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IMPROVEMENTS TO THE STRENGTH AND CORROSION RESISTANCE OF Al-Mg-Mn ALLOYS OF NEAR-AA5083 CHEMISTRY

DISSERTATION

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

By
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The Ohio State University
2001

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ABSTRACT

Aluminum alloys of the 5000 series (Al-Mg-Mn) are extremely popular in a wide range of applications that call for a balance of moderately high strength, good corrosion resistance, and light weight, all at a moderate cost. One of the most popular 5000 series alloys is designated Al-5083, containing, in addition to aluminum, approximately 4 wt% magnesium and 0.7 wt% manganese. In order to increase the range of versatility of this particular alloy, a number of modifications have been examined that will potentially improve the strength and corrosion resistance characteristics while maintaining a chemical composition that is very close to the proven 5083 alloy.

The strength of the 5083-based alloys under study are investigated with two goals in mind — to maximize the potential strength characteristics in a “standard” 5083 form through changes in minor processing parameters or through minor alloying additions. Increasing the standard alloy’s potential is possible through improved efficiency of “pre-processing” heat treatments that maximize the homogeneous dispersion of secondary manganese-based particles. For the modified alloy study, additions of scandium and zirconium are shown to improve strength not only by forming secondary particles in the alloy, but also through substitutional solid solution strengthening, even when added at very small levels.

Corrosion resistance of these 5083-based alloys is investigated once again through minor alloying additions; specifically zinc, copper, and silver. Zinc is particularly effective in that it changes the corrosion-susceptible binary aluminum-magnesium phase
that would otherwise form on grain boundaries following exposure to moderately elevated temperatures for extended periods of time to a ternary aluminum-magnesium-zinc phase. This chemical composition of this ternary phase that forms following zinc additions can be further altered through minor additions of copper and silver.

By determining threshold levels for these modifications while maintaining a chemical composition that is very near that of standard Al-5083, it can be shown that even minor modifications to processing and alloying parameters can have a favorable effect on the final bulk properties of the alloy. The increased range of strength and corrosion resistance of these lightly modified alloys make them more attractive in a broadened range of potential applications.
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PUBLICATIONS


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Major Field: Materials Science and Engineering
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Aluminum alloys of the 5000 series have long demonstrated a great deal of versatility; their light weight, moderately high strength, and weldability have made them ideal for heavy usage in the building and construction industry (welded girders and support trusses), the automotive industry (automobile frames and structural components), and in the land-based shipping industry (storage tanks, truck and train car bodies). Additionally, the resistance of 5000 series alloys to corrosion, even in seawater environments, have made them ideal in marine applications. Shipbuilders use 5000 series alloys not only for hull stiffeners and structural support, but also in exterior applications such as in construction of the hull, decking, and superstructure. The nature of 5000 series alloys has also made them ideal for pressure vessels and other systems that will be subjected to extremely low temperatures, with extremes approaching absolute zero [1, 2].

Registered in 1954, aluminum alloy 5083 has been described as the "work horse" of the 5000 series alloy system due to its very versatile characteristics and extensive usage. 5083 contains magnesium levels in the range of 4.0-4.9 wt% and manganese in
Table 1.1: General chemical composition ranges (ASTM standards) of aluminum alloy 5083. There is no approved amount of Zr or Sc in 5083, although those elements will be evaluated and discussed.
greater than 3.5 wt% are prone to decomposing and forming a secondary Mg-Al β-phase \((Al_3Mg_2)\) along slip bands and on grain boundaries [2]. 5083, which contains levels of Mg that exceed this maximum value, is therefore susceptible to β phase formation. Because the β phase precipitates heterogeneously along grain boundaries, it does not provide any real precipitate strengthening effect to the bulk material, but rather has the undesirable effect of making components constructed of 5083 susceptible to intergranular corrosion (IGC) and stress corrosion cracking (SCC) [3].

The material's susceptibility to IGC and SCC can be substantially reduced through an appropriate processing sequence. One of the sequences which has proven effective is the H116 temper [4], consisting of an extended hot work reduction, which can be in the vicinity of 50:1, followed by a minor cold work step (15-20% reduction), and a final stabilization heat treatment. This practice can vary based on proprietary industrial processing parameters from mill to mill. Because this temper is being extensively used in order to limit the alloy's susceptibility to IGC and SCC, this study will address the issue of strengthening based on a reasonably consistent processing sequence; that which produces the H116 temper.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Yield strength, [MPa]</th>
<th>Tensile strength, [MPa]</th>
<th>Elongation, (A_e), %</th>
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<td>5083-H321</td>
<td>215</td>
<td>305</td>
<td>10</td>
</tr>
<tr>
<td>5383-H116</td>
<td>220</td>
<td>305</td>
<td>10</td>
</tr>
<tr>
<td>6082-T6</td>
<td>260</td>
<td>310</td>
<td>10</td>
</tr>
<tr>
<td>7108-T79</td>
<td>290</td>
<td>330</td>
<td>10</td>
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Table 1.2: Some design values for common aluminum-based shipbuilding material.
The driving force behind this study is to gain a thorough understanding of the established strengthening and corrosion mechanisms in 5083-based alloys, and to improve on these properties by making compositional changes that elevate the effectiveness of these mechanisms. Preferably, these chemistry changes can be made in a manner which will allow ingots to be cast and processed in a fashion which does not require any radical deviations from established practices for producing the favored H116-type temper. Ideally, a competitive 5083-based alloy can be developed and produced with a minimum of changes to standard practices both in casting and in processing. Such an alloy has a market in established as well as emerging industries; new 5000 series alloys are presently being developed and registered that are generating a great deal of interest in the marketplace. These alloys are commanding much higher prices (and associated profit margins over standard 5083) by improving on the aforementioned desirable properties of strength, corrosion resistance, and weldability. A sampling of basic design properties for popular materials used in the shipbuilding industry is given in Table 1.2 [5]. Difficulties exist in producing entirely new alloys, however. Even recently, developments requiring experimental evaluations based solely on chemistry changes have been performed and have led to the introduction of improved alloys, but only after an extreme number of total “test” castings. Each of these castings had to be evaluated in a manner which took the effect of each individual alloying element as a variable in the trend of bulk property improvements [5, 6].

This study is concerned with improving the favorable properties of standard 5083 by approaching the strengthening and corrosion mechanisms with three major areas of focus. First, the level of strengthening which can be reasonably obtained in a standard chemistry by varying pre-processing parameters (specifically preheat treatments) will be investigated. Second, the amount of precipitation/dispersion hardening contributions that can be improved upon will be evaluated. This will be investigated by adding additional elements which will also form precipitates during decomposition of
the solution from a supersaturated state. Third, the corrosion susceptibility due to Mg levels will be addressed by focusing on the mechanisms for β phase formation. Based on published studies that have addressed this particular matter, limiting β-phase formation will improve the material’s resistance to IGC and SCC [4].

The roles of Mg and Mn in the Al-Mg-Mn system are known well enough to pursue these three areas of focus while maintaining a core material which is based on the common 5083 alloy. Increasing solid solution strengthening effects not only through increased Mg levels but also through the addition of other stable solute atoms is not an unrealistic goal. An increase in overall precipitation/disruption hardening also appears to be a very tangible goal. Several alloying elements have received attention as of late for their abilities in providing barriers to dislocation motion through homogeneous precipitation of fine, coherent particles. The role of Mn can therefore be evaluated along with promising additional elements, such as scandium and zirconium, and the effects that these and other alloying elements have on producing favorable microstructures that translate to favorable bulk properties. Finally, knowledge of the β phase has been in print since the 1960’s, but the structure and behavior of the β phase continues to be elusive. Studies which help to clarify the role and behavior of the β phase, along with evaluations of its contribution to corrosion in high-Mg aluminum alloys, will aid in determining chemistry changes which will limit its detrimental effects.

The bulk of the work contained in this document will concentrate on addressing the three issues outlined above. Following the introductory chapters (Chapters 1 and 2), Chapter 3 will evaluate preheat practice with respect to standard 5083 by investigating microstructural changes to the alloy that occur with more aggressive heating prior to process reductions of the material. The reduction process serves to not only to homogenize the non-uniform as-cast chemistry profile in the material, but also to refine the as-cast grain structure. More efficient precipitation-inducing preheat practice prior
to this reduction could aid in rendering the overall processing more efficient and more effective in increasing final strength. Chapter 3 will continue to evaluate strengthening processes through a study of the effects of minor additions of scandium and zirconium to a standard 5083. The resulting additional precipitates that form will have an effect on final strength parameters, perhaps without significantly altering other favorable properties of 5083.

Chapter 4 will continue the study of improving 5083 by examining methods of reducing the alloy's susceptibility to stress corrosion cracking. As with the scandium and zirconium additions, very minor additions of other elements may not have a large effect on overall bulk characteristics of the alloy, but may have a mitigating effect on the propensity of the alloy to form the detrimental β phase along grain boundaries. The study contained in Chapter 4 will examine additions of zinc, copper, and silver in varying levels, evaluating the effects of each when added in various levels. In addition to performance with regard to SCC, other observed characteristics of promising additions will be directly compared to standard 5083.

References

CHAPTER 2

EXPERIMENTAL PROCEDURES

Due to the wide range of experiments undertaken over the course of this study, each with differing specific conditions, more precise experimental procedures will be outlined in many sections of this document. Each will generally precede the specific section to which those experimental parameters apply.

2.1 Introduction

The purpose of this brief introductory chapter is to give the background and general capabilities of some of the major equipment that was used to perform a wide variety of tests throughout the course of this study. It is meant as nothing more than an overview to familiarize the reader with the equipment; specific parameters for individual experiments will be addressed in the sections that report the actual information gained.
2.2 Casting/Processing

The material used in this study is all based on the standard composition for aluminum alloy 5083. There were three sources for the material from which all castings were generated: Reynolds Aluminum Corporation, Pechiney Rolled Products, and The Ohio State University.

Initial observations were made on a series of castings that were generated under contract by the Reynolds. This investigation was carried out as a comparison of four alloys. One is of a standard Al-5083 chemistry, one 5083 with 0.13 wt% Zr, one 5083 with 0.09% Sc, and finally one with 5083 plus 0.13 wt% Zr and 0.09% Sc. The ingots were provided by Pechiney Rolled Products (formerly Century Aluminum Corporation, Ravenswood Operations), for investigation at the Ravenswood facility as well as at The Ohio State University.

Studies on as-cast materials and associated microstructures were carried out on industrially-produced sections of full-sized ingots cast at the Ravenswood plant of the Pechiney Rolled Products division of Pechiney Aluminum.

The studies on alloys with modified compositions were performed on material that was melted and re-cast following minor additions of copper, silver, and/or zinc at The Ohio State University. The base metal was Pechiney Al-5083, or, in the Sc- and Zr-modified alloys, Reynolds castings, which were re-melted using an Inductotherm 50 kW induction furnace and cast in a graphite mold (Figure 2.1). Hot and cold processing of test ingots cast in graphite molds (Figure 2.1 inset) was performed on the rolling mill shown in Figure 2.2; elevated temperatures for hot working of material was achieved by heating ingots in the resistance box furnace directly adjacent to the roll mill.
2.3 Microscopy

Two types of electron microscope are used during the course of this study – the scanning electron microscope (SEM) and the transmission electron microscope (TEM).

The scanning electron microscope used is a Philips XL-30FEG. It is equipped with EDAX for energy dispersive spectroscopy (EDS) evaluation. It is generally operated in one of two detection modes, either detecting backscattered electrons or...
Figure 2.2: Roll mill and adjacent furnace used to mimic industrial hot and cold work practices on test castings.

secondary electrons. It was most often used in the backscattered electron mode, which was often necessary to discern features that are invisible to observation when detecting secondary electrons.

Two transmission electron microscopes are utilized for this study depending on the specific information desired and the magnification level needed. For structure and chemical analysis at lower resolution, a Philips CM200 with a LaB₆ cathode was employed, generally operated at 200 kV. The CM200 is also equipped with EDAX for energy dispersive spectroscopy (EDS). Imaging at higher magnifications, which also includes high resolution TEM imaging (HRTEM), was performed on a Philips CM300 FEG (field emission gun) operated at 300 kV (Figure 2.3).
One of the vital features of the CM300 utilized extensively over the course of this study is the EMiSPE system. EMiSPE is a system that uses the EDS capabilities already in place on the microscope column (EDAX), and as such the same EDS probe is used to determine chemical enrichment in selected areas. Unlike "manual" EDS control, however, EMiSPE takes a pre-selected line or two-dimensional area and automatically scans and records a pre-determined number of complete EDS spectra and "fills in" this selected area with EDS data. From these stored spectra, energy windows of selected elements can be highlighted and a complete contrast map of the relative peak height of the selected element in each spectrum is generated.
2.3.1 Sample Preparation

Transmission electron microscopy studies are carried out by preparing 3 mm foils of the material to be studied. As will be addressed in future chapters, electropolished samples were initially utilized. Electropolishing was invariably done under the same conditions; at -20°C in a 25% nitric acid/75% methanol solution, operating at 15V.

In some cases, for example on as-cast materials and in studies where electropolishing of TEM foils would otherwise be overly corrosive to features of interest, samples were dimpled to 25 μm and ion milled on a twin gun mill at 10-12 degrees incidence, 6 kV, and 1 mA gun current.

To remove artifacts due to potential surface contamination, samples were prepped on an E.A. Fischione plasma cleaner immediately prior to insertion in the microscope column.
2.4 Tensile Testing

2.4.1 Standard Tests

Standard tensile testing was performed on flat, 0.375 in dog-bone type samples using a 0.5 in Interlaken extensometer for extension readings that are converted to strain levels. The test rig used is an MTS model 810 (Figure 2.4).

Figure 2.4: Model 810 MTS™ tensile test machine and associated control computer.
Figure 2.5: M-CERT\textsuperscript{TM} constant extension rate test rig and associated control computer. The rig (right) is shown without a tensile sample mounted.

2.4.2 Slow Strain Rate Tests

Slow strain rate testing (SSRT), or constant extension rate testing (CERT), is performed on an M-CERT tensile test rig (Figure 2.5) on cylindrical samples. The samples were machined to the dimensions shown in Figure 2.6; the M-CERT system allowed testing not only in ambient air but also in aqueous environments through the use of an integrated environment vessel.
Slow Strain Rate (SSR) Specimen
Drawing # SD01003

Notes:

1 - Machining of the specimen must be done carefully to avoid overheating and cold working in the gage section.
2 - The final two machining passes should remove about 0.002" of the metal.
3 - The gage section must be a uniform diameter within the ±0.005" tolerance.
4 - The specimen is finished to a surface roughness of 10 micro-inch or finer.
5 - Tolerance of dimensions ±0.005" unless otherwise specified.

A - 0.150"
B - 1.000"
C - 0.250"
D - 2.750"±0.01"
E - 0.500"±0.01"
2.4.3 Compression (Creep) Tests

Creep testing is performed on rectangular aluminum samples of interest fixed in a compression cage. Testing was performed at elevated temperatures in a 3-stage furnace mounted directly to an ATS creep rig (Figure 2.7). Temperatures are carefully measured by using a thermocouple tip wired directly against the sample surface.
CHAPTER 3

STRENGTHENING MECHANISMS

This chapter will endeavor to describe the basics of strengthening in alloy systems and how those mechanisms might apply to 5083-based aluminum alloys. Experimentally, two strengthening approaches will be investigated. The first is based on standard 5083 chemistry and the inherent ability to maximize the efficiency of the most common precipitates in the 5083 system, Al₆Mn, in strengthening the material. One way to accomplish this is by increasing the volume fraction and homogeneous distribution of Al₆Mn particles prior to the generation and mobilization of dislocations accomplished during hot and cold work reductions.

A second strengthening method to be investigated is through additional precipitate structure not common to a standard 5083 alloy. To be specific, through minor chemistry modifications that will produce a second precipitate structure. In the case of this study, the "additional" precipitates to be investigated will be produced through minor additions of scandium and zirconium.

Evaluation of the resulting microstructure of the material modified through both of these methods will be discussed, as will the associated changes in strength and other bulk properties.
3.1 Introduction

The inherent strength of a metal is based largely on the ability of dislocations to become mobile and continue to move through a material’s microstructure. Limiting the ability of dislocations to move, or even limiting the initial dislocation density of a material, can have a profound effect on the yield strength of a material. Whiskers have been produced that contain few dislocations, and as such have strength levels approaching theoretical values, requiring shear stresses approaching \( G/30 \) in order to cause motion between slip planes. The actual yield strength of real metals, however, requires stresses on the order of only about \( G/(10^4-10^5) \) in order to cause the same slip [1], with a value of \( G/10^4 \) more common at room temperatures. From a practical standpoint, whiskers can only be produced in exceedingly small samples of material, and not on any scale that would allow widespread use following casting or forming operations. Such a technique for raising the strength levels in metals is clearly not feasible.

Aluminum in a commercially pure state does not contain a great deal of inherent strength. Once again, dislocation mobility is not hindered to any great extent such that strengths on the order of only about 10-12 Kpsi (kips), or 70-85 MPa, are common [2]. The degree to which commercially-pure (CP) aluminum can be strengthened is based largely on the ability to promote dislocation-dislocation interactions, thus hindering further mobility and raising the overall strength level. This interaction has been recognized not only as interactions between parallel dislocations, through the repulsive stresses which exist between dislocations of like sign and orientation, but also in the “crossing” of dislocations on different planes, or cutting, which can create immobile
jogs and kinks [3]. This genuine strengthening technique, called strain hardening, is quite important in the area of aluminum processing and production. For stress vs. strain of a single crystal, shown in Figure 3.1 [4], the increment of stress increase per unit of strain can be divided into three basic regions. Each corresponds to a different degree of dislocation-dislocation interactions [5]. In Stage I, a rotation of the crystal occurs as slip planes line up in order to orient themselves for multiple slip. In this region, dislocations begin to mobilize, but have not begun to interact with one another to any great extent. Interaction between dislocations begins to occur in Stage II as slip distances shorten; the associated strain hardening rate increases as dislocations intersect one another and form immobile kinks and jogs along their line lengths. The crystal hardens as the dislocation density increases during the interactions of dislocations on different slip planes. Stage III work hardening is reached when dislocations begin to interact with others of opposite sign, annihilating both dislocations and reducing dislocation density within the crystal. This phenomenon is commonly referred to as dynamic recovery. Although it appears so in the associated figure, this region is not

![Diagram showing three distinct stages for stress vs. strain for a single crystal.](image)

**Figure 3.1**: The three distinct stages for stress vs. strain for a single crystal.
linear; rather it exhibits a positive curvature. Additionally, cross slip of dislocations back onto their original slip planes may allow increased mobility due to bypassing of obstacles on the original slip planes. It has been experimentally established that in Stage III the dynamical recovery processes are mainly due to thermally activated cross slip of screw dislocations aided by some applied stress [5]. The hardening rate is somewhat parabolic in this stage, as dislocation interactions which increase the local hardening within the microstructure are countered by increased mobility of dislocations in other areas of the microstructure.

Although this generic model is based on the deformation of a single crystal of face-centered cubic (FCC) material, polycrystalline materials behave in a similar fashion. The initial region of stress vs. strain is steeper than for single crystals, but the following stages mimic the behavior of single crystals. For FCC materials at room temperature, most of the stress vs. strain behavior observed occurs in Stages II and III; Stage I behavior does not apply.

For the purposes of this study, however, strain hardening behavior is a component of the strength equation which will remain relatively constant in terms of the processing deformation (both cold work and hot work) which is applied to the alloys under investigation. Just as dislocations will interact in the microstructure and strengthen CP aluminum, dislocations will interact in a multitude of different ways with foreign atoms in an alloy system in order to optimize the strain-hardening characteristics of a material. Elements added to a matrix of metal to form an alloy will provide a strengthening effect as a result of distinctly different mechanisms. The two most common strengthening methods are outlined as follows [6]:

- Disperse alloying elements in solid solution and cold work the material to instigate dislocation/solute interactions (work hardening alloys)
- Dissolve alloying elements in solution and precipitate them as finely dispersed coherent particles (precipitation hardening alloys)

Both of these basic mechanisms will be examined more closely in the next sections.
3.2 Solid Solution Strengthening

The introduction of magnesium (Mg) into an aluminum matrix produces a solid solution over a wide range of compositions; common alloys of the Al-Mg system contain magnesium in solution ranging from 0.8 to over 5.0 wt% [7]. The effect of increasing Mg levels in Al-Mg-based systems is illustrated for a group of common alloys in Figure 3.2 [6]. Solid solutions in general can retain such a large range of solute atoms in solution based on the method by which the solutes occupy space within the lattice structure. Depending on the size mismatch between solute atoms and the solvent matrix atoms, solutes may position themselves either in the spaces between sites of the solvent atoms (interstitial solid solution) or occupy atomic positions that would normally be occupied by solvent atoms (substitutional solid solution).

