This second scan is depicted in figure 1 showing the intermetallic containing no Mg and the resulting agglomeration of Mg and again a slight depletion of Al at the top, indicated by the arrows. Effectively what has occurred is that the Mg found at 200°C flowed via grain boundary diffusion at 300°C to the top of the intermetallic and precipitated as a β equilibrium precipitate as shown in previous studies[121, 151] and compositional change agreeing with previous works[7, 21]. Following this the sample was then heated to 325°C and the precipitate was found to be stable at this temperature so a different area of the sample was observed. In the figure at 300°C a clear depiction of grain boundary enrichment of Mg is seen along with Al depletion. This result is fascinating and confirms that both enrichment and β precipitation is possible at temperatures above the solvus detailed in the binary Al-Mg phase diagram[25, 26] which has been shown in our previous studies[121, 151]. This result contradicts the understanding that remediation at 280°C, outlined by works[18, 89], removes or heals the material back to its original state. While it is agreed that the temperature range may reduce the overall degree of sensitization as we[176] and others have shown[18, 89], it in fact does not mean that the Mg has been removed from the GBs and that in fact in some cases further enrichment of Mg to the grain boundary may be occurring. Continuing, the next step was in attempt to see what temperature was required to actually remove the Mg from the GBs and back into solution. A temperature of 400°C was used, as it appeared to remove the β equilibrium precipitation in the in situ cyclic annealing experiment above. As a result once the 400°C temperature was reached Mg was found to be successfully
removed from the grain boundary. However, while the sensitization was removed from the boundary, the distribution of Mg was not homogenous. Figure 1 400°C shows a scan taken at the same boundary as the 300°C example, showing areas of high concentration agglomerations of Mg next to the grain boundary within the matrix (400°C arrows). These agglomeration next the boundary contained ~15% Mg while the boundary area reverted back to the normal 5% level of the 5456 alloy. A schematic of the Mg segregation over the range of temperatures is expressed in the figure below.

![Figure 59: Schematic of observed β phase/Mg segregation during in situ experiments](image)

In order to assure that the in situ results were accurate, ex situ bulk annealing was completed on new as received 5456-H116 plate. Samples were annealed in a box furnace at 325°C for 20 minutes and analyzed via STEM EELs for local Al and Mg concentrations. Examples of resulting precipitation are shown in images a-c. Two
different examples of high temperature precipitation is shown via HAADF images (d and g) as well as the local Al (e and h) and Mg (f and i).

Figure 60: (a-c) Bright field TEM images of bulk furnace annealed AA5456-H116 at 325°C for 20 minutes. STEM EELs results with HAADF image and Al(green) and Mg (red); (d-f) Example 1 of precipitate on intermetallic plate and Example 2 (g-i) of precipitate at triple point.

Example 1 (images d-f) shows precipitates located around a Al-Cr-Fe-Mn intermetallic (a typical location reported in the literature [7]) in an almost identical situation as presented in the in situ results. The signature depletion of aluminum and enrichment of Mg are exhibited. In the second example (g) precipitation located at a triple point was observed and shown to have similar enrichment of Mg and depletion of
Al. From this it is clear that the in situ heating experiments have shown strong agreement with real world ex situ bulk sensitization treatments. These results also confirm that Mg can be stable at temperatures 45°C higher above the solvus.

In order to further test the stability, remediation treatments were applied to the high temperature samples in an attempt to remove sensitization from the boundaries. High temperature sensitized plate was heated ex situ at an additional 375°C for 15 minutes and another sample at 400°C for 15 minutes for comparison to see the temperature necessary to remove sensitization. These results are presented in figure 3.

Figure 61: Bright field TEM images of: sample sensitized at 325°C for 20 minutes with an additional annealing of 375°C for 15 minutes (a-d) and sample sensitized at 325°C for 20 minutes with an additional annealing of 400°C for 15 minutes (e and f).