The degree to which these solute atoms will have a strengthening effect on the mechanical properties of an alloy depends largely on the mechanism by which the solute will hinder dislocation motion in a material due to irregularities or distortions in the crystal lattice. Some materials react much more profoundly in terms of strength increases than others; body-centered cubic (BCC) materials can have tremendous increases in strength due in particular to non-symmetrical (tetragonal) distortions in the matrix when solutes occupy interstitial sites [8]. Although the strength increases in FCC materials may not be as large by comparison, the positive effect on mechanical properties is large enough to justify utilizing the benefits of solid solution alloying.

The main contributions to strength due to solute atom occupation are a result of the interaction of dislocations with the different types of solute irregularities. These irregularities can be classified into three major categories. First, size differences between solute and solvent atoms can cause lattice distortions whether the solution is
Figure 3.2: Correlation between tensile yield, elongation, and magnesium content for some common commercial alloys.
substitutional or interstitial. Second, solutes can reach a lower energy state through short range ordering or clustering within the matrix, causing regions in the crystal which have different dislocation mobility characteristics. Third, dislocations can become effectively locked by solute atoms which segregate to the “open” spaces along a dislocation’s line length.

The effect of randomly oriented solute atoms within a matrix on dislocation mobility is based on two principles. In the case where there is a size mismatch between the solute and solvent atoms, elastic distortions in the crystal will lead to an increased frictional force on dislocations as they move through the associated strain fields. The most prolific interaction between solutes and dislocations can be described by this size mismatch, or local dilatation, within the lattice structure [9]. In the case of magnesium in aluminum, where the solution is substitutional, the average lattice dilatation can be described using a misfit parameter, \( \delta \):

\[
\delta = \left( \frac{1}{a} \right) \left( \frac{\partial a}{\partial c} \right)
\]

where \( a \) is the lattice parameter and \( c \) is the concentration solute atoms in the solution. The interaction effects between dislocations and solute atoms with a defined misfit parameter varies as a \( 1/r \) relationship, with \( r \) defining the relative distance separating the dislocation and the solute atom [10].

In the case where there is no real size mismatch between the solute and solvent atoms, dislocation motion can still be affected by the difference in elastic modulus between the atoms along the dislocation’s path. An additional stress is required to move a dislocation through a region with a higher modulus, or away from a region with a lower modulus. This local change in shear modulus (\( \partial \mu \)) and its associated
effect on the mobility of dislocations through occupied glide planes, can be defined in terms of a characteristic known as elastic polarizability, $\eta$ [11], where:

$$\eta = \left( \frac{1}{\mu} \right) \left( \frac{\partial \mu}{\partial c} \right)$$

and $\mu$ is defined as the shear modulus and $c$ is the concentration of the solute species. In the case of local shear modulus changes due to the presence of solute atoms, the interaction effect between non-screw dislocations and solutes will vary as a $1/r^2$ relationship in FCC materials.

Clearly the effect of solute atoms, regardless of the mechanism, will be greater when the fraction of the atomic sites occupied by solute atoms is greater. This is evidenced by the concentration term in each of the above equations. It can be inferred that even with a small size mismatch or difference in shear modulus between solute and solvent atoms, increasing concentrations of solute will have an increasing impact on associated bulk properties. For Al-Mg alloys, increasing Mg content will increase frictional stress ($\sigma_o$) in a relatively linear fashion, as evidenced by the plot in Figure 3.3 [12].

![Figure 3.3](image.png)

**Figure 3.3**: The influence of Mg concentration on frictional stress $\sigma_o$ in 5000 series alloys.
Solute atoms have also been shown to have an affinity for faulted regions within a lattice structure [11]. In contrast to an interaction between a mobile dislocation and a stationary solute atom, solutes can have an effect on the hardness of a material by essentially preventing a static dislocation from becoming mobile. This can occur as a result of several conditions. In the case of FCC structures with substitutional solute atoms, the presence of strain fields surrounding both dislocations and misfit solute atoms can cause a re-ordering of solutes as a method of providing relief to the system. The stress field surrounding a dislocation with edge character will contain both compressive and tensile components on opposite sides of the dislocation line. For misfit substitutional atoms that are larger than the surrounding atoms, the solutes will segregate to the energetically favorable side; i.e. the side in tension. Smaller solute atoms will be attracted to the compressive side. In either case, a lower energy atmosphere of solute atoms is formed due to these elastic interactions. In order for the dislocation to mobilize, it must be subjected to a stress which either frees it from the dislocation anchors or effectively drags them along [13, 14]. This type of dislocation-solute interaction is known as Cottrell atmosphere locking. Cottrell atmosphere locking can also lead to reductions in the forming limit. The locking effect has been shown to increase work hardening at low strains, but produces a decrease in hardening at large strains [6].

Another type of dislocation mobility loss due to the presence of solute atoms is a result of chemical interactions. First suggested by Suzuki [15], this type of locking is based on the stacking faults that will occur in FCC materials when dislocations split into partials and consequently change the periodic stacking arrangement of the lattice. The atomic planes on either side of a stacking fault in an FCC crystal will have hexagonal close-packed (HCP) structure, which generally has a different solid solubility than an FCC structure. Whether the solubility is raised or lowered in the region of the stacking fault, the local concentration of foreign atoms will shift to reach a more favorable
energy state (by solute atoms segregating into or out of the region of the stacking fault). Unlike atmosphere locking, this Suzuki locking does not require dislocations to have an edge component in order to interact and subsequently affect mobility: it will hinder the motion of both edge and screw dislocations.

Differences in valence between solute and solvent atoms can also have an effect on the mobility of dislocations [11, 15]. This electronic interaction is a result of the sea of electrons that surrounds atoms and tends to resist compression. Areas of tension will carry a negative charge as electrons are attracted, while areas of compression repel electrons to an extent and hence carry a positive charge [16]. The extra valence in a solute atom may therefore be attracted electrostatically to the charge dipole along a dislocation's line length. It should be noted that this effect is minimal in metallic materials when compared to elastic interactions [17].

The overall effect of solid solution strengthening is an increase in the initial flow stress of a metal as foreign atoms are dissolved in it [17]. This increase, brought on by the dislocation-solute interactions described above, cannot be effectively thought of as single interactions between a dislocation and a solute atom. Pronounced strengthening effects can be realized not only from the singular interaction mechanisms outlined above, but also through the more macroscopic interactions between dislocations and widespread solute concentration gradients. The concentration levels of solutes are unlikely to be completely uniform throughout a matrix of material; the interaction models described above can also be applied at differing levels throughout these gradients. This gives rise to additional strengthening mechanisms. For example, a change in lattice parameter may exist across a region where solute concentration varies over many atomic distances. If a dislocation moves along this area in such a manner that a dislocation-like displacement or misfit across the slip plane is reduced, the resulting increase in energy within the lattice structure will place an appropriate reduction on the mobility of the moving dislocation [18].
3.3 Precipitation/Dispersion Hardening

At elevated temperatures approaching the melting point, the solid solubility of the alloying elements in 5000 series alloys can be quite high. Upon cooling to low temperature, many of the alloying elements become supersaturated in the solution, being at concentration levels much higher than their respective solid solubility limits. These elements will achieve a lowered energy state through the decomposition of the solution which is accompanied by a solid-state precipitation reaction. This precipitation reaction can be hastened by holding the material in the supersaturated condition at some moderately elevated temperature for some period of time, a process known as aging. Natural aging will occur at room temperature as a mechanism for lowering system energy, but at such low levels of thermal activation the process could take tens or hundreds of years. For the purposes of this study, a number of different precipitation processes and the effectiveness of the particles that result on bulk properties will be evaluated. For this reason, a very general description of the precipitation/dispersion process will be outlined here, with the understanding that these processes will differ from element to element in the alloy. The basic precipitation process for a "generic" aluminum alloy is as follows:

\[ SSS \rightarrow GPZ \rightarrow A'' \rightarrow A' \rightarrow A \]

As the supersaturated solid solution begins to decompose, atoms migrate together and form tiny clusters, or zones, known as Guinier-Preston (GP) zones. GP zones will often nucleate homogeneously throughout the matrix, providing a dispersion of coherent particles which result in a uniform strengthening effect throughout the material. In the
case of some alloying elements in an aluminum matrix (Cu and Zn, for example) [6], a
dispersion of GP zones is the most effective precipitate structure for increasing material
strength. As GP zones continue to grow, larger coherent particles may form that are
sometimes referred to as GPlI zones.

The $A''$ phase forms as the GP zone “clusters” grow and begin to take on some
crystalline structure. This phase generally remains coherent and also provides some
strengthening effect, but is not so homogeneously dispersed as GP zones. Often this
precursor to the final stable phase requires some form of energy “sink”, or catalyst for
a drop in system free energy (such as dislocations, grain boundaries, or incoherent
interfaces), in order to nucleate and grow. Such heterogeneous nucleation will typically
be detrimental to the strengthening potential that the growth of these particles would
otherwise provide.

Continued growth of the $A''$ phase will produce a larger particle with a more
advanced precipitate crystalline structure, the $A'$ phase. In the case of many alloy
additions, this stage of the precipitation process provides the most profound
strengthening effect, although this depends on several factors which include the degree
of coherence that each particle retains and the extent to which it nucleates and grows
homogeneously throughout the matrix.

The final stage of the precipitation process has been reached when particles
achieve their most stable state. The strengthening effects associated with the
precipitation process are often lost as precipitates coarsen in reaching this stage, and
are more heterogeneously distributed due to the Ostwald ripening mechanism for
advanced precipitate growth, whereby large particles continue to grow at the expense
of smaller ones. This behavior necessarily dictates that interparticle spacing will
increase. The effect that this will have on hindering dislocation mobility will be
discussed in the next section.
3.4 Dislocation Interactions with Foreign Particles

The degree to which interactions between foreign particles and dislocations will affect the final bulk properties of a material can be modeled in a variety of ways. One of the first generalizations to make lies in determining whether the type of interaction that occurs is one in which thermal activation can play a role. The interactions between dislocations and mobility barriers can be divided into two categories; those that can be overcome with the aid of thermal fluctuations and those that cannot. The interaction between a large second-phase particle and a dislocation will be quite different than an interaction between a solute atom and a dislocation. The same is true for interactions between one dislocation and a second dislocation. An obstacle which possesses a physical dimension or a long-range stress field on the order of 10 atomic diameters or greater cannot be overcome with the aid of thermal fluctuations; such an obstacle would be termed an athermal obstacle. Examples of athermal obstacles, along with the aforementioned second-phase particles, would include large precipitates or dislocations on parallel glide planes. Conversely, a thermal obstacle is an obstacle with a short-range stress field that can be bypassed by dislocations with the aid of thermal activation. Common thermal obstacles would include the Peierls-Nabarro barrier, dislocation glide through forest dislocations, the dragging of jogs on screw dislocations, or climb of an edge dislocation [19]. In a crystal system containing both types of barriers, the applied stress can be modeled as having two components; both an athermal component $\tau_\mu$ which is dependent on the shear modulus $\mu$, and a thermal component $\tau^*$, which depends on temperature $T$ and strain rate $\dot{\gamma}$ [20]:

$$\tau = \tau^*(T, \dot{\gamma}) + \tau_\mu$$
As strain rate decreases or temperature increases, the thermal component $\tau^*$ will become less and less of a contributor to applied stress, until such a threshold is reached where the short range stress fields are "transparent" to the mobile dislocation. At this stage, only the long range stress fields of the athermal components are contributing to the applied stress term $\tau$, which is in agreement with many experimental observations [19].

A second generalization would include the extent to which these interactions occur. Clearly the modeling of a single dislocation moving along a glide plane and interacting with a precipitate or solute atom will not effectively describe the measurable increases in strength and hardness. Many authors have described the methodology for these interactions on a more macroscopic scale by illustrating the effect of dislocations crossing through multitudes of foreign particles. Consider the case of a single dislocation encountering a field of solute atoms. If this field of atoms contains a distribution whereby each atom occupies an area of the glide plane equal to the square of the Burgers vector ($b^2$) at a spacing of $l$, the dislocation will bend around each obstacle until a critical bowing radius ($R=l/2$) is reached. At this point the dislocation will move past the obstacles; the shear stress required to do so is defined as the critical shear stress:

$$\tau_c = \frac{\alpha \mu b}{l}$$

where $\alpha$ is equal to some constant (generally 0.5 - 1.0) [1], $\mu$ is the shear modulus, and $b$ is the Burgers vector. This reasonably simple model can then be rewritten in terms of
the concentration of solute atoms. The fraction of the area in a glide plane taken up by solute atoms some distance $l$ apart can be written as:

$$c = \frac{b^2}{l^2}$$

and therefore the critical shear stress for a dislocation to overcome obstacles in its path can be given as:

$$\tau_c = C \cdot c \left(\frac{1}{2}\right)$$

where $C$ is some constant equal to $\alpha\mu$. Using this relationship, it can be estimated that the critical resolved shear stress goes as a function of the square root of the solute concentration.

Modeling of dislocation interactions with particles is similar to that of modeling solute interactions. The distinct difference between the two is that the size of the precipitate or dispersoid will have an effect on the method by which the dislocation can pass by each obstacle. Dislocations will choose the more favorable path for moving past each particle; whether by shearing it, moving around it, or by looping around it and "rejoining" at the opposite side.

The first method, cutting through the particle, requires enough applied energy to break bonds in the particle. Following this shear, the surface area of the cut precipitate is increased. The amount of energy produced at this sheared interface is dependent on the coherency of the particle. In the case where a particle is coherent, the energy produced, $\Gamma$, has been estimated in an Ag-Al alloy to be about 0.1 J/m$^2$ [21]. For an incoherent particle, such as a largely different precipitate crystal structure, $\Gamma$ can be modeled more on the order of a large angle grain boundary. A much larger interfacial
energy is therefore involved, nearer to $1 \, \text{J/m}^2$. The stress to force a dislocation through a zone of particles of radius $r$ and separated by some distance $l$ can be described by:

$$
\tau_c = \left( \frac{\Gamma}{b} \right) \left( \frac{r}{l} \right)
$$

This manner of modeling the motion of a straight dislocation through some number of particles must be further modified if the particle is some ordered phase which becomes disordered [11], or if the there is some difference in stacking fault energy between particle and matrix [22].

A dislocation can also move past a particle by avoiding it altogether. This can be accomplished by cross slip onto a particle-free plane or by climb around the particle.

If the spacing between particles is large enough, a condition often encountered when sufficient coarsening of precipitates has occurred, particles can by bypassed through an Orowan looping mechanism [23]. In this method, a dislocation bends between obstacles in the same manner as was outlined above for solute atoms:

$$
\tau = \frac{\alpha \mu b}{l}
$$

where $\alpha$ for Orowan looping is 0.8 [1]. Whether it is energetically favorable for a dislocation to cut through a particle or loop around it is not only based on the interparticle spacing, but also on the size of the particle as well as on the particle's shear modulus, $\mu$. Although looping will generally occur when a material is "overaged" and has begun to lose its strength properties, the loops left around each particle bypassed via the Orowan method can actually continue to have a work hardening effect on the crystal. Not only is the spacing between particles effectively reduced with each loop, but a repulsive stress between moving dislocation and the dislocation loop will provide further hindering of dislocation mobility.
It should be noted that the interactions between dislocations and particles continue to build on one another during the strain hardening process. That is to say, multiplications and interactions of dislocations depend on the concentration of impurities in the system. The overall effect of hardening by impurities and hardening through strain is multiplicative in nature rather than additive [9], and as such it can clearly be seen why these interactions play such an important role in the final properties of the material.

3.5 Precipitating Alloying Elements

3.5.1 Manganese Additions

Manganese plays a variety of important roles in the Al-Mg-Mn system. The solubility limit of manganese is much lower than that of magnesium; any solid-solution strengthening effect is merely secondary to its importance as both a precipitation hardener and as a grain refiner. Although Mn, a substitutional impurity, can be a very effective solid-solution strengthener in levels up to 0.5 at% [24], a large portion of the manganese which is retained in solution following solidification will precipitate out as dispersoids during elevated temperature sequences of the alloy processing phases. The maximum solid solubility of Mn is 2.0 wt% at the eutectic temperature of 958.5K, a solubility value that decreases rapidly with a decrease in temperature [25]. The equilibrium solid solubility of Mn, even at elevated temperatures for preheating or for hot work is only 0.2-0.3 wt%. Common trace impurities in aluminum alloys, such as silicon or iron, will further reduce the solubility limit of Mn.

The contributions of manganese to the final properties of 5000 series alloys can be traced back to the behavior of this principal alloying element during the solidification
and processing stages which the alloy undergoes. The following sequence of events is based on achieving the final H116-type temper outlined in Chapter 1.

3.5.1.1 The Solidification Phase

As the solidification interface moves through the melt during the alloy ingot casting process, the manganese precipitates out during the cooling phase from liquid to solid, forming a structure of widely distributed $\text{Al}_6\text{Mn}$ dispersoids. The typical manganese-based particle distribution consists of two types: large dispersoids formed during casting which generally contain trace amounts of Fe and Cr, and submicron-sized particles that precipitate at a later stage of the cooling process [26]. These dispersoids can reach a finer size and distribution during a hot working phase, but the initial state of the ingots following solidification will have an effect on the final distribution. The equilibrium phase $\text{Al}_6\text{Mn}$ has a body-centered orthorhombic structure with a lattice parameter of $\approx0.75$ nm [25]. The final dispersoid distribution will provide a marked effect on grain and subgrain size and shape, due to heavy interactions and subsequent pinning of boundaries [27]. Hence, the state of the alloy in terms of size, shape, and distribution of the manganese eutectic constituents (ECs) will have a measurable effect on final macroscopic properties.

Pertinent literature reports the as-cast microstructure of the Al-Mg-Mn alloys contains both blocky $\text{Al}_6(\text{Mn,Fe})$ particles as well as plate-like particles of similar composition. The solidification sequence of the alloy begins with the reaction:

$$L \rightarrow \alpha-\text{Al} + L'$$

The remaining liquid then becomes continually enriched with Mn until the concentration level at the liquid-solid interface reaches a point where the $\text{Al}_6\text{Mn}$ begins to solidify.
The solidification process is confirmed in other works which demonstrate the as-cast structure of the material as having precipitate-free dendritic regions (α-Al) and interdendritic regions which contain the Mn-based precipitates. During final homogenization, it has been observed that Mn will precipitate non-uniformly near dendrite boundaries, resulting in a banded structure in material that has been hot worked [28].

3.5.1.2 Effect of Manganese Content

Increases in beginning Mn content (\(C_0\)) would lead to a more rapid enrichment of the liquid as α-Al forms, leading to a more widespread formation of the Al\(_6\)Mn particles in the final as-cast microstructure. The interesting aspect of the solidification process is caused by the presence of excess Mg in the remaining liquid, which effectively lowers the final solidification temperature and allows for continued enrichment of Mn and Mg and subsequent formation of the much smaller plate-like Al\(_6\)Mn precipitates [29]. The importance of these plate-like precipitates is realized in the dislocation substructure, whereby low-angle subgrains are pinned by these precipitates leading to a much finer overall subgrain structure. It should be noted that these plate-like particles do not form entirely during the solidification process. Manganese will also remain, to some extent, in solution following solidification and continue to precipitate and coarsen the plate-like precipitates during subsequent processing operations [30].