Figure 3 a-d exhibits precipitation remaining at the grain boundaries after sensitization of 325°C for 20 minutes and remediation treatment of 375°C for 15 minutes. Precipitates are observed at grain boundaries (a-c) as well as near intermetallics (d). Examples of the 325°C for 20 minutes and remediation treatment of 400°C for 15
minutes show no signs of precipitation with “clean” GBs(e) and no precipitation on or near intermetallics (f). Again agreeing with the in situ results, the bulk material required temperatures up to 400°C to fully remove the high temperature β equilibrium phase precipitation. These results contradict the idea that remediation can be completed at the solvus of 280°C suggested by the phase diagram. From both the in situ and ex situ experiments Mg enrichment was found at temperatures well above the commonly used remediation temperatures of 250-280°C. Most likely this is due to some other element in the alloy allowing for stability of Mg at the grain boundary at the high temperatures, which would require further experiments to clarify.

Despite the concept of remediation or reversal of sensitization being somewhat new there is still a major lack of information in terms of the dissolution process of β phase particles. The majority of studies rarely utilize high resolution techniques to resolve “remediated” β phase and base the concept solely on ASTM G67 values. Also typical sensitization treatments try to mimic in service conditions concentrating on low temperature sensitization rarely heating to the temperatures like that within this work. While the G67 values may decrease and have been shown to do so in previous works[18], it does not mean that the material has been brought back to its original state. This concept only strengthens the case that the metastable β’ phase leads to the most deleterious corrosion effects[35, 175]. It has been shown that there is still Mg enrichment and Mg particles at GBs at temperatures above 280°C but the resulting G67 values do not account for this. Another downside is that the high temperatures required for remediation does not bode well for maintaining mechanical properties post treatment. Works have found the onset of diminished mechanical properties can begin as low as 250°C after
In reality the only advantage of a remediation treatment is to minimize the β’ phase as much as possible to extend service life but most likely material failure will be inevitable.

10.5 Conclusions

In situ heating STEM EELs experiments allowed for the tracking of Mg throughout the remediation process. Mg was found to enrich at the GB at temperatures much higher than previously reported. When held at temperatures above the solvus, in this case 325°C, the magnesium was shown to stay within the grain boundary rather than fully diffuse back into solution. While remediation may lower the overall DoS the material is not fully reverted back to its original state.

Attempts to remove Mg from the GB were made and it was found that temperatures of 400°C were required. While the high temperature treatment did remove the Mg from the boundary agglomerations of Mg were found around the GB. These agglomerations were found to contain ~15% Mg compared to the 5% in the remediated GB. Upon reheating to 300°C the Mg redistributed evenly in the matrix with some areas of the GB containing elevated Mg. These results show that removal of Mg from the boundary after initial sensitization has occurred is much more difficult than previously thought. Also any benefit from removal of Mg from the boundary is overshadowed by the potential recovery of the material from the required temperature.

The in situ results were compared to high temperature bulk ex situ heated material and were found to be consistent. Bulk material heated to 325°C for 20 minutes exhibited the same characteristic Mg enrichment and Al depletion at the grain boundaries. This
shows that even at temperatures ~50°C higher than the solvus that Mg precipitation can still occur. It has been suggested by this work that a reexamination of the Al-Mg phase diagram is necessary and that it may be possible that some other solute atom from material production is allowing for stabilization of Mg at the boundaries.
Chapter 11: Conclusions

The approach of this work has utilized a combination of multi-scale techniques to better understand the entire life cycle of β phase precipitation. A combination of high resolution in situ TEM with complementary bulk ex situ studies has allowed for a more complete picture of sensitization in terms of boundary coverage, temperature regimes, precipitation mechanism, and microstructural effects. Direct visual evidence of the β phase precipitation has been shown for the first time allowing for growth kinetics and activation energy calculations. The wide range of temperatures used has set this work apart from others which have only focused on low temperature ranges. By extending the range of temperatures tested a clearer delineation has been made between the metastable and equilibrium β phase precipitates. The metastable phase has been shown to be not only the more prevalent form found within in service material, it has been shown that it exhibits a more corrosive potential as well. Finally an examination of the stability of β phase precipitation has been given, showing that the precipitation can exist at temperatures much higher than suggested by the phase diagram. Once Mg has segregated to the grain boundary it requires temperatures much higher than previously thought to remediate or return back into solution. This discrepancy between the results and the phase diagram can possibly be attributed to the following: a need for a re-calculation of the Al-Mg phase diagram, a better understanding of the other solute additions impact on sensitization, a more cohesive examination of the relationship between starting microstructure and β phase precipitation. A schematic presenting the entire live cycle of β phase precipitation based on this work is shown in the figure below:
As it has been shown in the previous chapters above the temperature regimes can vary greatly based on starting microstructure and dislocation levels. In general both ex situ and in situ experiments using various starting materials and confirmed though countless trials, are in excellent accordance with this diagram. These and all other findings of this work are summarized in the following:

- We have shown that initial β phase formation occurs at low angle grain boundaries, which conflicts with previous observations of β phase growth only occurring on high angle grain boundaries. Low angle boundaries are susceptible to sensitization. Also, it has been shown that the β’ phase does not transform into β; rather, the β forms on its own after the β’ has begun to dissolve which agrees with what has previously been suggested. The primary nucleation sites observed during in situ experiments are intergranular defects and low angle subgrain boundaries. In many instances, the β
phase formation preferred low angle rather than high angle grain boundaries. Although formation on low angle boundaries was more prevalent, precipitate growth on low angle boundaries was halted at a maximum size, most likely dependent on boundary energy, whereas precipitates on high angle boundaries shows signs of uninhibited growth. Moreover, as the misorientation angle increased, the precipitate area increased. Studies to better connect the dependence of $\beta$ phase precipitation on both boundary structure and energy are underway.

- The results show that an increase in dislocation density via cold rolling has an impact on the overall sensitization of the 5xxx series Al-Mg alloy. The size of the precipitates found samples with elevated degrees of cold rolling were very similar to those found in the H116 samples. While the size of the precipitates did not change dramatically between the rolled and H116 conditions the density of $\beta$ phase precipitates did increase, which is attributed to the increased dislocation density (heterogeneous sites). The coverage on the grain boundary was found to be drastically different in the pre-strained samples, with the rolled samples having much less space between nucleation sites compared to the H116 which showed large spans between precipitates.

- An increased rolling reduction did increase the rate of growth of $\beta$ phase. There was a difference observed in rates due to misorientation angle with high angle boundaries showing faster precipitate growth than found on lower angles. The largest impact due to the cold rolling on $\beta$ phase growth was that on the lowering of the nucleation
temperature. The rolled samples saw a much faster nucleation regime rate which occurred at lower temperatures than the H116 sample. The H116 sample took a longer time to nucleate and grew at a slower rate than rolled samples even when higher temperatures were achieved. Initial activation energies of the rolled samples were lowered due to increased dislocation density coinciding with the pipe diffusion mechanism. When higher levels of rolling reduction were used the rate did drop and the material mimicked the H116 sample. This was attributed to some material recovery during the heating process.

- Two studies were compiled within this work using two different plates of 5083-H116 focusing around comparing the effect of thermomechanical processing on corrosion resistance. This work showed that additional thermomechanical treatment in addition to the H116 temper of AA5083 can result in a material with improved corrosion resistance. A key downside observed is that due to the wide specification of the H116 treatment a singular thermomechanical treatment that may improve one lot/manufacture of material may actually lead to more corrosion in another. For instance in this work a 5% reduction with 500°C anneal in plate A performed best but in a secondary study plate B required a treatment of a 15% reduction with a 400°C anneal to achieve comparable corrosion resistance.

- A general reduction of mass loss was shown as a result of having a larger grain size which in turns reduces the grain boundary area susceptible to β phase precipitation and sensitization. However, the treatment induced recrystallization throughout the entire cross section resulting in a homogenous microstructure consisting of equiaxed
grains in plate B. Initial trials using this treatment with a different AA5083-H116 (plate A) did not experience recrystallization at the center of the plate. Ultimately, the variability in the H116 temper was shown to produce inconsistent results across different plates under the same material designation. Finally the majority of the corrosion resistance was attributed to larger grain size which while extending service life would regrettably lower mechanical properties.

- The type of precipitate within the failed in service material is that of the β’ phase, as determined using in situ TEM coupled with high resolution analysis and bulk ex situ heating. It is clear from our work that low resolution, bulk SEM, EDS or use of the phase diagram alone, is not enough to delineate between β’ or β unless perhaps a purely binary material is used.

- A new precipitate evolution of β equilibrium in AA5456-H116 has been defined. Here, the metastable β’ exists from room temperature to ~275°C where it begins to dissolve. The β’ phase continues to dissolve and eventually the stable β equilibrium phase forms around 300°C. The high temperature β equilibrium phase remains stable well above the binary phase solvus in this alloy.

- ASTM G67 testing has confirmed that the low temperature treatment yielded the highest level of mass loss. The in service material follows the same trend as the low temperature treated samples which shows that the β’ precipitate is the more corrosive form and a need for a clear delineation between β’ and β in future works is crucial.
• In summary, both low angle and high angle grain boundaries showed depletion of Mg to 1.5 at% in sensitized 5456. The LEAP experiments conducted clearly show that in sufficiently low angle boundaries the Ga concentrates around individual dislocations. Dislocations, both in the low angle grain boundary and separate from it, provided pathways for accelerated transport of solute atoms to the sinks into the specimen from the surface. This pipe diffusion was visualized using the penetration of the Ga into the sample, the areas around which are depleted of Mg in the low angle grain boundary, which diffused from the implanted region at the surface of the sample to precipitates at least 70 nm below the nearest free surface, highlighting these structures for analysis in the APT reconstruction. Precipitates connected by a GB or dislocation network contained Ga while precipitates formed from the melt, despite high levels of Mg, did not, thus showing that a high diffusivity path is required to allow pipe diffusion or grain boundary diffusion of the Ga through the Al matrix.

• These properties pose issues in use of Ga FIB-SEM instruments in the preparation of TEM and LEAP specimens of aluminum; while they present an opportunity to study the diffusion paths available to Mg during sensitization, the amount of Ga present in the precipitates both distorts the chemical analysis and likely changes the precipitates crystal structure as well.

• In situ heating STEM EELs experiments allowed for the tracking of Mg throughout the remediation process. Mg was found to enrich at the GB at temperatures much
higher than previously reported. When held at temperatures above the solvus, in this case 325°C, the magnesium was shown to stay within the grain boundary rather than fully diffuse back into solution. While remediation may lower the overall DoS the material is not fully reverted back to its original state.

- Attempts to remove Mg from the GB were made and it was found that temperatures of 400°C were required. While the high temperature treatment did remove the Mg from the boundary agglomerations of Mg were found around the GB. These agglomerations were found to contain ~15% Mg compared to the 5% in the remediated GB. Upon reheating to 300°C the Mg redistributed evenly in the matrix with some areas of the GB containing elevated Mg. These results show that removal of Mg from the boundary after initial sensitization has occurred is much more difficult than previously thought. Also any benefit from removal of Mg from the boundary is overshadowed by the potential recovery of the material from the required temperature.

- The in situ results were compared to high temperature bulk ex situ heated material and were found to be consistent. Bulk material heated to 325°C for 20 minutes exhibited the same characteristic Mg enrichment and Al depletion at the grain boundaries. This shows that even at temperatures ~50°C higher than the solvus that Mg precipitation can still occur. It has been suggested by this work that a reexamination of the Al-Mg phase diagram is necessary and that it may be possible
that some other solute atom from material production is allowing for stabilization of Mg at the boundaries.
Chapter 12: Future Work

The chapters within this thesis have helped to redefine the process of Mg segregation and β phase precipitation regimes in 5xxx series alloy. Although this work has improved the understanding of sensitization, there is still no simple solution to assure minimal corrosion within these materials. Topics such as remediation and thermomechanical treatments have been discussed as ways to mitigate corrosion, but have proven to be difficult to apply due to wide variances in the H116 treatment, and once applied act only as temporary solutions with potential to lower mechanical properties. As with most topics in materials science there is always a tradeoff and in this case it is no different, the relationship between strength and corrosion in this material appears to be a complicated one. Additions of Mg aid in the potential for significant strength increases but also tend to increase the potential for corrosion. There may be a proverbial “sweet spot” where microstructure, Mg concentration, and dislocation density meet but much more work is required to solve this problem. As a result this and other topics are outlined in the following sections.