The first Mn particles to form, the large and block-shaped Al-based particles which, in addition to Mn, also commonly contain chromium, iron, and silicon in various ratios [26], serve a different role in the microstructure. The eutectic constituents (ECs) can serve as nucleation sites for particle stimulated nucleation (PSN) of primary grains [31], which Humphreys [32] has shown requires some critical particle size. As such, the distribution of the ECs will have an instrumental effect on final grain structure.
These ECs are generally blocky in shape, and will often break up and be drawn into stringers during subsequent hot rolling operations [30]. A micrograph revealing the shape and post-rolling “breaking up” of ECs is given in Figure 3.4 [33]. This effect will potentially lead to the deleterious formation of microcracks and voids, reducing desired mechanical properties. Additionally, excess trace elements common to industrial production can combine with Mn, forming intermetallic particles that enrich the outer layers of cast ingots, leading to excess fractures in the form of edge cracks during hot rolling operations [34]. While it is the trace impurities that are the catalyst for these undesirable fracture surfaces, it is the presence of excess manganese that provide the basis for intermetallic particle formation.

It has been reported, however, that these same manganese-based blocky constituents which break up during hot rolling operations can actually be beneficial to final properties. The breakup of these particles leads to a more widespread dispersion
of large particles which are instrumental in PSN of new grains during processing at elevated temperatures [31]. Evidence for the nucleation of grains owing to the presence of ECs is given by Vetrano in Figure 3.5 [27]. The grains formed are therefore finer in areas throughout the microstructure, leading to a more favorable effect on overall strength properties [12] due to the Hall-Petch mechanism of hindering dislocation motion as a function of grain size \( d \):

\[
\sigma_y = \sigma_o + kd^{-1/2}
\]

where \( \sigma_y \) is the frictional stress due to solute atoms, generally 40-60 MPa for Al-Mg alloys (see again Fig. 2.3), and \( k \) is a constant. The Petch parameters \( \sigma_o \) and \( k \) are heavily influenced by Mg content in the 5000 series alloys, while grain size uniformity and shape are parameters heavily influenced by dispersoid content due to Mn levels [12].

**Figure 3.5**: Unetched (a) and etched (b) sample of 5083 cold rolled 50% and recrystallized for 10 minutes at 510°C. The decrease in grain size near the eutectic constituent (EC) particles indicates particle-stimulated nucleation (PSN). Dark spot in upper right is a microindent used as a position reference.
The addition of Mn has also been shown to increase the recrystallization temperature of the alloy. Goel, et. al. [35] demonstrated that for an Al-7 wt% Mg alloy with an Mn addition, annealing treatments on cold worked structures are characterized by three temperature ranges:

- \( T > 390^\circ C \) – recrystallization complete prior to precipitation.
- \( 390^\circ C > T > 350^\circ C \) – precipitates form mainly at grain boundaries of recrystallized structure; final grain size is uniform and small.
- \( T < 320^\circ C \) – continuous recrystallization is found, resulting in fine grain size.

These observations serve to support the role of manganese particles in hindering dislocation motion, even at elevated temperatures.

3.5.2 Zirconium Additions

Zirconium has been evaluated as an alloying addition to 5000 series alloys as a grain refiner, promoting a higher resistance to recrystallization and subsequent retention of strength. Zirconium will precipitate in a fine dispersion of Al₅Zr in this system [36, 37], producing a microstructure containing an array of homogeneously dispersed particles which interact with dislocation mobility on a much smaller scale than the larger Al₆Mn dispersoids.

Zirconium has a very low solubility in aluminum, having an equilibrium solid solubility of 0.08 wt% at 350°C. In rapidly solidified Al-Zr alloys, the precipitate that forms is a metastable L1₂-type structure with a lattice parameter of 0.407 nm [24]. For alloys cooled at a much lower rate, i.e. slower than about 10³ K/s, an equilibrium phase with a tetragonal D₀₂₃ structure will form. Schematic diagrams of these unit cells are given in Figure 3.6 [37]. A structural state diagram of the Al-rich section of an Al-Zr phase diagram at cooling rates of between 5 and 10⁵ K/s shows the separation between precipitates having L1₂ or D₀₂₃ structures (Figure 3.7) [24]. The precipitate will exhibit
Figure 3.6: The unit cells of the two structures observed in Al-Zr systems; (a) cubic L1$_2$ structure, and (b) tetragonal DO$_{22}$ structure.

Figure 3.7: The structural states for Al-Zr precipitates as a function of wt% Zr and the cooling rate of the melt.
a variety of shapes after forming, from needle-like precipitates to star-shaped particles, depending on the amount of zirconium added and the cooling rate of the melt [24].

\( \text{Al}_\text{X}Zr \) particles can have a measurable precipitation hardening effect on an aluminum matrix, although for very minor levels of Zr this effect is not tremendous. Precipitates generally reach a size of 50-100 nm in diameter in observations that follow moderately low heat treatments [31, 38, 39]. These Zr-based precipitates will coarsen at higher temperatures, however, and lose their effectiveness as precipitation hardeners as their coherency in the matrix is lost. It is unclear where this thermal stability is lost, however, as there are conflicting reports over how large the particles grow at elevated temperatures. Nes [36], for instance, showed growth of the \( \text{Al}_\text{X}Zr \) precipitate to reach average radii no greater than 400Å (40 nm) following heat treatments at 460°C for up to 700 hours. A graph of the growth of Zr particles at this temperature is given in Figure 3.8 [36]. The real interest in pursuing the effects of very minor Zr amounts on the strength of the 5000 series alloys is in taking advantage of this stability, as well as in the proven effectiveness of the precipitate in interacting at the smallest scale within the microstructure. It is these precipitate interactions that can behave in such a manner that recrystallization and recovery dynamics are altered.

Zirconium gained favor in the eyes of metallurgists seeking to develop aluminum alloys containing the necessary characteristics for superplastic forming. One of the important criteria for the superplastic characteristics is an extremely refined grain size. In extreme cases, favorable results have been demonstrated with grain structures less than 1 μm in diameter [40]. Formation of a microstructure containing the evenly dispersed particles of \( \text{Al}_\text{X}Zr \) has helped to suppress recrystallization and aid in desired grain refinement 5000 series alloys. It is unclear, however, the extent to which these \( \text{Al}_\text{X}Zr \) particles can actually pin grain boundaries. Based on a grain boundary interaction with a particle through a Zener drag process, zirconium can play an active role in pinning boundaries, although that effect may be minimal compared with that of larger
precipitates [41-43]. Zener drag is, among other parameters, dependent on particle size and spacing for effective interactions that can pin high angle grain boundaries [44]. The Zener drag pressure ($P_z$) can be modeled [45] in a precipitate system by:

$$P_z = \frac{\beta \gamma f}{r}$$

where $\beta$ is a constant, $\gamma$ is the surface tension term, and $f$ and $r$ are the volume fraction of and distance between precipitates, respectively. Although the $\text{Al}_8\text{Mn}$ particles are large enough to effectively fill this role, $\text{Al}_2\text{Zr}$ particles may be too small to perform this function to any great extent [26]. These $\text{Zr}$-based particles can certainly interact heavily with dislocations, however, and as such may perform an important role in substructure development by interacting with arrays of dislocations that can eventually limit grain and subgrain size. Work by Kannan at. al. [45] demonstrated that $\text{Zr}$ acts synergistically with Mn in promoting fine grain sizes. Their experiment in a low Mn

![Figure 3.8](image_url)

**Figure 3.8**: Precipitate radius of $\text{Al}_2\text{Zr}$ annealing time at 460°C, demonstrating a square root dependence on time.
5083-based alloy actually revealed an increase in grain size by 10% with a 0.2 wt% addition of Zr. Additions of Zr in the same amount to an alloy with a higher Mn content, however, actually lowered grain size by three times the percent that the higher Mn content did alone. Results of the stability, or retained hardness, shown by this experiment are given in Figure 3.9 [45].

It should be noted that the superplasticity development in 5000 series alloys has depended greatly on a large amount of cold work [40] prior to any final annealing process used to stabilize a highly refined grain structure. Such studies have also attempted to correlate additional precipitation structure to changes in strain hardening characteristics and the associated transition point for strain rate sensitivity in highly deformed Al alloys [46]. At low strain rates (or increasing temperatures), climb is

---

**Figure 3.9**: Hardness variation with time for 5083-based alloys containing 0.2 wt% Zr and/or excess Mn.
easier and the work hardening rate does not increase to levels which will cause premature failure of a material undergoing deformation. At high strain rates (above the "transition point"), dislocations accumulate as geometrically necessary dislocations at barriers, leading to large increases in work hardening rates [47] and possible fracture during elongation. For the purposes of this particular study, the amount of cold work is limited by comparison as superplastic characteristics are not of primary interest, although the interaction between Al₃Zr precipitates and mobile dislocations is very germane to the ultimate development of strengthened 5000 series alloys. In actuality, the formation of fine Zr-containing particles, Al₃(Sc,Zr), which are discussed in further detail later in this chapter, have been shown to contribute to refined grain sizes even with comparatively low levels of cold work than the 5:1 reduction often prescribed for superplasticity characteristics [39].

The positive effects of Zr on Al-Mg-Mn alloys is not limited to that particular system; questions over the effectiveness of Zr as a grain refiner have also been addressed in other Al-alloy systems. Nieh [48] showed that additions of 0.6 and 0.7 wt% Zr to alloys 2124 and 7475 greatly increased the ability of those alloys to undergo high strain rate superplasticity (HSRS). HSRS is a phenomenon that inherently requires an extremely fine grain structure in order to allow the necessary elongations through grain boundary sliding [40]. Chinh et al [49] also demonstrated that Zr additions of 0.12 wt% contribute a strong grain refining effect to Al-5.7%Zn-2.0%Mg alloys in superplasticity studies. The 2000 and 7000 series alloys displaying positive Zr contributions differ from the Al-Mg-Mn alloys in that they are moderately heat treatable. As such, they are dependent on a totally different mechanism for the bulk of their strengthening properties when compared to the non-heat treatable alloys, which include those of the 5000 series.
3.5.3 Scandium Additions

Studies of the effects of scandium on final material properties of aluminum alloys have been carried out since the early 1980's by groups of Russian scientists. These studies have noted the potential strength increases not only in Al-Sc binary systems, but also when Sc is added to existing alloy systems such as the popular Al-Mg-Mn 5000 series [50]. The impressive gains made through Sc additions, both to CP Al and to Al-Mg systems, is shown in Table 3.1 [51]. There is a distinct similarity in precipitate size and structure with that of Al-Zr systems as well as in the associated hardening improvements that have been demonstrated. Sc precipitates form from the decomposition of an Al-Sc supersaturated solution in the form of Al₃Sc particles, having a face-centered structure (space group Pm₃m) with a lattice parameter of 0.4106 nm, as a eutectic transformation at 655°C. The speed of transformation is quite high; the rapid coagulation of Sc atoms is several orders of magnitude higher than that of other transition metals [52]. Sc-based precipitates are like Zr-based precipitates: they are

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Sc. wt-%</th>
<th>Mg. wt-%</th>
<th>Density, g cm⁻³</th>
<th>Yield strength, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation, %</th>
<th>Hardness, HV10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-0.25Sc</td>
<td>0.23</td>
<td>...</td>
<td>2.702</td>
<td>126</td>
<td>138</td>
<td>24</td>
<td>40</td>
</tr>
<tr>
<td>Al-0.5Sc</td>
<td>0.56</td>
<td>...</td>
<td>2.692</td>
<td>277</td>
<td>287</td>
<td>21</td>
<td>71</td>
</tr>
<tr>
<td>Al-0.75Sc</td>
<td>0.77</td>
<td>...</td>
<td>2.694</td>
<td>322</td>
<td>347</td>
<td>19</td>
<td>97</td>
</tr>
<tr>
<td>Al-1.1Sc</td>
<td>1.14</td>
<td>...</td>
<td>2.687</td>
<td>346</td>
<td>352</td>
<td>15.5</td>
<td>114</td>
</tr>
<tr>
<td>Al-2Sc</td>
<td>1.9</td>
<td>...</td>
<td>2.699</td>
<td>238</td>
<td>393</td>
<td>20.7</td>
<td>120</td>
</tr>
<tr>
<td>Al-1.1Sc-6Mg</td>
<td>1.13</td>
<td>5.39</td>
<td>2.622</td>
<td>526</td>
<td>548</td>
<td>9.2</td>
<td>156</td>
</tr>
<tr>
<td>Al-1.9Sc-6Mg</td>
<td>1.93</td>
<td>5.47</td>
<td>2.628</td>
<td>567</td>
<td>595</td>
<td>13.1</td>
<td>172</td>
</tr>
</tbody>
</table>

Table 3.1: Some experimentally obtained properties for Sc- and Mg-containing aluminum alloys.
not only more effective than other transition metals in the overall increase in precipitation hardening seen when alloyed with aluminum, but are also more adept at producing and stabilizing a finer grain structure [53]. Sc is superior to Zr (and all other transition metals, for that matter) in that it is the most potent strengthener known in Al-based systems [54].

The \( \text{Al}_3\text{Sc} \) particles that form in the \( \alpha \)-aluminum matrix following a normal processing sequence are on the order of 50-90 nm in diameter [31, 39] for dilute solutions and, like \( \text{Al}_3\text{Zr} \), are spherical in shape. Heavy interactions with dislocations have an apparent significant effect on microstructure by helping to stabilize low angle (less than 4-5°) subgrain boundaries. This subgrain boundary observation was supported by Nieh et. al. [48], who also attributed grain boundary pinning to \( \text{Al}_3\text{Sc} \). It should be noted, however, that the study by Nieh was performed on an Al alloy that was Mn-free. The sequence of events he describes (a 91% cold work reduction, subgrain formation during annealing treatments, and finally conversion of low-angle subgrains to high-angle grain boundaries under dynamic conditions at elevated temperatures) might infer that \( \text{Al}_3\text{Sc} \) particles were the primary grain-pinning vehicles. This conclusion might well be based on the fact that they were the only secondary phase and hence were instrumental in forming the subgrain structure. That scandium can have a grain refining effect to alloys that have received higher levels of cold work cannot be argued, based on recent work. While again it may not have a grain boundary pinning effect on alloys which have received low levels of cold work and hence have had limited opportunity to interact with dislocations, the effectiveness of scandium particles on alloys that have undergone extreme grain-refinement procedures has been aptly demonstrated. Such a extreme treatments would include equal-channel angular pressing (ECAP); a study which investigated ECAP grain refinement in an Al-3%Mg-0.2% Sc alloy showed final grain sizes of about 0.2 \( \mu \)m, from initial grain sizes of 200 \( \mu \)m prior to ECAP [55]. An important aspect of this study was the determination of the most effective heat

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treatments for maximizing the effective distribution of Al₃Sc particles. Without an appropriate solution heat treatment, the fine distribution of Al₃Sc particles cannot be achieved, as not enough of the available scandium goes into solution and subsequently nucleates upon cooling. As the purpose of grain refinement in this study was to achieve superplastic properties in the alloy, the lower bound to the solutionizing temperature is demonstrated by the final elongation to failure of the material, which is directly related to the degree to which fine grain sizes have been achieved. The solutionizing temperature limit lies between 873 and 878 K for the most effective distribution of Al₃Sc particles. Of course, this “solutionizing limit” is also based on the concentration of scandium in the alloy. As shown in the Al-Sc binary phase diagram of Figure 3.10, the eutectic temperature is only slightly below the melting point of aluminum. For hypereutectic alloys, even only to a slight degree (>0.55 wt% Sc), nucleation and growth of Al₃Sc particles is far more developed with regard to size and shape in the as-cast microstructure. Extended times at or near the eutectic temperature can lead to the growth of much more complex Al₃Sc primary particles [56, 57] that are highly effective in refining grain structure during solidification of the alloy.

Studies have also shown that the precipitation process in the Al-Sc binary system can actually make the alloy age-hardenable, although this effect occurs in alloys with amounts of Sc far in excess of those that would be investigated in this study (1 wt% and greater vs. less than 0.2 wt%, respectively) [54]. One example of this type of behavior is clearly shown by the increases in strength over time demonstrated in Figure 3.11 [58].

The precipitates that were produced in the higher Sc alloys formed in a variety of shapes. In addition to spherical geometries, rod-shaped and dendritic precipitates were predominant. Blake [54] notes that these shapes are analogous to those found in aged, chill cast Al-Zr and Al-Hf alloys; both of which form a similar metastable L1₂ structure in the early stages of precipitation. It is interesting to note that for high-Mg
alloys, it has been shown that the optimum level of Sc in this system is only about 0.15%. Although even these small additions provide impressive increases in strength, further additions hardly provide an increase in measurable properties [59]. This range is surprisingly close even for binary Al-Sc systems; the maximum strength or hardening increases occur at 1 wt% Sc or less [50].

An interesting aspect of the thermal stability of these precipitates lies in the elevated temperatures that are required to cause extensive precipitation growth. As was mentioned in the previous section, much of the literature that deals with Zr- or Sc-containing 5000 series alloys is interested in the development of superplasticity. The focus of studies that evaluate the precipitates of Sc and Zr, therefore, is to determine the effects of these elements on the recrystallization and recovery processes. The ultimate goal is to limit recrystallization at elevated temperatures in order to retain

![Figure 3.10: Dilute scandium region of the Al-Sc binary phase diagram showing the phase equilibrium compositions for $\text{Al}_3\text{Sc}$ formation.](image)

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refined grain sizes. The ability of Sc precipitates to retain bulk hardness levels over the course of an elevated temperature (artificial) age is demonstrated in Figure 3.12 [31].

It is incumbent on the precipitates to retain their effectiveness in interacting with dislocations even through any final stabilizing annealing treatments. While Zr has a tendency to coarsen and lose coherency even at only moderately elevated temperatures, AlSc has shown a tremendous amount of thermal stability, demonstrating proficiency at resisting coarsening effects even at temperatures approaching 450°C. The particulate structure has shown the ability to retain a completely non-recrystallized microstructure in cold rolled sheets annealed at temperatures of 300-400°C and higher [60]. Additionally, the particles have retained coherency up to temperatures of 550°C [60] and particle sizes of 1160Å [61].

![Graph](image)

**Figure 3.11**: Aging response of Al-0.54Sc and Al-4Mg-0.56Sc at 561 K.
The scope of Sc strengthening effects go beyond those in the binary system or even in the window of 5083-type alloys. Promising effects on hardening characteristics attributed to minor Sc additions (up to 1 wt%) were demonstrated in a wide range of Al alloys that contained various amounts of Mg, Zn, and Ag [62].

The positive effects of Sc additions are not limited to the potent strengthening effects. Alloys with minor Sc additions have displayed improved hot cracking resistance during welding along with enhanced weld strength. These improvements were observed in both weld filler and base material; the alloys studied included 2000, 5000, 6000, and 7000 series alloys [63]. Additionally, industrial practice in high-grade applications has demonstrated that Sc additions contribute to improved weldability. Additions of Sc have been shown to densify the grain structure in welded joints, leaving a joint that is fine grained and more resistant to hot cracks [60]. Sc additions have also demonstrated improved fatigue strength in a variety of alloys [53].

![Graph showing hardness as a function of time](image)

**Figure 3.12:** Change in hardness as a function of time at 300°C for Al-4Mg-1Mn with and without 0.3 wt% Sc. The hardness for Sc-containing alloy levels off after ~1000 s.
3.5.3.1 Scandium + Zirconium

With the amount of study that has gone into various levels of scandium and zirconium and their effects on microstructural behavior, it should be noted that there is evidence in the literature to support an enhanced, if not synergistic, effect on final bulk properties in alloys which contain both Sc and Zr [52, 63]. Elagin [52] reports that to maximize the effects of the Sc-based precipitates, Zr can be added in levels of up to 50 at% of Sc. Increased resistance to recrystallization as well as improved overall thermal stability has also been reported when chemistry contains amounts of both Sc and Zr in amounts such that an $\text{Al}_3(\text{Sc},\text{Zr})$ particle can precipitate.

Reports have made the assertion that the $\text{Al}_3(\text{Sc},\text{Zr})$ particle is finer and even more thermally stable than $\text{Al}_3\text{Sc}$ particles, maintaining a large fraction of strength levels above annealing temperatures of 350°C [24]. An illustration of the synergistic effect of Sc and Zr added together is clearly demonstrated in Figure 3.13 [64]. The

![Figure 3.13](image-url)

**Figure 3.13**: Volume fraction of recrystallized material for aluminum alloys containing Zr, Sc, or Sc+Zr.
combined effect in preventing recrystallization is far superior to that of either element added alone. A higher tensile ductility and higher microcrack propagation resistance has also been attributed to the presence of coherent Al$_3$(Sc,Zr) particles.