12.1 Compositional experiments

One of the more significant findings in this work is that discrepancy of the experimental results with the binary phase diagram. Both in situ and bulk ex situ experiments showed that the β phase was stable at higher temperatures than explained by the binary phase diagram. The solvus at 5% Mg should be 280°C but on almost every experiment when exposed to 280°C or even higher Mg rich precipitates were still found at the GBs. There are a couple of potential reasons for this; 1 the binary phase diagram
may be incorrect, the other solute atoms within this material may help to stabilize the precipitation. In regards to the first reason a newer first principle calculation should be completed to re-confirm precipitate regimes. Another way this could be done is to make “cleaner” binary phase materials and test them either in or ex situ and see if it follows the phase diagram. If the binary phase material does follow the phase diagram start to add the other commonly alloyed elements, Cr, Mn, Fe, Si, and Cu to see if they have any impact on the precipitation. As a note in extremely thin samples Cu was found within the precipitates due to thin film effects. This did not appear to happen in bulk processed material so while this may be only in very thin samples it may be a good place to look. Also varying the amounts of added solute and seeing their impact sensitization would make for a very nice study.

12.1.2 Modification of composition

One of the most defeating aspects of this material is that while Mg has an incredible effect on strength and aids remarkably in the ability to work harden, it also leads to its ultimate failure in harsh environments. One suggestion would be to modify the alloy with lower amounts of Mg and add some other element in its place. Some work has gone into alloying with Sc[2], Zr[11], and other elements[177] but there is still room for improvement on the impact of each element on overall sensitization.

12.2 The impact of grain boundary plane

As discussed in this work the staring microstructure of the material can have a great impact on corrosion resistance and overall DOS values. This was clearly shown in the thermomechanical treatment section where different H116 treatments were compared. These variations were attributed primarily to the H116 treatment and the starting
microstructure controlled by that treatment. While recent work appears to be addressing the impact of grain boundary character on sensitization there is still a great deal of information missing in regards to the grain boundary plane and its influence on sensitization. One of the interesting things observed in kinetics section of this work is that GB misorientation only had an impact between low and high angle precipitation. When comparing precipitation on similar grain boundaries or same misorientation angles it was found that even though on boundary of angle $x^\circ$ may have precipitation another boundary of the same angle $x^\circ$ may have nothing. It is appears that some other factor is playing a role in sensitization and most likely that grain boundary plane. Work by Yuan[38] observed a relationship between the $\langle 112 \rangle$ and close packed $\langle 111 \rangle$ plane as a prime location for sensitization but there are not many other works on this topic. A study similar to the misorientation dependence section of this work regarding boundary plane would be very interesting, possibly comparing GB relationships and angle divergence to the precipitate coverage.

12.3 Remediation treatments

It is clear from the work in this thesis that the regimes of $\beta$ equilibrium and $\beta'$ phases are stable at much higher temperatures than previously thought. As a result of this there is a need for studies which focus on all thermal regimes not just low temperature. These studies also need to be coupled with high resolution techniques to assure that remediation is successful. The G67 NAMLT test provides a good representation of the degree of sensitization, but as show in this work, a low value does not mean the boundaries are devoid of sensitization. In order to truly understand the process of remediation an experiment coupled with high resolution TEM would be required.
Sample material could be sensitized at a given temperature range for a given time, afterwards a remediation treatment could be applied and G67 samples made for various temperature throughout the entire process of remediation. In order to confirm removal of β precipitation at the GBs simultaneous TEM examinations of the GBs could be completed until the no more β precipitation was observed. The information which could be extracted from this type of study include; a comparison of β equilibrium and β’ G67 values, the understanding of these exact temperature regimes in the given material, and the observation of kinetics involved in remediation. As discussed in this work and others, remediation even at short time scales reduces the mechanical properties of the material so it is important to know the exact temperature regime and time required to remediate the specimen to avoid as much material degradation as possible which an experiment along this lines would provide.