Additions of Zr to Sc-containing Al-alloys has also been reported to instigate changes in the as-cast microstructure. In the presence of Zr, a non-dendritic structure is formed in cast billets with an Sc content of 0.2 wt%. Without Zr, a non-dendritic structure is observed only when the alloy contains hypereutectic (above 0.5 wt%) additions of Sc [52].

3.5.3.2 Scandium + Additional Alloying Elements

Other alloying elements that are soluble in the Al$_3$Sc particle include titanium and hafnium. The Ti atom can replace the Sc atom in Al$_3$Sc, although the solubility is significantly less than that of Zr. Ti may not actually strengthen the effect of Sc in the manner which Zr does, but it does have the ability to reduce the critical amount of Sc required to procure Sc’s modifying effect [52].

Unlike Ti, additions of Hf will enhance the strengthening effect of the Sc-based precipitates. Hf can be added in amounts of up to 50 at% of Sc to become part of the Al$_3$Sc unit cell. The result of this addition is, like Zr, a synergistic strengthening effect following the decomposition of the solid solution as well as an overall increase in recrystallization temperature [52]. Hf appears initially to be a positive contributor to the desirable effects of Sc additions, but it is unclear where the threshold lies for maximum or most-efficient additions.
3.6 Strengthening Results and Discussion

3.6.1 Manganese

3.6.1.1 Background on Manganese Behavior

As described earlier in this chapter, the common Al\textsubscript{6}Mn dispersoids found in Al-Mg-Mn alloys play an important role in overall microstructural development. For the purpose of this study, the development of the manganese particle substructure will be investigated with an eye toward maximizing the dispersion of particles in a "pre-processed" condition. These particles will subsequently provide a major contribution to grain and subgrain size and shape following industrial hot- and cold-working processes. The goal, therefore, will be to study "preheat" treatment on as-cast material in order to develop a relationship between these treatments and Mn-based particle dispersion.

In an as-cast state, the two most common forms of the manganese particles are the large ECs that take on the "Chinese script" morphology and the pill- or plate-shaped dispersoids. While the ECs appear in the manganese-rich dendritic arms of the solidification structure at the eutectic composition, the pill-shaped dispersoids appear at a later stage; whether during cooling from melt temperatures, homogenization anneals, or during elevated hot working processes. Several processes will occur in relation to the manganese particles during the processing sequence of the material. The ECs will be broken up and re-distributed along the rolling direction in stringers of large, blocky particles. While the resulting particle distribution has the potentially beneficial effect of refining grain size, both through particle-stimulated nucleation (PSN) in the local high energy regions surrounding the particles following cold work and through simple
pinning of migrating grain boundaries, the particles also are a detriment to material properties. Particularly in sheet applications, these sharp-edged, brittle particles can adversely affect formability. This property is directly related to the density of these coarse constituent particles observed in the final gauge sheet [65]. Additionally, the loss of manganese to the highly enriched dendritic regions during solidification effectively reduces the amount of manganese left in solution to contribute to the overall volume fraction of the potentially beneficial pill-shaped dispersoids.

The benefit to grain refinement of the pill-shaped Al$_6$Mn particles is a product of the Zener drag pressure exerted on the migrating grain boundaries. This pressure, as outlined earlier, is a product of the volume fraction of particles and the particle radius. Increased numbers of these particles lead to a decrease in overall mobility of grain boundaries and decreased final grain size of wrought material [66]. The size of these particles can also have an effect on the dynamic recrystallization properties of the material. When these particles reach a size greater than 0.6-0.75 μm, they are large enough to store enough local energy to allow recrystallization to occur in a dynamic condition [31, 67, 68]. In smaller sizes, they can also help to stabilize subgrain structure.

Figure 3.14: Commonly-seen Al$_6$Mn particles decorating grain boundaries.
Figure 3.14 shows an example of the commonly observed grain boundary interaction with the distribution of Al$_6$Mn particles.

The goal of the following study is twofold; one, to minimize the amount of ECs that are present in an as-cast microstructure following experimental homogenization treatments, and two, to maximize the most efficient distribution of the pill-shaped Al$_6$Mn particles from the standpoint of both volume fraction and homogeneous distribution.

### 3.6.1.2 Experimental

For the purpose of this study, several alloys were tested based on the common Al-5083 chemistry. As the intent of the study is to illustrate a general behavior for this class of alloys, the exact composition of each alloy tested is not necessary. Designated Alloy A and Alloy B, the detailed individual chemistries will not be revealed due to proprietary considerations. Information on the chemistry analysis for the constituents of concern in each alloy is listed in Table 3.2. Each of the alloys studied in this section are observed entirely in an "as-cast" state; i.e no further processing steps were instituted beyond solidifying the ingots using a direct chill process. Each of the samples observed are taken from actual production alloys produced at Pechiney Rolled Products, removed

<table>
<thead>
<tr>
<th></th>
<th>Mn</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloy A (5083)</td>
<td>0.76</td>
<td>0.09</td>
</tr>
<tr>
<td>Alloy B (5083)</td>
<td>0.85</td>
<td>0.08</td>
</tr>
</tbody>
</table>

*Table 3.2: Compositions of test alloys with varying levels of Mn and Cr.*
from full-sized ingots prior to any further homogenization treatments or hot and cold work reductions. The significance of this study, therefore, is that any reaction to heat treatments given to the material are representative of the behavior that could be expected in actual production ingots. Of course, there is some deviation expected due to thermal mass constraints (full-sized ingots take longer to heat up through the thickness of the material) and furnace heating constraints (time to equilibrate temperature will be longer), but microstructurally and compositionally speaking this study is a good representation of production alloy response to the different preheat treatments given, although applied in a small-scale laboratory environment.

An initial and rapid testing method for the level of manganese in solution for alloys that have received a preheat treatment is the eddy current conductivity test using a Zetec DC-2 conductivity probe. Units are measured in terms of values normalized as a percentage of the international annealed copper standard (%IACS). Conductivity will necessarily behave as the reciprocal of resistivity, which will change according to the Nordheim rule

\[ \rho(T) = \rho_{Al} + \sum K_i C_i \]

where the \( \rho \) terms are the total resistivity at temperature \( T \) and the resistivity of pure aluminum, respectively. The final summation term includes \( C_i \), which represents the atomic concentration of solute elements that remain in solution while neglecting the resistivity due to primary particles (Al\(_2\)Mn).

TEM and SEM study in this section was carried out on the Philips CM200 and the Philips XL-30FEG, respectively.
3.6.1.3 Reduction of Eutectic Constituents

Again, it should be stated that the objective for this portion of the study is to delineate the behavioral changes that are possible through treatment of as-cast material. In the case of ECs, solidification parameters would have the most profound effect on the ability for the cast microstructure to contain highly enriched zones that reach eutectic concentrations in the inter-dendritic regions. A faster solidification rate would reduce the time available for diffusion to transport manganese before the solidification interface. Novel approaches have been discussed for agitation of melt pours for the purpose of mixing dispersoids during casting [70]; such techniques might also be effective in reducing concentration gradients in the melt through more complete mixing steps during the direct chill process.

Over the course of an effective solutionizing or homogenization treatment, it is expected that conductivity will go down (i.e. resistivity will increase as the $C_i$ term increases) over the course of exposure to elevated temperatures as more manganese particles dissolve and are driven back into solution. In truth, a full re-solutionizing of the ECs is not an expected outcome for several reasons. First, it is difficult to ascertain where the solubility phase field exists for this alloy; the $\text{Al}_5\text{Mn}$ eutectic is a stable structure that may only be soluble in temperatures extremely close to the melting point. Second, the diffusion rate of manganese in aluminum is particularly slow even up to these elevated temperatures. The as-cast microstructure also is marked by larger grains, which would necessitate even longer-range diffusional processes to occur. Still, there are reports [71] of the annealing effect of elevated temperature on the as-cast constituents that demonstrate some degree of spheroidization to the extended script-like particles. The solubility of manganese in aluminum being as low as it is, as can be seen from the Al-Mn binary phase diagram shown in Figure 3.15 [72], we might expect some
Figure 3.15: Al-Mn binary phase diagram reveals the narrow phase field for Mn solubility.

demonstrated changes in the preheated as-cast distribution of the manganese particles.

Three samples of slightly different compositions, all well within the normal manganese range for 5083 alloys (including Alloys A and B, shown in Table 3.2), were given an extended heat treatment at 1100°F in order to facilitate this decrease in conductivity due to increased fraction of manganese in solution. Following the incremental times at the solutionizing temperature, samples were quenched and subsequently cut in half to reveal a clean surface area well distant from the exposed surface of the material. Conductivity measurements were recorded from each exposed face of the cut samples; the averages of these values are graphed in Figure 3.16.
Obviously, the expected decrease in conductivity, which would correlate to an increase in the level on manganese in solution, is not seen. Quite to the contrary, the conductivity continued to increase steadily over the entire period of exposure. Clearly the behavior demonstrated through these measurements indicates that the eutectic constituents prevalent in 5083 are not re-dissolving to any great extent within the matrix.

Magnified SEM images of the exposed samples (Figure 3.17) support this observation, as the script-like shapes of the large ECs that are prevalent following solidification (Figure 3.17) are still prevalent (Figure 3.18) even following the most extreme times at the elevated temperature. Also demonstrated in these images are a

![Graph](image)

**Figure 3.16**: The increase in conductivity over time at 1100°F indicates a decomposition of the solid solution.
Figure 3.17: The as cast microstructure demonstrates the presence of the eutectic constituents in a uniform, precipitate-free matrix.

number of additional pill-shaped precipitates in a size range of 2-4 μm that have formed over the course of the preheat treatment. It is evident, then, that the change in conductivity which indicates a reduction in the amount of manganese in solution is due to additional dispersoid nucleation and growth. This phenomenon is made even more clear in the sequence of SEM images of Figure 3.19, in which the growth of large numbers of these Mn-based precipitates is quite obvious. Preheat treatments, therefore, do not decrease the size and shape of primary ECs, but rather lead to the growth of additional precipitates - a phenomenon which leads directly to the behavior detailed in the next section.
Figure 3.18: Extended heat treatment from an as-cast state reveals the growth of needle-shaped Al₆Mn precipitates up to 10 μm in length.
Figure 3.19: Precipitation of Al₆Mn particles from as-cast samples; note the denuded regions around the eutectic precipitates.
3.6.1.4 \textit{Al}_6\textit{Mn} Particles

Further investigation must be made into the presence of these additional particles that form over the span of the heat treatments outlined above. As has been described in previous sections, additional dispersoids can be extremely beneficial to the desired material properties of interest such as strength and refined grain size.

It cannot be assumed, however, that the path to the most desirable \textit{Al}_6\textit{Mn} distribution is extraordinarily long periods of time at elevated temperatures prior to hot line processing. Just as with many heat-treatable aluminum alloys, there exists an optimal window of temperature and time to achieve the best possible distribution of precipitates with respect to both size and interparticle spacing. Additionally, there is a factor of the time and resources involved to achieve the properties of interest without sacrificing additional effort in exchange for diminished improvements. To further extricate information concerning the optimal balance between \textit{Al}_6\textit{Mn} dispersion and time/temperature parameters, conductivity measurements were again used to gain information on dispersoid morphology. A pseudo time-temperature-transformation plot was generated in order to achieve this endeavor, using information gained from conductivity measurements over time at different temperatures, example results of which are illustrated in Figure 3.20. To give some perspective on the conductivity changes shown, consider that in a fully processed state conductivity values approach 34-36 %IACS for similar 5000 series alloys depending, of course, on the alloy composition. How a small increase in %IACS is reflected in microstructural characteristics (particularly precipitate structure) is the most important focus of this section of the study. Figures 3.21 and 3.22 show the plots of Alloys A and B (additional tests on like alloys were similar in shape) over a span of time at different temperatures. Since the
Figure 3.20: Graph of conductivity vs. time for one of the 5083 samples preaged at the temperatures shown.

The plot is not depicting an actual phase transformation, it is not a TTT diagram per se; rather it is an illustration of the level of decomposition of the solid solution at given temperatures and times. Each of the lines represents an iso-conductivity level, which directly corresponds to the amount of manganese left in solution.

The importance of such a diagram is that it clearly illustrates the optimum temperature and time to reach a certain level of saturation in the aluminum matrix. Since there exists a “nose” on the time/temperature axes, the optimum level of decomposition is *not* achieved at the highest temperature for the longest time. In this case, the most rapid decomposition on the supersaturated solid solution from an as-cast state occurs at around 950°F, regardless of the “end” conductivity level desired.
Figure 3.21: Diagram showing iso-conductivity profile for decomposition of Alloy A.
Figure 3.22: Diagram showing iso-conductivity profile for decomposition of Alloy B.
Figure 3.23: Conductivity measurements of 2 samples taken prior to TEM investigation.
Of course, conductivity does not give a direct measure of the particle size and distribution within the matrix. As illustrated via TEM investigation (Figures 3.24-3.29), following direct conductivity measurements for the samples observed (Figure 3.23), for a given conductivity level the size, shape, and interparticle spacing varies greatly over the ranges of heat treatments. Furthermore, it can be seen from the Figure 3.24 and 3.29 images at lower magnifications (images on upper right) that a true "homogenized" microstructure does not exist. Clear bands of dense distributions of particles can be seen extending through the width of the foil, indicating that the distribution of particles is still segregated into distinct areas of the matrix. Precipitates are often observed in a banded substructure in sheet metals. This structure is attributed to the application of cold work to the material, but in the case shown in the figures of this study, an as-cast material, no cold work has been applied. It must therefore be concluded that the short-range diffusion limit of manganese in aluminum constricts the formation of these excess particles to the interdendritic regions of the solidified material where manganese enrichment is greatest.

The effect of this type of distribution will have a distinct contribution to the eventual substructure of the processed material with regard to the roll bands that will form. These pill- or plate-shaped dispersoids will tend to orient themselves with the "plate" normal parallel to the normal of the rolling direction [31]. As a result, the cross-sectional radius of the precipitates and their local volume fraction will be extremely effective at preventing grain boundary migration in a direction normal to the rolling plane. This contributes to the continued flattening of grains, a physical characteristic that can lead to geometric dynamic recrystallization (GDRX) where serrated grain boundary edges are pinched together and annihilate [67], which can subsequently lead to a refinement of the otherwise pancake-shaped grain structure.

Returning to the issue of particle size, shape, and distribution based on preheat treatments, a study was carried out based on specific preheat treatments tailored for the immediate onset of the hot work cycle upon completion of the treatment. As was
Figure 3.24: 875°F treatment - Alloy A.
Figure 3.25: 925°F treatment - Alloy A.
Figure 3.26: 1000°F treatment - Alloy A.
Figure 3.27: 875°F treatment - Alloy B.
Figure 3.28: 925°F treatment - Alloy B.
Figure 3.29: 1000°F treatment - Alloy B.
previously delineated in Figures 3.23-3.29, three temperature ranges were investigated, 875°F, 925°F, and 1000°F. The times given to each sample at the appropriate temperature are listed on the respective axes. Following each of these heat treatments, the conductivities for each temperature and time were recorded (Figure 3.23); again, the trend in conductivity demonstrates to now-expected decomposition of the Al-Mn solution. TEM investigation was carried out in order to correlate times, temperatures, and conductivity measurements with dispersion characteristics, the results of which are shown in the correlating figures. Note the overall increase in average particle size as the time at each temperature increases. Regardless of the alloy or temperature, as the preheat time increases the average particle size also increases. Small particles may be seen in several of the longer preheat times, but it is believed that these particles are additional precipitates that have nucleated and are also growing — a concept which will be explained further later in this section.

It is important to note from the outset that one of the major constituents in the particle distribution are extremely long needle-shaped precipitates in excess of 1 μm. These particles are present at each of the heat treatment levels, but are difficult to quantify effectively due to their random distribution with regard to TEM size scales. It should be noted, however, that these particles do, in fact, increase in length over the course of the heat treatments given. For a more qualitative evaluation, we will look more closely at the distribution of sub-micron-sized particle dispersion and attempt to illustrate the growth of these precipitates following their nucleation. One of the observations worth identifying is the lack of a singular nucleation event for the dispersion of AlₓMn. As the micrographs show, there appear to be secondary and tertiary nucleation events which contribute smaller particles to the overall distribution. The increased particle density over the length of the heat treatment would indicate that these smaller particles are not, in fact, precipitates that have lost atomic mass to larger precipitates due to a surface energy reduction process (ripening), but are indeed additional
precipitates that have nucleated. Consider, then, that the nucleation and growth of Mn-based precipitates does not follow a single, widespread, nucleation event, but rather a series of nucleation events. The "secondary" nucleation events will occur at much lower levels of Mn saturation, so the opportunity for growth is limited. Likewise, further (tertiary) nucleation events will have even less of a saturation state from which to draw Mn atoms, and as such are decreasingly significant contributors to final precipitate structure. The two alloys with near-5083 composition are evaluated in terms of precipitate size (diameter) over the course of preheat treatments ranging from 14 to 80 hours at the temperatures shown. In order to more closely mimic an industrial preheat process, the samples were held at 650°F for 4 hours prior to exposure to the preheat temperatures listed.

It can be seen from Figure 3.30 that the growth of Al₆Mn particles coincides with the increases in conductivity for the given temperatures. As expected, 925°F gives a faster rate of growth of precipitates over the period of time shown; raising or lowering of the preheat temperature to any significant degree will only slow the growth kinetics of Al₆Mn. Note the growth of secondary precipitates delineated by dashed lines on each of the graphs. The lower temperature preheats display a greater propensity for secondary nucleation and growth than does a 1000°F preheat, quite possibly due to the easier long range diffusion of Mn at the elevated temperature. It should be duly noted that Figure 3.30 is a representation of average long-axis measurements of Al₆Mn particles for what was deemed to be a representative number for each treatment given. While the particle diameter values shown in Figure 3.30 do not give the reader a feeling for the wide range of actual particle sizes measured for each treatment, they are a suitable representation for the "average" size computed from measurements of a large number of particles. In effect, the values represent a peak for a Gaussian-type distribution of Al₆Mn particles for each condition. Maintaining a preheat temperature of 875°F reveals a distribution that is much smaller in size than the other treatments given, both
Figure 3.30: Resulting mean particle diameter for Mn-based particles following preheat treatments.
for primary and secondary precipitates, but one must remember that there is a minimum size at which these particles can be expected to provide a grain-refining effect. As was mentioned earlier in this chapter, several authors have given indication that for $\text{Al}_6\text{Mn}$ to provide any appreciable barrier to grain boundary migration, a mean particle diameter of 0.6 $\mu$m is necessary. While that figure has not been evaluated for these particular alloys, it is clear that the most efficient temperature for achieving some minimum particle size and distribution in an as-cast microstructure is between 900-950°F.

### 3.6.1.5 Manganese Behavior Summary

Of considerable importance to overall grain refinement in 5083-based alloys is the distribution of manganese ($\text{Al}_6\text{Mn}$) particles in the cast microstructure prior to hot and cold work of the material. This distribution can be greatly influenced by post-solidification (preheat) treatments prior to commencing hot work operations. For this reason, preheat treatment could conceivably provide an enhanced effect on grain and subgrain refinement during subsequent hot and cold working stages of the processing sequence. In terms of maximizing the efficiency of these preheat treatments, a basic understanding of the time and temperature relationship for $\text{Al}_6\text{Mn}$ morphology is outlined.

1. Lines of iso-conductivity reveal the most rapid decomposition of the Mn-saturated solid solution will occur at or near 950°F for the Al-5083 alloys studied.

2. TEM investigation reveals that small increases in conductivity measurements do, in fact, correlate to decomposition of the supersaturated solid solution via $\text{Al}_6\text{Mn}$ nucleation and growth.
3. TEM investigation also supports the results of the conductivity measurements by demonstrating the growth of Al₆Mn particles over the course of preheat treatments at different times and temperatures. Heating at 925°F demonstrates not only a faster growth of “primary” Al₆Mn particles, but also more rapid nucleation and growth of secondary and tertiary precipitates.

3.6.2 Microalloying Additions — Zirconium and Scandium

In contrast to the previous section, which dealt with potential microstructural and physical properties based on heat treatments to existing compositions, this section will investigate the effects of alloying elements added to the base 5083 material in levels not to exceed 0.15 wt%. The effect of these extremely small additions will provide a focus of study into the behavior of the material when modified by an extremely fine dispersion of additional precipitates.

It must be made clear that unlike the previous study, which made observations on actual industrially-cast material, this study is carried out on “custom” castings of specifically-engineered composition. While certainly based on standard 5083, the ingots cast for this study were done so under contract at the Reynolds Aluminum Corporation, and contained the following chemistries for direct study of any strengthening effect realized through minor additions of scandium and zirconium (Table 3.3). Since the as-cast microstructure is of little interest for this portion of the study, the following processing schedule was employed to produce an H31-type temper:

- **Preheat** - 920°F
- **Hot Roll** - 400+/-50°C for a reduction ~90%
- **Cold Work** - 18% reduction
## Composition - Reynolds-Cast Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>%Mg</th>
<th>%Mn</th>
<th>%Zr</th>
<th>%Sc</th>
</tr>
</thead>
<tbody>
<tr>
<td>5083</td>
<td>4.66</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5083+Zr</td>
<td>4.81</td>
<td>0.54</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>5083+Sc</td>
<td>4.63</td>
<td>0.56</td>
<td></td>
<td>0.099</td>
</tr>
<tr>
<td>5083+Sc+Zr</td>
<td>4.63</td>
<td>0.59</td>
<td>0.13</td>
<td>0.096</td>
</tr>
</tbody>
</table>

Table 3.3: Compositions of 5083 alloys modified with Zr and Sc.

The hot work reductions started at approximately .05 inches/pass, decreasing to .01 inches/pass over the course of the hot working cycle as the material thickness was reduced, based on rolling mill power constraints. Reductions for cold work remained at .01 inches/pass. The work on this material will concentrate on classifying the precipitation structure and subsequent microstructural behavior of Zr and Sc when added to Al-5083 in small amounts. Rather than evaluating the effects of these additions on grain size and shape, the focus will be on material that has received a thermo-mechanical treatment schedule similar to that used in the industrial processing of 5083 sheet. A hot work schedule followed by a minor cold work addition will be the extent of the processing which is performed on each sample, hence a heavily modified grain and subgrain structure is not expected. This particular work will investigate not only
Figure 3.31: (a) Dark-field image of Zr-based particles (b) Diffraction pattern demonstrating the common [100] orientation in matrix and precipitates. Several \{100\} and \{110\} superlattice reflections from the precipitate are indicated.
the microstructural effects of minor Zr and Sc additions to a baseline 5083 chemistry, but also to investigate the effect of adding the two elements in concert.

3.6.2.1 Microstructural Characterization

3.6.2.1.1 Zirconium Additions

The 5083 + Zr alloys show a much wider distribution of precipitate sizes within the matrix, although the sizes seen are consistent with previous reports. Figure 3.31 shows an array of "coffee bean"-shaped Zr-based particles within an area of the matrix; the smallest are approximately 10-15 nm in size while the larger particles approach 60 nm. HRTEM imaging of diffraction contrast was difficult to achieve for Al-Zr, greatly limiting the ability to classify their coherency through high-resolution analysis. Selected area diffraction pattern analysis at several orientations confirmed that these particles are in the metastable cubic (L1₂) phase (Figure 3.31(b)). The stable tetragonal phase of Al-Zr is achieved only through elevated temperature exposure (>460°) for extended periods of time [36]. A common [100] orientation relationship exists between particle and matrix, while the size and shape distribution of the Zr particles varies widely, ranging between 10-60 nm in diameter. Although some subgrain structure is apparent in the microstructure, there appears to be very little interaction between particles and subgrains.

3.6.2.1.2 Scandium Additions

Scandium has been identified as a potent strengthener [50] in binary Al-Sc alloys, but its contribution in minor amounts to the 5083 system is largely unidentified. As shown in the micrographs of 5083+Sc, the Sc-based particles are relatively widely
Figure 3.32: (a) Sc-based particles (b) Cubic orientation between Al₃Sc and α-Al matrix.

spaced and range in size from 50-90 nm in diameter following the casting/processing sequence (Figure 3.32). Based on these observations of relative size, the Sc-based precipitates appear to have a larger propensity to coarsen even under the moderate processing sequence employed for these observations when compared to the Zr-based particles. Like the Zr-based particles, Sc-based particles do not appear to interact heavily with the observed subgrain boundaries. Note the proximity to a grain boundary of the Sc particles in Figure 3.33; no associated grain or subgrain boundaries appear to be interacting with the particles. Simple dislocation interactions are apparent, however, which would lend microstructural support to the observed strength increases even though the size of these secondary particles is quite small when compared to the commonly present manganese-based precipitates. An orientation relationship also exists between Sc-based particles and the matrix (Figure 3.32(b)), with [001]||[001] and {100}||{100}. 

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3.6.2.1.3 Zirconium + Scandium

A profound effect exists in precipitate structure when zirconium and scandium are added together. Although the macrostructural effects on bulk properties have been identified in published reports [44, 73], there has been little reported in terms of microstructural characterization to support these effects. Credit is given to the formation of Al₃(Sc,Zr) particles which are similar in structure (L₁₂) to both Al₃Sc and Al₃Zr, but are actually more potent as strengtheners and less susceptible to coarsening when exposed to elevated temperatures [74, 75]. As shown in Figure 3.34, the effect of the two elements in concert was to form a very fine, homogeneous dispersion of particles which remain in a very narrow size range; between 8 and 12 nm in diameter. Again, the particles demonstrate a lack of interaction (Figure 3.35) with the subgrain boundary.

Figure 3.33: Sc-based particles near a subgrain boundary. (a) Overall view (b) Higher magnification showing interaction with dislocations.
Figure 3.34: (a) $\text{Al}_3(\text{Sc,Zr})$ particles in vicinity of subgrain boundary (b) Diffraction pattern shows $(001) || (0001)$ orientation relationship between particle and matrix.

shown, as compared to the distinct interaction shown by the larger Mn-based particles in the figure. EDS confirmed previous reports [27] of the precipitate that at least the \{111\} planes are fully coherent between precipitate and matrix. In addition, apparent facets of the precipitate can be observed which are consistent with \{100\} habit planes for the particle/matrix interface. As with Sc- and Zr-based particles, they are too small to interact to any extent with grain or subgrain boundaries (as are the Mn-based precipitates shown in Figure 3.14), but the strengthening effect cannot be ignored.

High-resolution transmission electron microscopy (HRTEM) is quite helpful in determining the characteristics of these particles. Observation of one particle imaged in high resolution (Figure 3.36) mode demonstrates several of these important characteristics. First, there is a definite coherency between particle and matrix. Rather
than relying on diffraction contrast to determine the presence of coherency, HRTEM allows the investigator to determine coherency more directly, by actually observing the continuation of lattice fringes as they pass from matrix to particle and back again into the matrix.

A second benefit is the characterization of the crystal structure of the particle by comparing the HR image to a simulation produced by the EMS software developed by Stadelmann [76]. By assuming the suspected Al$_3$(Sc,Zr) composition and L1$_2$ crystal structure, it can be seen that the simulation (for a defocus value of 65 nm and a crystal thickness of 20 nm) correlates very well with the contrast seen in the image. The observed difference in contrast between particle and matrix is due to the (110) superlattice fringes that are present only in the particle. For this viewing direction, the
Figure 3.36: High resolution image of Al₃(Sc, Zr) particle in matrix. Note the continuity of atomic plane channels along matrix and particle. Lines parallel to apparent cubic facets are highlighted.
(111) lattice fringes are resolvable in both the matrix and precipitate; it is the superlattice fringe contrast that generates the contrast difference between particle and matrix. Hence, coherency of at least the {111} planes between particle and matrix is present.

Finally, such high resolution imaging also indicates an apparent presence of facets in certain orientations between the particle and matrix. Figure 3.36 shows a highlighted line parallel to these apparent facets which are consistent with {100} habit planes of the particle and matrix.

Studies have shown that the positive effects on strength levels due to scandium additions are increased significantly by adding zirconium as well [52]. The positive effects of zirconium on the hybrid Al$_3$(Sc,Zr) precipitates are limited to the maximum solubility of Zr in Al$_3$Sc. It has been estimated that levels of up to 50 wt% of Sc may be replaced by Zr, as excess Zr in the precipitates may lead to excessive coarsening of the particles. Although difficult to estimate the fractions of Zr and Sc in the particles identified and evaluated via EDS, the wt% of Zr in the alloy examined is actually 50% higher than that of Sc. No Al$_3$X particles containing Zr exclusively were detected, hence the excess Zr is either exceeding 50% in the Al$_3$(Sc,Zr) particles or, more likely, is actually providing some solid solution strengthening. The positive effect of Zr may actually be greater due to the fact that this alloy contains a relatively low amount of Sc. Scandium will show positive effects on strength up to levels of 0.6 wt %, while Zr has been shown to be beneficial for alloys having a lower Sc content (<0.2 wt%).

The effect of these additions on strength have been demonstrated by an outside source via tensile testing of samples of the material used for the TEM studies. An increase in yield strength of 8-19% for Zr additions, 10-20% for Sc additions, and between 16-28% for Sc+Zr additions was found even for the minor amounts added. The increases in ultimate tensile strength were similar (in terms of the effects of each
### Strength - Reynolds-Cast Alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>UTS</th>
<th>YS</th>
<th>% Elongation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5083</td>
<td>47.3 / 53.1</td>
<td>29.9 / 42.4</td>
<td>10.5 / 13.7</td>
</tr>
<tr>
<td>5083+Zr</td>
<td>49.0 / 54.2</td>
<td>36.9 / 46.2</td>
<td>7.6 / 14.5</td>
</tr>
<tr>
<td>5083+Sc</td>
<td>48.4 / 54.8</td>
<td>37.8 / 47.6</td>
<td>7.5 / 14.3</td>
</tr>
<tr>
<td>5083+Sc+Zr</td>
<td>53.1 / 56.6</td>
<td>41.6 / 50.9</td>
<td>4.5 / 12.9</td>
</tr>
</tbody>
</table>

**Table 3.4**: Strength and ductility data for modified alloys. The first set of numbers is for an unstabilized condition, the second set of numbers is following a 2 hour stabilization at 225°F.

Element added alone vs. the two added together) although not as great; at 2-3%, 2-3% and 6-10%, respectively (Table 3.4). More detailed analysis of the physical property changes of these zirconium- and scandium-modified alloys will be addressed in the next section.
3.6.2.2 Strength and Stability Testing

While the previous section discussed the qualitative increase in yield and ultimate tensile strengths, this section will provide a more detailed study of the effects of varying levels of scandium in 5083-based alloys containing zirconium. The level of zirconium will remain fixed at 0.13 wt% based on favorable results in precipitate distribution at this level and also based on using the Reynolds castings as base metal master alloys. Another reason for determining a more quantitative effect of varying scandium levels goes beyond the pure science aspect of this study; scandium is tremendously expensive as an alloying agent. Any gain in physical properties of material, from an industrial standpoint, must be great enough to overcome the increased production cost of the alloy. The cost factor is extremely sensitive in scandium-modified alloys. For the experiments over the course of this study, the cost of scandium cast in the original master alloys was $2200/pound [77]. Although the price of such rare metals is subject to large fluctuations on the open market, even at $2000/pound a 0.05 wt% addition to an aluminum alloy will immediately raise the production cost by $1.00/pound; a cost figure that includes nothing more than the addition of scandium and discounts increased wear and tear to capital equipment. This conceivably pushes the final price for such a modified alloy into the regime of high-performance aluminum alloys – able to command higher prices but limited in useful applications from a cost standpoint. Certainly such modifications are still useful for study; whether the final conclusions on increased mechanical properties justify increases in the final cost of the alloys remains to be seen.

The compositions used in this study are listed in Table 3.5. The reader should also take note of the fact that the alloys (being directly compared to a standard Al-5083 chemistry) also contain minor levels of zinc and copper, along with a very minor amount of silver. While the reason for these additions may not be clear to the reader at this
Sample 1x 5083 + Zn + Cu + .13 Zr
Sample 2x 5083 + Zn + Cu + .13 Zr + 0.03 Sc
Sample 3x 5083 + Zn + Cu + .13 Zr + 0.06 Sc
Sample 5a 5083 + Zn + Cu + .12 Zr + 0.09 Sc

Table 3.5: Compositions of test alloys with varying levels of Sc and Zr

point, a far more comprehensive analysis on the effects of zinc and copper in these alloys will be presented in Chapter 4, which deals directly with corrosion issues.

3.6.2.2.1 Experimental

Tensile testing was performed on the alloys listed in Table 3.5 (along with standard 5083), which were recast from the Reynolds castings studied in the previous section in order to vary Sc levels. It should be made abundantly clear to the reader that in order to more accurately compare the material properties of modified alloys to a standard 5083, casting and processing conditions must be identical! For this reason, standard 5083 was re-cast and re-processed under the exact conditions as the modified alloys, right down to the amount of reduction per processing pass. Under no circumstance is modified material compared to 5083 that has been industrially produced. Again, it should also be noted that the modified samples contain equivalent additions of Cu (0.12 wt%), Ag (0.04 wt%), and increased Zn levels (0.6 wt% and 0.3 wt% for sample 5a and samples 1x-3x, respectively). As with the previous section, the goal of the study is to determine the effects of these additions on final material properties in a material ready to be put into service, hence a full processing sequence was given to
each sample. The processing parameters were identical with one notable exception -
the total amount of cold work given. Following a hot-work cycle there was a cold
work reduction of 20% for cylindrical samples and 80% for flat tensile samples. The
high degree of cold work was applied to the flat samples in order to provide a
microstructure suitable for stability studies, a point which will become clear as that
section is addressed. Following the cold work cycle on the five alloys, a stabilization
treatment at 250°C was given for various times in order to measure the subsequent loss
in strength from a fully work hardened (no stabilization) condition.

Tensile testing was performed on one of two platforms as noted; either an M-
CERT constant extension rate rig on threaded cylindrical samples at very low strain
rates ($10^{-4}$/second) on an MTS 810 on flat .375 inch samples at a more rapid strain rate
of .04/second. Sample strain is measured either as a function of crosshead deflection
or through the use of an attached extensometer.

3.6.2.2.2 Test Results

Figure 3.37 shows a detailed section of the yield strength of the zirconium- and
scandium-containing cylindrical samples pulled at slow speeds ($10^{-4}$/sec) at a constant
extension rate. For these particular constant extension rate tests, the samples again had
a relatively minor cold work reduction of 20%, but were also given a “flash”
recrystallization treatment of 500°C for 15 minutes. Although we expect Sc- and Zr-
containing samples to be more stable than standard 5083, hardness testing has indicated
that this recrystallization treatment is complete enough to render any further stabilization
treatments superfluous. Evidence of this recrystallized stability under tensile test
conditions, rather than hardness test conditions, is demonstrated in Figure 3.37. Although
heat treated, after 250 minutes at 350°C the sample shown has retained almost entirely
its “pre-stabilization” strength as compared to untreated samples (not shown).
Figure 3.37: Detail of yield point of 5083, 5083+Zr, and 5083 + Zr + increasing levels of Sc, pulled at $10^4$/sec. Each additional level of Sc demonstrates a systematic and measurable gain in yield strength.
Regardless of recrystallized condition, these tests do indicate measurable and systematic increases in strength with increasing scandium. Even with additions at these very low levels, the increase in yield strength due to increases in scandium level is apparent. Increases of .03 wt% to a zirconium-containing 5083-based alloy equate to approximately 3 ksi in yield strength over the ranges tested.

For the following experiment, a more aggressive processing sequence was used. Cold working was increased to 80% in order to instigate a highly elevated dislocation density in each sample. Testing the highly deformed samples in an unrecrystallized state will give a more definitive indication of alloy stability, in terms of dislocation mobility, based on scandium and zirconium additions. Figure 3.38 is an example of
the changes in material properties that are readily observable via tensile testing. It demonstrates the marked change in stress/strain curve shape over the course of a moderate anneal lasting as long as 1000 minutes. While the gain in ductility over the course of the treatment is also quite measurable, the drop in yield strength from a fully hardened condition, and even from 10 minutes to 1000 minutes, is considerable.

"Recovery" Stability

Further testing of the Zr- and Sc-modified alloys in an unrecrystallized state may also offer a better representation of dislocation dynamics on bulk properties. In the following example (based on results obtained for each sample similar to those shown in Figure 3.38), tensile testing was performed on flat tensile samples that were subjected to an aggressive cold work cycle and then given a recovery treatment at 250°C. Such a "recovery" treatment at a low homologous temperature (less than 0.5T_m) is not expected to cause recrystallization, but is certainly high enough to inject the thermal energy necessary to allow dislocation motion and extensive annihilation within existing grains. This treatment does not mimic any standard industrial practice, but certainly is an indicator of the degree to which bulk strength is retained through heavily intertwined dislocation substructures. In an alloy without the impetus to hinder dislocation motion, i.e. through a stable precipitate dispersion, we would expect a high degree of recovery over time at 250°C and an associated loss of yield strength and ultimate tensile strength (along with a more complete recovery in overall ductility).

For this test, each of the Zr-and Sc-modified alloys as well as a standard 5083 alloy was given an extended recrystallization treatment (500°C for 75 minutes) at a moderate gauge, prior to an 80% cold work reduction. One can consider this treatment to render the material into a "fully hardened" condition. Tensile samples were pulled
to failure following treatments of 10, 100, and 1000 minutes at 250°C, to be compared
with tensile samples not subjected to a recovery heat treatment following the cold
work cycle.

Figure 3.39 demonstrates the measured retention in strength following the
recovery treatment, both in terms of yield and ultimate tensile strength. It is clearly
shown on both graphs that the initial transient toward recovery occurs rapidly; the first
10 minutes show a marked decline in strength for each of the alloys. This is
commensurate with the high degree of stored energy in the heavily worked
microstructure of each alloy and the ease with which this stored energy can be released
by thermal activation. The real measure of stability is therefore manifested in the
retention of strength following this initial transient. While the precipitate substructure
might not be effective in strength retention over this initial transient, the subsequent
retention of strength following this primary recovery transient can be largely attributed
to the differences in effective precipitate-dislocation interactions.

Figure 3.41 is a representation of retained yield and ultimate tensile strengths
based on a normalized value (the "retained strength factor") to the initial strength for
each of the alloys. The retained strength factor (RSF) is simply:

\[ RSF = \frac{\sigma_f}{\sigma_i} \]

where \( \sigma_f \) and \( \sigma_i \) are the final stress (after treatment) and initial stress (comparison stress
of interest), respectively. Each of the modified alloys demonstrates a remarkable in­
crease in retained strength over the time intervals measured. Noteworthy in this ex­
periment are the comparable values in both yield and ultimate tensile strengths for
each of the alloys (with the exception of the Zr + 0.9 wt% Sc alloy) in the fully hard­
ened state and even after the 10 minute recovery treatment. For the fully hardened
material, this may indicate that the dislocation density is more a product of dislocation-
dislocation interaction and subsequent "foresting" (tangling) rather than dislocation-
Figure 3.39: "Recovery" stability of yield strength of modified alloys from a fully hardened state.
Figure 3.40: "Recovery" stability of ultimate tensile strength of modified alloys from a fully hardened state.
precipitate interactions. The standard 5083 is well within a statistical equivalence, in terms of strength, for fully hardened material. The stability of the modified alloys beyond 10 minutes is measurably better than that of standard 5083, however. The modified alloys appear to have stabilized following the 10 minute recovery period, while the 5083 continues to recover (and lose associated strength levels) out to 100 minutes before reaching a stable state. In terms of yield strength, the Sc-modified alloys are the most stable; the Zr-only alloys continues to lose strength measurable even out to 1000 minutes, although overall the retained strength is much higher than that of standard 5083.
TEM Investigation

In order to more fully investigate the microstructural characteristics of the alloys containing Sc and Zr, TEM investigation was carried out on the samples which were subjected to the recovery anneal treatment at 250°C for 1000 minutes. While a full investigation of each of the heat treatments would seem, at least in theory, to be prudent, it must be understood that after 80% cold work the microstructure of each sample would be so tangled with dislocations that imaging any sort of features would be needlessly wasted effort. At best, such a microstructure might be classified as simply "heavily cold worked". After 1000 minutes, however, it might be expected that enough of a recovery process has occurred that features of interest may be more effectively observed. In this case, it can be hypothesized that these features will involve the strengthening role of Al\textsubscript{3}Zr particles in the case of sample 1x and Al\textsubscript{3}(Sc,Zr) particles for samples 2x, 3x, and 5a.