12.4 Early detection of sensitization

One very frustrating aspects to β phase precipitation is it is very difficult to detect until it is too late i.e. effectively when cracks form. There is a desperate need for early detection of sensitization. One way would be to estimate sensitization based on the thermal exposure of the material. A system like this may already be in place but if the exposure temperatures are known computer models could be set up to estimate the DOS for the given material and if a particular area of a ship or vehicle has been exposed to elevated temperatures, it could be replaced before failure occurs. In a way the Al-Mg materials can be treated similarly to radiation damage in steel. While this does not solve the problem and is understood to be an extremely daunting and expensive task, it would lower the risk of in service failure.
Another approach would be to find a visual cue for sensitization utilizing lower resolution techniques. Some works have attempted to use etchants[178, 179] highlighting the β phase on a macroscopic level but as shown in these works and of this thesis, many of the precipitates can only be viewed with electron microscopy techniques. Despite this fact, material which is heavily sensitized and has not cracked may be investigated using this technique potentially avoiding material failure.

12.5 Improvements to the H116 treatment

The wide range of potential starting material has led to a lot of misunderstanding of the 5xxx series alloy. It is clear that starting material even if it is deemed “H116” can be completely different from one plate to another. Due to these inconsistencies a myriad of temperature regimes have been proposed for sensitization and remediation which may all be true or equally wrong due to starting microstructure. These problems are exponentially compounded when it is considered the amount of different plates and lots required to build a naval ship. The odds of having two identical plates next to each other are slim. Even if a process was found for a given plate it may work for a few plates but for others it would reduce the mechanical properties or even cause the material to sensitize more. The H116 treatment is too broad and can include microstructures of all kinds. Work into further tighten and improve consistency of this treatment is an absolute necessity.
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Education

Drexel University
Ph.D. Materials Science and Engineering
Advisor: Mitra Taheri, Ph.D.

Undergraduate Degrees

Bachelor of Science in Materials Engineering (2010)  Drexel University
Bachelor of Science in Applied Physics (2007)  Shippensburg University

Professional Experience

Drexel University Dynamic Characterization Group  Philadelphia, PA
Graduate Fellow  June 2011 – Present
Thesis Topic: β phase precipitation in the 5xxx series aluminum magnesium alloy system via in situ TEM observations

• Redefined the understanding of precipitation process in 5xxx series aluminum alloys by interpreting results conducted via in situ TEM experiments and bulk heat treatments
• Establish theories for future material development, corrosion resistance, and industrial application by investigating previous literature and designing various experimental approaches to test hypotheses
• Improve future development of Al-Mg alloys by analyzing precipitation process data and publishing experimental results to materials based journals for the advancement of corrosion resistance
• Design experiments conducted primarily via advanced microscopy based technics such as in situ TEM and EBSD (SEM) requiring extensive sample preparation and advanced lab technics to further the understanding of the precipitation process
• Create yearly reports, communicate new findings and research status to project manager, and conduct formal presentation to secure renewal of funding
• Present research and findings at various global materials conference proceedings
Teaching Assistant / Mentor

• Manage senior design students to ensure on time delivery of results by aiding with the fabrication of samples, conducting experiments, defining project goals, and teaching various microscopy techniques
• Prepare, organize, and teach lab portions of undergraduate classes via obtaining required lab materials, experiment setup, and responsible disposal and storage of lab materials
• Grade lab reports and proctor and grade exams for various classes and labs

Undergraduate Senior Design Project - Nuclear Reactor Stainless Steels
September 2009 – June 2010

• Conducted in situ TEM straining experiments at Argonne National Laboratory to find correlation between microstructure and mechanical properties in commonly used nuclear reactor stainless steels
• Applied various characterization techniques such as EBSD to understand relationship between crack formation and grain boundary type in relation to grain boundary engineering and irradiation damage
• Responsible for formal project proposals and presentations to assure compliance with project timeline

Lyophilization Technology Incorporated
Ivyland, PA
Development Lab Technician
March to September 2009

• Formulated and researched various Active Pharmaceutical Ingredients and excipients for client projects needed in the freeze drying process to elongate product shelf life
• Inspired new tactics and ideas to guide various research projects that were dependent on the freeze drying process and client requests