Figure 3.42(a) shows the residual dislocation density and refined grain size of sample 1x. Since no Sc is present in this sample, a careful investigation of precipitates should reveal the presence of Al\textsubscript{3}Zr particles if decomposition of α-Al, or precipitation of Zr, from a saturated state has occurred. Extensive fine-probe EDS analysis of particles in the 2-50 nm range failed to uncover the presence of any such Zr-containing precipitates. The apparent absence of Al\textsubscript{3}Zr particles is puzzling; previous observations made on an ingot of the same composition (alloys 1x-3x used sections of the same castings as base material for re-casts) showed a clear distribution of particles. It is possible that the particles are in a less developed state and as such are particularly elusive to image. While bright field imaging (Figure 3.43(a)) sometimes lacks the resolution necessary to image small particles, even a dark field image (Figure 3.43(b))
Figure 3.42: The zirconium sample (1x) shows a refined grain structure (a) following the 250°C recovery anneal for 1000 minutes, but no obvious presence of Zr particles. Several regions surrounding Ag/Cu particles (b) appear to be depleted.

does not reveal that presence of particles that are similar in size or shape to those $\text{Al}_2\text{Zr}$ particles observed in earlier investigations. Another effective test for Zr-based particles relies on information shown in a diffraction pattern. In the expected $\text{L}_1_2$ structure of $\text{Al}_2\text{Zr}$, we can expect to see reflections halfway between major planes in a $\{100\}$ zone diffraction pattern. Even though the grains are quite small, even an "invisible" dispersion will give reflections that give the presence of $\text{L}_1_2$ particles away. Figure 3.44(b) is a 150 second exposure of a $\{100\}$ zone in the matrix. Several "extra" spots can be seen, but none are present in positions that reveal $\text{L}_1_2$ particles. Immediately one must consider the possibility that a) the Zr particles are monumentally elusive in the imaging conditions
Several regions appeared to have been electrochemically attacked; resulting close-up microdiffraction patterns (b) (inset) do not, however, show amorphous rings.

Figure 3.43: Several regions appeared to have been electrochemically attacked; resulting close-up microdiffraction patterns (b) (inset) do not, however, show amorphous rings.

used, or b) Zr is largely retained in solution for the casting/processing conditions utilized for the sample in this study. Some other features of interest are present, however, beyond the fruitless search for Zr-based particles. Figure 3.45(a) shows two Mn particles sandwiching an apparent depleted region that contains a small particle. In sample 1x, in which the foil was prepared through an electropolishing process, one might assume that this region is more susceptible to electrochemical attack than the surrounding region. Figure 3.45(b) is a more detailed investigation into one of these features; the close-up
Figure 3.44: (a) Kickuchi pattern demonstrating [100] zone axis, (b) associated diffraction pattern showing clear Al reflections but no L1_2 reflections.

view of the zone again shows a particle at the apparent center of the lightened zone. Extremely fine-probe EDS reveals this region to be rich in copper, while the particle has an apparent silver peak. It is possible that these regions are more electrochemically active due to an enrichment of free copper in the vicinity of these small Ag-bearing particles. What is surprising, however, is that while the regions do appear to have been degraded by electrochemical attack, an associated diffraction pattern Figure 3.45(b) does not reveal the presence of any sort of amorphous structure (manifested by diffraction pattern rings) that might be expected in a highly degraded region. It should be noted that a region of this extremely minute size is beyond the limitation of true selected-area diffraction imaging – most of the pattern shown is that of the surrounding matrix. This
Figure 3.45: (a) Bright field and (b) dark field image of [100] grain shown in Figure 3.44. No Zr-based precipitates appear to be present in either condition.
Figure 3.46: The “tied up” grain structure is evident in Sample 2x (a), while the increased Mn precipitation due to the extensive cold work is clear in (b).

does not, however, discount the observation that the resulting pattern demonstrates an apparent absence of any amorphous rings.

Continuing the investigation with sample 2x, Figure 3.46(a) demonstrates once again the refined grain structure resulting from the aggressive processing treatment. Additionally, one can observe from Figure 3.46(b) that an extremely developed Al₆Mn dispersion has resulted, indicating that a highly elevated dislocation density has a pronounced effect on manganese precipitation rate. Not at all surprising as one would expect the diffusion rate of Mn atoms to be greatly enhanced by the increase in the number of dislocations. With regard to Al₅(Sc,Zr), however, once again an extensive search of the microstructure reveals little in terms of an Sc/Zr-based precipitate distribution. EMI SPEC compositional mapping does reveal a scarce number of particles,
although rather than being randomly dispersed they are commonly found in the subgrain/Al_{6}Mn interface regions so prevalent in the highly refined substructure. Figure 3.47 demonstrates the presence of two of such Zc/Zr-containing particles nestled against an Al_{6}Mn particle.

Figure 3.48(a) is the resulting microstructure following processing in sample 3x. Again, the highly refined grain and subgrain structure is apparent as is the increased distribution of Al_{6}Mn particles. Also similar to samples 1x and 2x is the conspicuous absence of any obvious distribution of Sc/Zr-based particles. Figure 3.48(b) is an image of another type of commonly observed precipitates found in each of the samples. The dimensions of these tiny particles are consistent with previously observed Sc- and Zr-based particles (see Section 3.6.2.1), but the only compositional anomaly revealed by EDS is a silver and small copper peak. Figures 3.49 and 3.50 further support this observation; the particles are relatively common while EDS profiles at high magnifications demonstrate only a presence of sharp silver peaks. The matter at hand is still to determine the role of Zr and Sc in these modified alloys, however, and Sc/Zr-based particles are indeed present in the microstructure. As with sample 2x, though, they are quite few and far between and are most commonly found in the near vicinity of common Al_{6}Mn particles. Figure 3.51 demonstrates the presence of such a particle, all but invisible until a compositional map is produced to reveal its presence. Interestingly enough, while the composition of the alloy has twice the level of Zr (in wt %) than Sc, the contrast in the Sc map is much clearer than that of the Zr map. While other factors can contribute to the amount of detector counts compiled during an EDS collection, the most obvious contributing factor would be a stronger presence of Sc in the precipitates observed. Couple this with the lack of Zr-based precipitates in sample 1x and one can consider the possibility that the Zr is actually more stable in solution for the processing treatments given. It is therefore possible that the Sc, not the Zr, that is driving the precipitation process in modified alloys with Sc and Zr in such small
Figure 3.47: EMiSPEC mapping of sample 2x demonstrates the formation of Sc/Zr particles in the Mn particle interface.
Figure 3.48: Scattered particles are shown throughout the matrix in sample 3x (a); high magnification "inverted" BF image (b) shows the shape and size dispersion common to the observed Ag-based particles.
Figure 3.49: TEM micrograph, SEM digital image, and EDS spectrum profile demonstrate the presence of tiny Ag-based particles.
Figure 3.50: Small particle distribution of Sample 3x indicates dispersion of Ag-based particles.
Figure 3.51: Composition map shows Sc/Zr particle in the vicinity of an Mn-based particle.
concentrations. In other words, the driving force, or energy barrier, for nucleation of an Sc-based precipitate or zone is more favorable than that for a Zr-based particle or zone. This is further illustrated in Figure 3.52, an EDS profile of a particle on a subgrain boundary (notice once again that the particle is in close proximity to an Al-Mn particle). The resulting profile shows a slight increase in Zr counts at the particle, but not nearly so dramatic as the Sc peak. An even closer view is shown in Figure 3.53, generated at an extremely high magnification (in terms of compositional mapping — 500kX) in nano-STEM mode on the CM300. Even with this extraordinarily fine probe, the peak generated for Zr is not as high as that of Sc. One must be very cautious in attributing increased enrichment or initial nucleation to peak height or map contrast, however. It should be noted that there are other factors which contribute to EDS intensity that would have the same effect, and therefore the assertion that scandium-based particle nucleation and growth being more energetically favorable than zirconium is merely speculative in nature and not based on concrete evidence.

Based on the observations for samples 1x, 2x, and 3x, the presence of Sc/Zr-based particles is not nearly as widespread as would have been expected, based on previous observations. It must be considered, then, that two possibilities for the lack of precipitate structure exist; a) that the processing parameters are such that the amount of precipitation seen in Section 3.6.2.1 has not had the opportunity to occur, or b) that the Sc concentration drives the precipitation process to the extent that a threshold level exists for widespread precipitation of Sc/Zr-based particles. Since earlier observations on an Sc- and Zr-containing alloy had a higher concentration of Sc (0.9 wt%), perhaps this precipitation threshold exists at or just below this level. Two arguments may be made against this possibility. One, that there was limited or no precipitation in the Zr-containing sample (1x) while earlier observations on Zr-containing samples of the same concentration of Zr showed extensive precipitation, and two, that the incremental increases in strength were systematic with regard to Sc level; i.e. were not in any way
Figure 3.52: Sc/Zr particle along grain boundary confirmed by EDS spectrum profile (insert).
Figure 3.53: HR - NanoSTEM image of Sc/Zr particle on Sample 3x grain boundary, confirmed by EDS spectrum profile.
indicative of a "threshold" level and subsequent wholesale change in microstructure having been achieved. To further discount the validity of possibility b), observations were made on sample 5a, made from the same base alloy that produced the homogeneous dispersion of 8-12 nm particles observed in Section 3.6.2.1. The processing parameters, of course, were the same as those used in producing samples 1-3x. As expected, the refined grain structure seen in the other samples is present (Figure 3.54), but the observed particles in the range of dimensions seen earlier are again silver-based particles.

The puzzling lack of Sc- and Zr-based particles was further investigated by a more extended precipitation heat treatment. Samples 1x (Zr-only) and 3x (Zr + .06 Sc) were aged at 350°C for 60 hours in order to allow a more complete precipitate structure

![Image of microstructure](image)

**Figure 3.54**: The highly refined grain structure of Sample 5a following the 250°C recovery anneal for 1000 minutes.
development. If Sc- and Zr-based particles were, in fact, on the verge of forming under the previous conditions given, then a more complete treatment might make them more readily observable. Following the 60-hour treatment, samples 1x and 3x were observed via TEM. Figure 3.55 shows sample 1x in the more developed state; once again the Mn-based structure demonstrates continued development, but fine-probe EDS investigation reveals no Zr-rich particles. A long-exposure diffraction pattern of along a cube zone direction shows the allowed Al FCC reflections, but no superlattice reflections indicative of an L12 structure. Once again, the Al1Zr particles do not appear to have formed. Figure 3.56 tells a slightly different story for the sample (3x) containing 0.06 wt% Sc in addition to the Zr. Unlike Figure 3.55, EDS analysis not only shows several particles (Figure 3.55(a)) that did demonstrate Sc and Zr peaks, but the cube orientation diffraction pattern reveals (albeit very faintly) the L12 superlattice reflections indicative of Al1(Sc,Zr).

Figure 3.55: Sample 1x aged at 350°C for 60 hours to allow more complete precipitation. Precipitate structure is well developed (a) but no L12 diffraction spots are seen (b).
Figure 3.56: Sample 3x contains a number of precipitates (a) which demonstrate a Zr/Sc peak on a fine-probe EDS spectrum. The diffraction pattern (b) of a [100] zone demonstrates faint L1₂ reflections, shown by arrows.

Summary

The key to widespread distribution of Sc/Zr-based particles is based on the processing parameters of the alloy. While the alloys observed were subjected to an extended post-processing heat treatment at a moderate temperature (250°C) were not sufficient to cause readily observable precipitation events to occur. The major differences between the alloys observed in section 3.6.2.1 and in this section were in the solidification parameters and in the amount of hot work each was subjected two. In the first case, solidification parameters, the samples of Section 3.6.2.1 were cast using a direct-chill process. By contrast, the samples of the previous section were cast in small batches in a graphite mold; the cooling rate for the small batch, while not using aqueous mediums for control of cooling rate, is nonetheless a much more rapid means of
solidification for the two cases being compared. Additionally, the amount of hot work that went into the samples of section 3.6.2.1 were on the order of a 16:1 reduction, vs. a 4:1 reduction for those samples in the previous section.

Interestingly enough, while it was expected that the strength and stability increases were due to precipitation of Sc- and Zr-based particles, it appears that the increases were in actuality due to a solid-solution mechanism. The fact that these increases in strength were as readily obvious as they were must not be discounted, in light of the fact that the only real differences in composition were the systematic increases in Sc levels. It must therefore be concluded that Sc and Zr can have a profound effect on strength as a substitutional impurity as well as through a dispersion-hardening mechanism. This is not surprising if one considers the atomic radius mismatch between Sc and Zr compared to Al (each is approximately 15% larger), but is very surprising in light of the low levels at which they demonstrate the aforementioned effects.

3.6.2.3 Microalloying Summary

1. The addition of small amounts of scandium and zirconium to baseline 5083 have a pronounced effect on final levels of yield strength and ultimate tensile strength. The addition of Sc and Zr together have a more pronounced effect than either added alone; increasing Sc amounts for a given level of Zr also provide incremental increases in strength.

2. The fine precipitates formed appear to have little interaction with subgrain boundaries at this low level of cold work, and as such have little effect on subgrain size and structure as compared to the dispersion of $\text{Al}_6\text{Mn}$ particles. Studies by other authors have, however, shown a high level of grain and subgrain refinement for high levels of cold
work when alloying with zirconium and scandium.

3. The $\text{Al}_3\text{X}$ particles formed in the Zr- and Sc-only alloys are less prevalent in the matrix than the $\text{Al}_3(\text{Sc},\text{Zr})$ particles. The $\text{Al}_3(\text{Sc},\text{Zr})$ particles, in addition, are finer (10 nm) and remain coherent in the matrix.

4. The retained strength (stability) of Sc- and Zr-modified alloys is measurably higher than that of standard 5083. Thermally activated recovery processes are less effective in reducing strength levels for increasing levels of scandium in the aforementioned modified alloys.

5. The strength increases seen through additions of Sc and Zr are not limited to a dispersion hardening mechanism. Measurable strength increases were also observed for alloys in which TEM investigation revealed little or no $\text{Al}_3\text{X}$ distribution within the matrix of the alloy, indicating that solid solution strengthening is also a viable strengthening component, even for very minor additions.
References


CHAPTER 4

CORROSION

This chapter will examine one of the commonly believed drawbacks of AA5083 — potential premature failure due to stress corrosion cracking. The mechanisms for stress corrosion cracking will be discussed with regard to one of the most important strengthening mechanisms in many 5000 series alloys: solid solution strengthening by a supersaturated level of magnesium. As stress corrosion cracking is attributable to a magnesium-based phase that forms along grain boundaries under the right thermal conditions, an investigation will be made into possible chemical and kinetic modifications of this grain boundary phase. Modifications to a standard 5083 alloy will be made through the addition of very minor levels of elements not common to 5083 - zinc, copper, and silver.

The goal of the studies outlined in this chapter, therefore, will be to investigate the resulting characteristics of with regard to stress corrosion cracking of material modified by additions that are small enough as to have minimal effects on other bulk characteristics of the alloy.
4.1 Introduction

The improvements to the 5083-based alloys system would not be complete without addressing the issues of corrosion. Increases in magnesium levels to well above the saturation limit have been shown to continue to improve the strength of the system, but it has been stated that the strength increment gained is insufficient to compensate for the resulting drop in stress corrosion resistance [1]. A tradeoff exists in overall property improvements if corrosion susceptibility becomes a very viable failure mode for components constructed from the material. This is certainly the case with 5083-based alloys, which contain Mg in elevated levels beyond the saturation limit, and as such are susceptible to certain types of corrosion under specific conditions. The corrosion mode of ultimate concern is stress corrosion cracking (SCC).

It has been commonly reported that SCC occurs as a result of three conditions: an SCC susceptible alloy, a corrosive environment, and an applied tensile stress. It is generally defined as brittle failure at a reasonably low level of stress along localized areas of corrosion [2]. SCC is particularly worthy of concern because failures generally occur unexpectedly. SCC lacks the visible evidence of deterioration seen in uniform or localized corrosion. In the 5000 series alloys, the SCC susceptibility has been experimentally attributed to precipitation of the β phase along grain boundaries [3] when the Mg content exceeds the solid solubility level (about 3% at 200°C) [4].

\[
\text{GPZ} \rightarrow \beta'' \rightarrow \beta' \rightarrow \beta
\]

The β-phase is a complex in nature, containing an estimated 1168 atoms per unit cell of near-\(\text{Al}_3\text{Mg}_2\) stoichiometry [5]. Homogeneous GP zone nucleation occurs in the matrix as tiny, solute-rich clusters, 1-2 atoms thick, in plate-shaped zones on \{100\} planes.
The nucleation of β-phase precipitates is of interest since solid solution strengthening is the most significant contribution to overall strength in the 5000 series alloys. It is therefore important to understand where the trade-off lies between strengthening by Mg addition and SCC susceptibility, as well as the loss of solute strengthening, due to Mg-based precipitation of the β phase.

The concerns over SCC are not founded in the formation of GP zones within the matrix so much as they are over the more stable β phase. The early stages of β require a large level of vacancy concentrations in order to nucleate and grow: precipitation of the β phase is energetically difficult due to the large strain energy associated with the formation of its unit cell structure. This necessity is supported by early work, which demonstrated the formation of dislocation structures necessary to accommodate β-phase precipitates. Eikum showed that alloys with reasonably high levels of Mg, between 5.0 and 6.5 wt%, when aged for a period of time at 100°C, punched out prismatic loops along <110> glide cylinders upon growth of β phase particles in the matrix. This nucleation and growth in largely defect-free areas is likely due to the lack of grain boundary structure available for accommodating precipitation in the samples tested; each were given a 12 hour anneal at 500°C prior to aging treatments and subsequent observations. This point about the lack of grain boundary structure is important, because β phase precipitates in wrought Al alloys generally find the “space” necessary to nucleate and grow along grain boundaries, forming almost exclusively in these regions in Al alloys containing moderately high levels of Mg. Figure 4.1 provides a schematic of the enrichment of Mg at a grain boundary, presumably due to β formation. Beck [7] attributes this behavior to the necessity for considerable three-dimensional disregistry of the lattice in order to accommodate the large size mismatch between the α-Al matrix and the β unit cell. Additionally, grain boundary formation is favored due to a reduction in system interfacial energy; a precipitate at a grain boundary maintains a level of interfacial energy between its surface and the matrix, but the interfacial
energy between neighboring grains in the space occupied by the particle is eliminated. Whatever the energetically-favored reason for formation, this continuous or semi-continuous phase along grain boundaries is the real catalyst behind SCC failure in 5000 series alloys [3].

SCC has generally not been observed in alloys containing less than 3.5wt% Mg [8], although this is above the solubility limit for Al-Mg at room temperature (Figure 4.2). That is not to say that occurrence of SCC in this condition is never seen: Skoulikidis et. al. [9] performed an experiment on active path formation of SCC on samples of Al-2.5%Mg in a highly corrosive NaCl environment. In his study, Skoulikidis tested time to failure via crack growth rate for samples that were notched via a controlled etching process vs. those notched mechanically. It was noted that electrolytically notched

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Figure 4.1: A simplified model of the β-phase and the surrounding diffusion region; (a) the cylindrical shape and (b) the concentration curve. Experimental data of the profile of Mg across interdendritic regions (c) supports the illustrations.
Figure 4.2: Aluminum-rich detail of the Al-Mg phase diagram; the effect of Mg content and processing conditions on stress corrosion cracking susceptibility are plotted.
samples always failed faster than mechanically notched samples, and always along an active path. This might suggest that electrolytic notching occurred along precipitated Mg phases and continued on the same path to failure. Mechanically notched samples failed at a lower rate because they were not necessarily engraved near an SCC-susceptible Mg-rich precipitate structure.

The temperature at which the decomposition of the β phase aluminum will occur with respect to room temperature is not clearly defined. Even higher-strength alloys with up to 5.5% Mg and beyond might take many years for the β phase to precipitate and lead to SCC-susceptible zones [8]. An illustration of the susceptibility of Al-Mg alloys for various Mg levels and aging times is given by Sprowls and Brown (Table 4.1) [10]. Failures due to stress corrosion cracking become more and more of a concern as the material contains higher levels of Mg or is subjected to a larger amount of cold work. The presence of an aging environment at elevated temperatures will also make β-phase formation more likely. Such an environment need not be continually well above room temperature; accelerated corrosion rates in heat-affected weld zones has been attributed to the formation of an Mg-based grain boundary phase [11]. For material naturally aged (exposed to room temperature ranges only) for 12 years, it has been demonstrated through differential scanning calorimetry (DSC) that even for a high Mg alloy (8.0 wt% in Al), the precipitation phase did not get beyond the GP zone stage. If this same material is subjected to an elevated (300°C) temperature, however, the β phase forms within several hours [12].

### 4.2 β phase Formation

It has been speculated for many years that β-phase formation is the main culprit behind SCC susceptibility, mainly because of the anode-cathode relationship that exists between the β phase and the α phase. Sprowls [10] has shown that the β phase is
### Table 3 - Resistance to Stress Corrosion Cracking of Al-Mg Alloy Sheets\(^{(1)}\) After 20 Years of Natural Aging at Room Temperature\(^{(1)}\)

<table>
<thead>
<tr>
<th>Temper</th>
<th>F/N(^{(2)})</th>
<th>Days to Failure(^{(3)})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al-4.04% Mg Alloy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed</td>
<td>0/2</td>
<td>OK 180</td>
</tr>
<tr>
<td>5% cold reduction</td>
<td>0/2</td>
<td>OK 180</td>
</tr>
<tr>
<td>10% cold reduction</td>
<td>0/2</td>
<td>OK 180</td>
</tr>
<tr>
<td>20% cold reduction</td>
<td>0/2</td>
<td>OK 180</td>
</tr>
<tr>
<td>40% cold reduction</td>
<td>3/3</td>
<td>13, 105, 135</td>
</tr>
<tr>
<td>60% cold reduction</td>
<td>3/3</td>
<td>42, 42, 56</td>
</tr>
<tr>
<td>75% cold reduction</td>
<td>1/3</td>
<td>62 days, OK 180</td>
</tr>
<tr>
<td><strong>Al-6.01% Mg Alloy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annealed</td>
<td>0/2</td>
<td>OK 180</td>
</tr>
<tr>
<td>10% cold reduction</td>
<td>2/2</td>
<td>17, 17</td>
</tr>
<tr>
<td>20% cold reduction</td>
<td>2/2</td>
<td>2, 48</td>
</tr>
<tr>
<td>30% cold reduction</td>
<td>2/2</td>
<td>2, 2</td>
</tr>
<tr>
<td><strong>Al-6.15% Mg Alloy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% cold reduction</td>
<td>3/3</td>
<td>12, 13, 13</td>
</tr>
<tr>
<td><strong>Al-5.99% Mg Alloy (Aged 15.3 Years)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75% cold reduction</td>
<td>3/3</td>
<td>10, 10, 20</td>
</tr>
</tbody>
</table>

\(1\) Chemical composition: Cu, 0.01-0.05; Fe, 0.13-0.19; and Si, 0.06-0.08.

\(2\) F/N denotes number of specimens failed over number of specimens exposed.

\(3\) Test conditions: exposure, 3-1/2% NaCl alternate immersion; specimen, sheet tensile (X-grain) specimen stressed to 75% yield strength by dead weight loading as a simple beam.

**Table 4.1**: The resistance to SCC is demonstrated for alloys which have not received cold work reductions even after extended aging periods at room temperature.[75]
strongly anodic to the Al-Mg solid solution matrix, and in the presence of electrolytes
the β phase corrodes selectively at a high rate because of the very narrow path of the
anodic phase. The β phase, having a different potential than the more noble α-matrix,
effectively becomes the sacrificial anode in a galvanic couple. The relative surface
area difference between the whole of the matrix and the β phase precipitate greatly
exacerbates the situation by increasing the corrosion rate even further.

In terms of the corrosion behavior of Al-Mg alloys, it should be noted that the
various intermetallic phases which form are actually instrumental in allowing corrosion
to occur despite the passive oxide layer which rapidly forms on Al-based alloys.
Research has been performed [13] to demonstrate the behavior of these alloys as
sacrificial anodes, protecting steel in corrosive environments. The performance of
these anodes is based upon their ability to corrode in spite of the passive layers that
form which would otherwise inhibit such corrosion. The presence of these intermetallic
secondary phases is what actually allows a foothold for the corrosion process to continue
and allow the anode to perform its desired role (i.e. to corrode). Although research in
this area looks at the corrosion process with a distinctly different goal in mind, with
corrosion being the desirable result, the general mechanisms which occur help to
illustrate the role of the secondary phases in the overall performance of the material.

Although it has been shown that a continuous β phase along grain boundaries
under a tensile stress is not necessary for SCC susceptibility [3], the mere presence of
a β phase in an Al-Mg system will not guarantee that SCC will cause a component to
fail even under corrosive conditions. Consider the micrographs (Figure 4.3) by Vetrano,
which show the failure of Al-5083 (4.8 at%) undergoing a U-bend test in a 3.5% NaCl
solution. The sample shown was given a heat treatment at 175°C for 100 hours. Clearly
the failure was intergranular rather than transgranular, demonstrating the effect of
weakened grain boundary regions on overall material performance. The interesting
aspect of the Vetrano experiment is that materials were tested following different heat
Figure 4.3: Stress corrosion crack in a U-bend test specimen showing a) an SEM image of the crack, b) an optical micrograph of an etched sample demonstrating intergranular failure, and c) an SEM micrograph of the crack inner surface confirming intergranular failure.

treatment times. All specimens treated for 100 hours failed the U-bend test due to SCC. After 50 hours at 175°C, one of the three specimens failed. At 24 hours and below, the specimens all passed the U-bend test regardless of the length of time that each spent in the corrosive solution [3]. This demonstrates the fact that although a β phase may be forming and subsequently corroding, there is a critical amount of sensitization (Mg migration to grain boundaries) which must occur, in terms of the magnitude of grain boundary lining, prior to a failure of the material due to an intergranular SCC mechanism. Generally β phase forms first at triple points, then along grain boundaries, and, in many cases, in the interface between the aluminum matrix and Al₆Mn particles. Prior to formation of a distinct β phase, there is a localized enrichment of Mg along grain boundaries - a condition which may also be associated with SCC failure in alloys where continuous grain boundary lining of β phase is not present [14]. Remember, however, that based on the Vetrano work, while Mg enrichment
at grain boundaries might allow SCC to occur more readily than in an alloy which is not otherwise susceptible, the lack of a more complete β phase formation will slow the SCC mechanism down to rates that are of little concern.

It has also been suggested that formation of the Mg-rich (β phase) zones at grain boundaries will cause a coalescence of hydrogen bubbles [15]. While it is not clear what causes the hydrogen enriched areas, it is possible that magnesium and hydrogen atoms exist as some sort of Mg-H complex, and that the enrichment of Mg at the grain boundaries will cause a subsequent enrichment of hydrogen in these areas as well. While the authors making this claim do not substantiate it further, or delve greatly into the specific mechanisms by which hydrogen might weaken a grain boundary area, they do make the general claim that the presence of closely-spaced bubbles might lead to localized decohesion of the boundaries. It is interesting to note that there are differing schools of thought on the susceptibility of Al-Mg alloys to SCC. It has been suggested that the presence of the β-phase in a high-Mg (9 mol%) alloy leads to a low solute concentration in the immediate area surrounding the grain boundaries where the β precipitates have formed [16]. While this claim may be true, the further claim that it is the presence of these low-solute areas in the precipitate-free zones (PFZs) which causes the SCC failure of these materials is questionable. The first argument against the solute concentration level leading to SCC is the lack of explanation for localized brittle failure. Even if the material in the PFZ was pure aluminum, the failure mode should still be ductile although the fracture might occur at levels well below that of fully solutionized α-aluminum. The second argument against this claim lies in the failure to consider the likely galvanic effect, or the relative dissolution rates, between the differing phases.
4.3 SCC Resistance

An important benefit of determining the mechanisms that lead to SCC in aluminum alloys is that ways may then be rationally devised for preventing it, or at the very least limiting its deleterious effects. Based on the background information presented in the previous sections, there are several distinct strategies for reducing or eliminating SCC in Al-Mg alloys due to β-phase precipitation. Each of the strategies outlined may or may not be realistic in the scope of the present study; the major goal is to improve the material's properties rather than to simple limit component failure in certain applications. The aim of improving a material is to increase the scope of its applications rather than to further restrict their use.

4.3.1 Limiting Magnesium Content

The upper limit to avoid β-phase formation in Al-Mg alloys is about 3.5%. Several alloys (including Al-5086) have levels of Mg at the lower end of this range in order to avoid Mg segregation/grain boundary enrichment problems. Other elements are also often added to overcome the loss of solid solution strengthening due to the reduction in Mg levels, adding strength through dispersoid or precipitation strengthening. Examples might include manganese, chromium, and iron as dispersoid strengtheners, and zirconium and scandium as precipitation strengtheners [17].

If substantial strength gains can be made utilizing methods outside of the solute strengthening effect, this could become a viable avenue for material improvement. It is more likely, however, that materials with elevated Mg levels will be developed, evaluated, and refined to maximize desired properties.
4.3.2 Varying Tempers

β phase formation can be limited during the processing stage by avoiding the thermal activation required to allow the precipitate to coarsen extensively. As Vetrano et. al. demonstrated, even though β phase might be present, limiting its volume fraction through limited heat treatments can significantly delay the onset of SCC, even in corrosive environments. Certain temper designations have been devised which increase the SCC resistance of 5000-series alloys [8]. These designations include strain-hardened as well as strain-hardened and stabilized conditions. Examples for alloys 5083 and 5456 (both containing 4.5-5 wt% Mg) include not only the H116 temper mentioned in Chapters 1 and 3, but also the H117, H321, H323, the H343 tempers. This study will focus largely on improvements based on the ASTM H116 designated temper.

4.3.3 Environment

Two factors can be postulated to lead to SCC in high alloys. The first involves the continued evolution of the β-phase. It has been shown that exposure to increased temperatures will allow continued coarsening of the β phase [8]. This effect could cause a material which is suitable for a given application in the as-supplied state to eventually fail due to growth of the β phase past threshold levels for allowing cracks to propagate. The other condition of concern is the corrosive nature of the environment of the application. Although the coupling may exist between the β-phase and the α-matrix, corrosion will be greatly diminished if the environment is such that only limited electrolytic support, in terms of metal ion flow, is given for the reaction. An electrolyte with a high ohmic resistance (RΩ) will be far less corrosive in a galvanic reaction between precipitate and matrix than an electrolyte with low ohmic resistance. Clearly this cannot be a consideration for the scope of this study, however, as limiting the applications for any newly developed material would not be considered a material
improvement. Additionally, as stated in Chapter 1, 5000 series alloys receive extensive use in particularly corrosive environments when used in the shipbuilding industry, when exposure to seawater is essentially continuous.

4.3.4 Microstructural Control

In light of recent developments concerning SCC in Al-Mg alloys, the control of grain size to control SCC resistance is questionable. Theoretically, if the continuous β-phase can be avoided along grain boundaries, in effect by “breaking it up” through a more thoroughly refined grain structure, then potential cracks might have less of an opportunity to propagate through any extended amount of material [8]. This theory is called into question by this author due to the fact that it has been shown the β phase is not, in fact, continuous in the more extensively used 5000-series alloys (4.0-5.5% Mg) although they still may be SCC susceptible. Additionally, the β phase is formed by localized diffusion of Mg to grain boundaries, presumably to lower the lattice strain energy of misfitting Mg atoms in solution. This is supported by the presence of the narrow (extremely narrow with respect to grain size) PFZs which are also low in solute level [15], indicating that the Mg will not necessarily be reduced along one grain boundary simply because a nearby grain boundary has “robbed” the available Mg content.

Advances in thermomechanical processing (TMP) techniques to control microstructure have also claimed success in avoiding the formation of continuous β phase lining of grain boundaries. McNelley and Garg [18] used a binary high-Mg (10.2 wt%) Al alloy to demonstrate that by “warm” rolling the material at 300°C, well below the Mg solvus temperature, β particles were confined to grain and subgrain interiors. The structure within these grains and subgrains remained interspersed with tangled arrays of dislocations, and retained a strength level of over 500 MPa ultimate tensile strength, comparable to that of heavily cold worked material. When the same
material was hot rolled to the same thickness and quenched, then given an anneal at the "warm work" temperature, continuous β phase was prevalent along grain boundaries. It was unclear from the authors what would occur if the warm worked material was given an additional annealing treatment.

4.4 Chemistry Changes for Corrosion Control

As outlined previously, one of the promising methods to reduce the detrimental effects of β phase formation in aluminum alloys containing Mg in amounts greater than 3.5% [8, 10] is to limit the formation of the phase during decomposition of the supersaturated solid solution. Ternary Al-Mg-X systems exist that may form preferentially over the binary Al-Mg phase; if these ternary phases have a corrosion potential that would render them less susceptible to dissolution than the β-phase precipitates, it is certainly conceivable that the associated intergranular corrosion rates for the bulk material could be similarly reduced.

Three ternary phases of the general form Al-Mg-X that have the ability to form in an Al-Mg system include precipitates which contain zinc, silver, or copper. Each ternary system is quite similar; each can have an Mg_{32}(Al,X)_{49} phase that has a body-centered cubic (BCC) structure with a lattice parameter of about 14Å [19].

4.4.1 Al-Mg-Zn

There are two major ternary precipitate phases that will commonly occur in Al-Mg-Zn systems. The equilibrium η and τ phases - MgZn₂ and Mg_{32}(Al,Zn)_{49}, respectively - will form based on the relative amounts in either system. Alloys with lower Zn:Mg ratios will more naturally fall into the τ phase equilibrium phase field, although η has been observed forming in the τ + Al field. In such an occurrence, an
increase in time or temperature will eventually cause the \( \eta \) phase to be replaced by the equilibrium \( \tau \) phase \([10]\). The ternary \( \tau \) phase is the phase that will form in Al-Mg alloys that contain zinc in levels of interest to this study; specifically, in amounts not to exceed 1-2 wt\% \([7]\). Formation of the \( \eta \) phase is most prevalent in 7000 series alloys, which contain higher levels of Zn than Mg. Formation is particularly predominant when stoichiometry of the system is close to the 2:1 Zn:Mg ratio found in the \( \eta \) precipitate.

An extensive undertaking by Bergman et. al. \([20]\) has uncovered much of the characteristic structure of the \( \tau \) phase. The \( \tau \) phase has a BCC structure (space group \( T5h \)) with 162 atoms per unit cell. There is some disorder in occupancy of the unit cell with respect to Al and Zn atoms, but the atomic percentage of Mg remains relatively constant. This would certainly be expected as the metallic radius of Mg is about 15\% greater than that of Al or Zn. The most important characteristic of a Zn-containing phase in Al-Mg alloys is the reported reduction in alloy corrosion rates, presumably due to SCC, when Zn is added in small (less than 2 wt\%) amounts to the system \([7]\). Further investigations into the nature and characteristics of the phases that form is a logical objective of this study.

\subsection*{4.4.2 Al-Mg-Ag}

Polmear and Sargent \([21]\) showed that even minute silver additions to an Al-Mg system will influence the resulting precipitation phases. In an Al-7 wt\% Mg alloy, an addition of 0.5 wt\% Ag will cause a precipitate to form which is much finer and more homogeneously dispersed than that which forms without an Ag addition. A 7 wt\% Mg alloy would clearly be in the supersaturated region where \( \beta \)-phase would be prone to form extensively; the observation of precipitation changes with the addition of Ag demonstrates an interaction between the magnesium and silver atoms.

Further experiments conducted by Wheeler, et. al. \([22]\), demonstrate the effects of silver on alloys that are closer in composition to 5083 in terms of magnesium content.
Additions of 0.3 wt% silver to samples of Al-5 wt% Mg that were then sensitized at 150°, 175°, and 200°C exhibited a hardness peak owing to the precipitation hardening effect of a ternary Al-Mg-Ag phase. The composition of this phase was determined to be 43 wt% Al, 29 wt% Ag, and 28 wt% Mg. This phase closely resembled both the copper- and zinc-containing Al-Mg-X phases (Al₅CuMg₄ and Mg₁₂(Al,Zn)₉, respectively); with a body-centered cubic unit cell having a lattice parameter of 14.4Å.

The presence of increased hardening response due to precipitation of a ternary Al-Mg-Ag phase was supported in work by Lim and Rossiter [23], who used the Cluster Variation Method developed by Kikuchi to produce phase diagrams to classify the alloy phases in an Al-Mg-Ag system. Their interest in the project stemmed from the response of Al-Mg alloys to additions of Ag in the alloy’s ability to age harden. Small additions of Ag can effectively lower the prerequisite Mg level for an age hardening response from about 6% Mg to 0.5%. Enhanced hardening due to Mg-Ag precipitation can occur readily in alloys containing more than 5 wt% Mg.

**4.4.3 Al-Mg-Cu**

A great deal of interest in the characteristics of Al-Mg-Cu alloys was stimulated by the undesirable softening effect of Al-Mg alloys in car body applications, an effect that occurred during the paint-bake cycle of the automobile assembly process. Additions of small amounts of copper to the alloys counteracted this softening process [24]. Based on the established behavior of Al-Mg alloys at intermediate temperatures, the softening behavior is most likely due to β phase formation. Additions of Cu effectively change the alloy from one that is susceptible to softening to one that is precipitation-hardenable through the formation of a ternary Al-Mg-Cu phase. There is much more published material which examines Cu-rich alloys than that which covers Cu-lean material [24-27] (which would be more pertinent to the present study), or, more specifically, alloys containing between 0.11 and 0.29 wt%. In addition to forming a τ-type phase with a
lattice parameter of 14.35+/-.01 Å [19], the precipitation sequence of the major Al-Mg-Cu S phase that occurs is similar to the precipitation sequence of the τ phase outlined previously:

A → GPZ → S'' → S' → S

The Al₂CuMg S phase is the stable precipitate in these alloy systems. Unlike the BCC ternary τ phases outlined in the previous section, the S phase is a face-centered orthorhombic unit cell with lattice parameters a=0.4nm, b=.923nm, and c=0.714nm. The intermediate S'' and S' phases have slightly distorted structures compared to the S phase, with similar lattice parameters. Recent work has suggested that the hardening effects of the S'' and S' phases are greater than those realized by the clusters and/or GP zones which initially form. The nucleation and growth behavior is not unlike that in other alloy precipitates; that is, while the GPZ forms homogeneously throughout the matrix, the S'' phase prefers to nucleate and grow heterogeneously on dislocations. It has also been suggested that the S'' phase transforms into the S' phase at later stages of the annealing process.

One of the main differences in precipitation behavior between Cu containing Al-Mg alloys and Cu free alloys is in the speed of the precipitation process. The softening effect that was seen in Al-Mg alloys became a factor after a paint bake cycle of 20-30 minutes at 160-180°C [24]. Following additions of small amounts of copper, in Cu:Mg ratios of between 0.7 and 0.14% in weight, the precipitation sequence only progressed as far as the formation of GP zones following a 16 hour heat treatment at 200°C [28]. Clearly this Cu addition retained the integrity of the material's properties by limiting the morphological changes within the microstructure. As an additional benefit, the realization of further hardening could be expected with a more developed precipitate formation, i.e. the formation of the S'' or even S' phase.
The downside to the addition of copper to the Al-Mg-Mn system would be the ternary phase's effect on corrosion resistance. Copper-containing phases are notoriously corrosion-susceptible in terms of the phases that they form in Al alloys. S phase, in particular, is a phase of concern in high-strength 2000 series alloys due to its propensity for destructive localized corrosion. Studies by Buchheit on isolated bulk S phase compounds have demonstrated the active nature of this phase with respect to the aluminum matrix—a characteristic which leads to the widespread localized corrosion damage in Al-Cu-Mg alloys. The strong anodic polarization of S-phase particles within the α-Al matrix leads to a high rate of anodic dissolution of the phase under free corrosion conditions. Eventually, dealloying of the phase will lead to a reversal of the galvanic relationship with the surrounding matrix, slowing the active dissolution, but not until the mechanical integrity of these locally dissolved areas has been greatly compromised [29]. Since the major concern with β phase formation is corrosion along grain boundaries, which will invariably lead to SCC in any sort of corrosive environment, additions of an element that precipitates a potentially more corrosive phase would not be beneficial in improving the material's bulk properties, or of any practical interest to this study.