Pennsylvania Department of Transportation
Harrisburg, PA
ESTI Engineering Intern
May to August 2007

• Supervised contractors to assure that work was completed properly by taking measurements and referring to Penn DOT's specifications, Roadway construction designs, and plans
• Created the audits and invoices in cdx-nextgen which paid for the contractors work and materials

Skills

• JEOL 2100 Transmission electron microscope (advanced)
• Scanning Electron Microscopy (SEM) and Electron Backscatter Orientation Imaging (EBSD/OIM)
• General Optical Microscopy
• Ion milling, Polishing, and Electro Polishing
• Metal Heat Treatments and Processing (Cold Rolling), Mechanical Testing (Tensile and Charpy impact)
Leadership
• Responsible for managing and mentoring several graduate, undergraduate, summer interns (REUs), and High school students while working in the lab and conducting research
• Head teaching assistant for metals processing lab.

Personal Interests: Bread Baking, Music/Guitar, Movies, Woodworking

Publications, Presentations, and Patents
Publications to date
• D. Scotto D’Antuono, J. Gaies, W. Golumbskie and M.L. Taheri “Grain boundary misorientation dependence of b phase precipitation in an Al–Mg alloy” Scripta Materialia 76 (2014) 81–84

Publications in submission
• D. Scotto D’Antuono, J. Gaies, W. Golumbskie and M.L. Taheri “Metastable Precipitates in 5xxx Aluminum Alloys as Predominant Failure Mechanism in Aluminum 5xxx Alloys”

Publications in progress
• M. I. Hartshorne, D. Scotto D’Antuono, G. Vetterick, C. M. Barr, M. Miller, M. L. Taheri “Atom Probe Tomography analysis of pipe diffusion in 5456 aluminum alloy”
• D. Scotto D’Antuono, D. Foley, J. Gaies, W. Golumbskie and M.L. Taheri “Observation of β phase remediation during in situ TEM heating experiments and its bulk scale impact on corrosion resistance.”
• D. Scotto D’Antuono, A. Lang, A. Leff, J. Gaies, W. Golumbskie and M.L. Taheri “Mg Segregation in 5xxx Series Aluminum”

Contributed talks
• D. Scotto D’Antuono, J. Gaies, W. Golumbskie, and M. L. Taheri, 13th International Conference on Aluminum Alloys (ICAA13), Pittsburgh, June 2012: "A Study of Stress Effects on Beta-Phase Precipitation in Al-Mg Alloys Using In-Situ TEM"
• D. Scotto D’Antuono, J. Gaies, W. Golumfskie, and M. L. Taheri, MS&T, October 2012, Pittsburgh: "A study of stress effects on beta phase precipitation in Al-Mg alloys using in-situ TEM"

• D. Scotto D’Antuono, J. Gaies, W. Golumfskie, and M. L. Taheri, Spring TMS, March 2013, San Antonio: "An Investigation of beta Phase Precipitation in Al-Mg Alloys during In-Situ TEM Heating/Straining Experiments"

• W. Golumbskie, J. Gaies, D.Scotto D’Antuono, and M. L. Taheri, TMS Annual Meeting 2013: “Influence of Stress on Sensitization in Al-Mg Alloys”

• D. Scotto D’Antuono, J. Gaies, W. Golumfskie, and M. L. Taheri, Fall MRS 2013: Fall MRS, November 2012, Boston: "A Study of beta Phase Precipitation in Al-Mg Alloys Using in-situ TEM"

• D. Scotto D'Antuono, D. Foley, J. Gaies, W. J Golumfskie, M. L Taheri, An Observation of ß-phase Precipitation Cycling in Al-Mg Alloys during In Situ TEM Heating Experiments TMS 2014

• D. Scotto D’Antuono, D. Foley, J. Gaies, W. Golumfskie and, M.L. Taheri A comparison of β-Phase precipitation during varying heat treatments in Al-Mg alloys via in-situ TEM heating experiments and ex situ bulk studies. TMS 2015

**Patents**

• WO2015027037 A1: Annealing process -Cyclic Annealing Process for Desensitization

• WO2015027030 A1: Selective grain boundary engineering- Thermomechanical Process for Increased Corrosion Resistance