4.5 Corrosion Results and Discussion

As outlined in previous chapters, magnesium in a state of supersaturation in aluminum alloys can be a potent strengthener. The drawback to excess magnesium, however, lies in the susceptibility of the alloy to precipitate magnesium-rich phases along grain boundaries which make the alloy prone to stress corrosion cracking (SCC) and potential premature failure [3]. While 5000 series alloys with elevated magnesium levels may not exhibit these secondary phases in the as-produced state, subjecting the
<table>
<thead>
<tr>
<th>Alloy</th>
<th>Exfoliation</th>
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<tbody>
<tr>
<td>5083 (Standard)</td>
<td>50%</td>
</tr>
<tr>
<td>5083 + Zn</td>
<td>20%</td>
</tr>
<tr>
<td>5083 (High Mg - 5.45%)</td>
<td>95%</td>
</tr>
</tbody>
</table>

**Table 4.2**: Comparison of exfoliation ratings in terms of % lining of grain boundaries for three 5083-based samples following an additional two-hour anneal. The Zn-containing sample exhibits a considerably higher overall resistance.

Material to extended periods of time at elevated temperatures can provide the thermal energy required to precipitate these secondary phases. In the laboratory, precipitation is hastened through the use of sensitization treatments, or artificially extended aging periods that allow the material to reach a more stable state in terms of secondary phase formation. In 5000 series alloys with elevated levels of magnesium, this can and does include formation of Mg-rich phases along grain boundaries.

### 4.5.1 Zinc Additions

Additions of Zn to these Al-Mg alloys in levels of 1-2% have been suggested in early studies to be more SCC resistant due to the formation of a stable ternary Al-Mg-Zn phase [7], the τ phase. Recent studies have shown that Al-5083 variants which contain even minor levels of Zn (0.68-0.70%) perform in a much improved manner (Table 4.2) during exfoliation testing [30]. Table 4.2 represents the results obtained through ASTM testing (B209) for grain boundary lining, or "ditching", that occurs when grain boundaries are under considerably more severe attack than the surrounding...
material after being subjected to an aggressive etchant. Transmission electron microscopy (TEM) observations, coupled with energy dispersive spectroscopy (EDS) investigations, may provide some explanation for this change in behavior by demonstrating the formation of a ternary Al-Mg-Zn phase along grain boundaries when Zn is added in levels of between 0.68-0.70% to an otherwise standard Al-5083 alloy composition. Investigations of the microstructure as well as the crystal structure of the binary Al-Mg phase and the ternary Al-Mg-Zn phase, along with the pitfalls associated with classifying these phases, are compared and discussed.

**Experimental**

The following study is based on material that was cast under contract by the Reynolds Aluminum Corporation. Ingots were solidified using a small-scale direct chill process and provided to The Ohio State University for further processing. These castings of 5000-series alloys, which fell into the normal window of the common Al-5083 alloy, were either standard Pechiney 5083 composition or were modified by the addition of Zn in levels between 0.68 and 0.70%. All samples were processed in a manner that produced an H116-type temper, which, as was outlined for the Sc/Zr modified alloys of Chapter 3 (identical to the processing sequence of Section 3.6.2), included a small amount of cold work (18% reduction) followed by stabilization at 110°C for two hours. For comparison, several samples were also studied which contained elevated levels of Mg (5.4%) that was processed in an identical manner in order to maximize sensitization effects and β-phase formation. It should be noted that no samples based on the 5083 chemistry exhibit the formation of a secondary phase without an additional “sensitizing” artificial aging treatment at an elevated temperature. Samples for this study underwent a sensitizing treatment of 24 hours at 200°C in order
to allow precipitation of secondary particles to a readily observable level (Figure 4.4). All foils made from these samples were viewed on a Philips CM200 TEM; foils were prepared using either electropolishing with a 25% nitric acid/75% methanol solution at 15V and -15°C, or by dimpling foils with a diamond paste slurry to 25 µm and ion milling at 6kV, 1mA at 15°. The dramatic difference in the results obtained following these the two types of foil preparation techniques will be described below.

Figure 4.4: Strip of Mg-rich secondary phase in sensitized Al-5083 with 5.4wt% Mg.
Ion Milled Samples

An ironic effect of studying the corrosive nature of a secondary phase is that sample (foil) preparation in the form of electropolishing, which relies on a corrosion process to thin samples, may prove severely damaging to the phases of interest in foils prior to their being viewed under the electron microscope. The extent to which this degradation can occur will be discussed below. One way to avoid this effect and subsequently retain the crystalline integrity of the secondary phase particles would be to remove the corrosive process entirely from foil preparation. This was accomplished by dimpling followed by room-temperature ion milling of each foil. The results of this process are shown in Figure 4.5, where the presence of secondary phases is observed along grain boundaries in the 5083 alloy (Figure 4.5(a)), and in the 5083+Zn alloy (Figure 4.5(b)). Although somewhat blocky and almost polycrystalline in appearance, both phases are reasonably intact in terms of crystallinity and as such the structure of the precipitates can be evaluated and classified through selected area diffraction (SAD) analysis.

Due to the complexity of the β phase unit cell and associated volumetric change associated with its formation, it should not be surprising that these or similar precipitates seek areas with a large lattice mismatch. The lack of a "continuous" phase would indicate that a certain threshold energy level must exist at boundaries prior to nucleation and growth of the secondary phase. This volume-accommodating threshold is evidently not reached in a continuous fashion along subgrain or grain boundaries, hence growth of the secondary phase occurs sporadically along a given boundary.
Figure 4.5: Dark-field TEM images of grain boundary phases in sensitized samples of (a) 5083 and (b) 5083+Zn that have been ion-milled rather than electropolished during sample preparation.
Crystal Structure

Successful sample preparation reveals the crystal structure of the β-phase in the 5083 alloy. In previous work using X-ray diffraction, the crystal structure of the β-phase in the alloys has been determined to be cubic with space group Fd3m. The unit cell is quite complex, having a lattice parameter of ~2.5nm and containing 1168 atoms [5]. Figure 4.6(a) shows the diffraction pattern of the β phase; Table 4.3(a) demonstrates the correlation between d-spacings measured on the pattern and those published in the Joint Committee on Powder Diffraction Standards (JCPDS) file 29-48 [31]. The orientation relationship of the β-phase with either of the adjacent Al grains is not obvious based on observations along several zone axes. Figure 4.6(b) shows the diffraction pattern of the Zn-containing precipitate, along with an identification of several reflections from the α-Al matrix. It can be seen that there exists a discernable orientation relationship between particle and matrix (matrix and precipitate reflections line up). As shown in the figure, the [111] direction of the precipitate is parallel to the [111] direction of the matrix, while the (844) plane of the precipitate is parallel to the (220) plane of the matrix. Although morphologically these precipitates resemble β phase particles, this diffraction pattern is distinctly different, and is, in fact, consistent with the ternary Al-Mg-Zn τ-phase, Mg_{32}(Al,Zn)_{49}. This conclusion is based on a direct comparison between appropriate d-spacings measured on the pattern and those published in JCPDS file 19-29 [32] (Table 4.3(b)).

Electropolished Samples

The formation of a secondary phase along a grain boundary in a high Mg (5.45%) sample following electropolishing of the TEM foil is clearly shown in Figure 4.4. EDS analysis indicated that this and similar regions are Mg-rich in comparison to the
Figure 4.6: Diffraction pattern of (a) β-phase \((\text{Al}_3\text{Mg}_2)\) and (b) τ-phase \(\text{Mg}_{24}\text{Al}_{17}\text{Zn}_{45}\) along with surrounding matrix.
### β-phase

<table>
<thead>
<tr>
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<th>Measured d-spacing (Å)</th>
<th>JCPDS d-spacing (Å)</th>
</tr>
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<tr>
<td>8 8 0</td>
<td>2.51</td>
<td>2.496</td>
</tr>
<tr>
<td>7 7 1</td>
<td>2.85</td>
<td>2.838</td>
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<tr>
<td>10 2 2</td>
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<td>12 4 2</td>
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<tr>
<td>10 10 0</td>
<td>2.14</td>
<td>1.997</td>
</tr>
<tr>
<td>16 8 8</td>
<td>1.47</td>
<td>1.441</td>
</tr>
<tr>
<td>4 2 2</td>
<td>5.80</td>
<td>5.764</td>
</tr>
<tr>
<td>4 4 2</td>
<td>4.74</td>
<td>4.706</td>
</tr>
</tbody>
</table>

(a)

### τ-phase

<table>
<thead>
<tr>
<th>Reflection</th>
<th>Measured d-spacing (Å)</th>
<th>JCPDS d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1 0</td>
<td>10.0</td>
<td>10.10</td>
</tr>
<tr>
<td>2 2 0</td>
<td>5.06</td>
<td>5.030</td>
</tr>
<tr>
<td>2 1 1</td>
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<td>4.08</td>
<td>4.110</td>
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<td>2.519</td>
</tr>
<tr>
<td>6 1 1</td>
<td>2.34</td>
<td>2.307</td>
</tr>
</tbody>
</table>

(b)

**Table 4.3**: Diffraction pattern measurements of the (a) β-phase and (b) τ-phase correlate closely with those published in JCPDS files 29-48 and 19-29, respectively.
surrounding matrix. The general appearance and overall size, shape, and location of these phases are consistent with the $\beta$ phase identified in the ion-milled samples. Several observations can be made from the micrographs in Figures 4.4 and 4.5, which was representative of the secondary phase found in each of the samples. The first aspect of note is that the secondary phase tends to form in strips along grain boundaries. These strips are not continuous along the entire length of the boundary, and as seen from the “clean” subgrain boundaries surrounding the secondary phase, are not continuous along subgrain boundaries, either. These secondary phase strips have been seen along the boundaries of subgrains, however, and are also often observed in the interface between the matrix and or grain boundaries and the manganese-based ($\text{Al}_\text{Mn}$) dispersoids. The other aspect of note in this figure is the condition of the secondary phase; it appears to have been extensively eroded away at some point during processing or sample preparation. One possible cause of the severe degradation of the secondary $\beta$ phase is that it is preferentially corroding during the electropolishing process, as was addressed in the previous section.

It has been theorized that one of the causes of SCC in Al-Mg alloys is the galvanic coupling effect between the $\alpha$-aluminum matrix and the secondary $\beta$ phase, a phenomenon that is consistent with the extent of material loss in the $\beta$ phase following electropolishing. It has been reported that the $\beta$ phase precipitate is strongly anodic to the Al-Mg solid solution matrix in the presence of many electrolytes [10]. The aggressive corrosion environment associated with the electropolishing process, combined with the surface area difference between the large cathode (matrix) and comparatively small “sacrificial anode” ($\beta$ phase), would strengthen the argument for this type of corrosion. The TEM diffraction pattern, shown in the inset of Figure 4.7, contains both diffraction spots and amorphous rings. The spots seen in the figure index to the surrounding $\alpha$-aluminum matrix, while the secondary Mg rich phase (confirmed by EDS) exhibits
only the amorphous rings. These rings do not index to the \( \beta \) phase, and thus conclusive proof of the character of the secondary phase could not be performed on samples prepared by electropolishing.

The samples containing 5083+Zn exhibit a secondary phase along grain boundaries as well (Figure 4.7(b)). This phase, however, was not the same Mg-rich phase seen in the standard 5083 alloys. Through EDS peak comparisons, these particles were actually seen to contain a large amount of Zn in addition to the excess Mg, in levels well above those observed in the matrix. Various exfoliation tests performed on samples in this study showed that the samples containing Zn, even at levels well below 1%, were more resistant to grain boundary lining and exfoliation failure than those which contained no Zn. Support for the resistance of this Zn-containing secondary phase to corrosion during electropolishing is demonstrated by the remaining (although limited) crystal structure of the phase in the associated diffraction pattern. While the pattern is difficult to make out and all but impossible to classify, crystal reflections do exist, indicating that unlike the amorphous and degraded \( \beta \)-phase regions, the crystallinity of the Zn-rich grain boundary regions did not fully dissolve during the corrosive electropolishing process. Aside from this information, however, very little information could be gained from diffraction analysis due to the still-heavy erosion of the secondary phase during electropolishing. This observation is not conclusive evidence as to the corrosion susceptibility of each phase, but certainly indicates that sample preparation through "corrosion-free" means (dimpling/ion milling) is warranted.

4.5.2 Other Additions - Copper and Silver

Previous sections outline the observation that alternate phase will form in the presence of minor Zn levels, a ternary \( \tau \) phase \( \text{Mg}_{0.32}(\text{Al},\text{Zn})_{0.68} \), which is less susceptible to anodic dissolution at the grain boundaries when exposed to the aggressive
Figure 4.7: (a) secondary phase in 5083 alloy; inset shows matrix with amorphous rings from precipitating phase, while (b) 5083+Zn secondary phase is similar in appearance, some crystallinity is retained.
electropolishing environment [30]. This ternary phase that forms can also have Cu or Ag in the place of Zn in the τ phase structure [19]. It is not understood, however, how similar additions of copper or silver rather than zinc might perform under the conditions that proved favorable for the zinc-containing alloys. What is important to remember is that, based on the Zn studies, the potentially harmful β phase is replaced by the ternary phase; the same behavior might also occur in the presence of Cu or Ag. One would not expect the corrosion mechanics to be similar if for no other reason than each element’s relative position in a simple galvanic series. Cu and Ag are both far more noble elements than Zn, and hence the dissolution mechanism might not even be a major contributor to corrosion processes that might occur.

Initial corrosion studies provide a more direct comparison of the corrosion performance of these modified alloys. For this experiment, modified alloys were cast and processed entirely at The Ohio State University. Much like the Sc/Zr alloys of Section 3.6.2.2, base material was re-melted in the induction furnace and re-cast in graphite molds with additions of Zn, Cu, or Ag. The shrinkage cavities of each ingot was scalped off prior to a hot work reduction of 75% (.02-.03 in/pass) at 660-800°F and a cold work reduction of 20% (.005-.01 in/pass). This casting/processing treatment was used for all subsequent modified castings studied and reported over the remainder of Chapter 4. One sample each of 5083 containing copper, silver, or zinc of the chemistries listed in Table 4.4 was subjected to the standard exfoliation test for 5000-series aluminum alloys, ASTM G66, following a lengthy sensitization treatment (175 hours at 165°C), which was instituted in order to allow secondary phases to fully form. Following extensive polishing of the three samples (Figure 4.8(a)), they were immersed in a warmed corrosive environment consisting of ammonium chloride, ammonium nitrate, ammonium tartrate, and hydrogen peroxide (see Step 8, ASTM Test G66) for eight hours and examined. Figures 4.8(b-d) demonstrate the distinct differences in corrosion behavior of the three samples. The sample containing zinc (4.8(b)) performed
**Orig. 5083:**  
Mg - 5.0%  
Mn - 0.54%

**5083 + Ag:**  
Mg - 4.8%  
Mn - 0.54%  
Ag - 0.53%

**5083 + Cu:**  
Mg - 4.6%  
Mn - 0.52%  
Cu - 0.86%

**5083 + Zn:**  
Mg - 4.6%  
Mn - 0.51%  
Zn - 0.62%

**Table 4.4**: Compositions of 5083-based alloys re-cast with additions of Ag, Cu, and Zn.

adequately, showing some areas that retained their initial luster while other areas are showing the onset of mild pitting or exfoliation. The silver containing sample (4.8(c)) demonstrated a great deal of pitting. This would indicate that the corrosion was initiated at distinct points within the microstructure, and was not demonstrating a distinct degradation along grain boundaries which would be evident by exfoliation. The copper containing sample (4.8(d)) demonstrates a severe amount of this type of exfoliation corrosion; entire grains have begun to lift away from the sample due to the extensive degradation of grain boundaries. Further grain boundary lining study was performed via scanning electron microscopy (SEM) on each sample (Figure 4.9) following polishing and a mild 30 second etch in Barker’s reagent. Again, the attack seen at grain boundaries is comparably worse for the copper-containing sample than for the other two. Zinc, once again, appears to have performed in the most resistive fashion to grain boundary attack, at least for this particular G66 surface corrosion test.
Figure 4.8: ASTM G66 test of modified 5083 alloys. (a) Polished samples (b) 5083+Zn (c) 5083+Ag (d) 5083+Cu
Figure 4.9: SEM micrographs of the three test samples following light etch using Barker's reagent in order to observe degradation of grain boundaries.
While this preliminary test indicates that there is not any sort of direct correlation in performance between alloys modified with one of the three additions when compared to Al-5083, as each demonstrated vastly different corrosion behavior, it does indicate that there is room for further study into the behavior of the modified alloys. At first glance, the grain boundary phases that form are very similar in appearance to those seen in standard 5083 or in 5083 modified with zinc (Figure 4.10). Additionally, there are additional phases that apparently form in grain interiors for the composition levels studied (Figure 4.11), indicating that concentrations are high enough to alter matrix bulk characteristics as well as the grain boundary phase makeup. For the next section of the study, investigating the microstructural effects of minor additions of copper and/or silver, a more sophisticated means of identifying microstructural features and local compositions will be needed. As the zinc additions have demonstrated positive results in terms of modifying the existing phase (β) at grain boundaries in Al-Mg-Mn alloys, we will endeavor to further modify the Al-Mg-Zn τ phase with much less aggressive additions of copper and silver. An invaluable tool for this investigation is described in the next section.

4.5.2.1 EMiSPEC

A vital tool in this compositional analysis is the EMiSPEC software system used in conjunction with the CM300 FEG when operated in scanning mode (STEM). Like earlier observations on Zr- and Sc-modified alloys (Chapter 3), compositional maps can be an important piece of information regarding microstructural features of interest. A compositional map focusing on the grain boundary characteristics important to this chapter is shown in Figure 4.12. In this figure, a standard 5083 sample is mapped in the vicinity of a grain boundary, demonstrating the characteristic
Figure 4.10: Sensitized samples of 5083+Ag (a) and 5083+Cu (b) demonstrating a grain boundary phase that is similar in appearance to previously observed phases.
Figure 4.11: Sensitized samples of modified 5083 samples, (a) $+\text{Ag}$, (b) $+\text{Cu}$, and (c) $+\text{Zn}$, that have been heavily cold worked to refine grain size.
Figure 4.12: Composition map of standard 5083 that has been sensitized.

microstructure made up of large Mn-based precipitates within the $\alpha$ aluminum matrix (as was outlined in Chapter 3). The scanned image shows the contrast of a number of precipitates, the resulting EMiSPECT map shows that these precipitates are, in fact, the common Mn-based particles. Also of importance through this mapping technique is the condition of the apparent phase along the grain boundary. It clearly contains a significant amount of magnesium, and as such reveals the type of microstructure one can expect of sensitized aluminum alloys that contain elevated levels of Mg. It should be noted that this mapping does not reveal information about actual crystal structure of these precipitates, as selected-area diffraction (SAD) analysis will, but instead only reveals that they are rich in manganese with respect to the surrounding matrix.
For further sections in which more detailed studies of compositional gradients and chemical distributions are the focus, the EMiSPEC system will be used extensively in order to provide compositional maps. Revisiting the 5083+Cu and 5083+Ag alloys, compositional maps aid in revealing immediate differences in grain boundary makeup when compared to standard 5083 and 5083+Zn. TEM investigation of these alloys, carried out on samples dimpled to 30 µm and ion milled at 6 kV, 1 mA, at 12°, with a finishing mill at 9°, allow EMiSPEC observations on the CM300 microscope. Figures 4.13 and 4.14 show a grain boundaries enriched with Mg, but also decorated with discrete Cu- and Mg-bearing particles. Such discrete particles of the “extra” modifying element were not seen in Zn-containing samples (i.e. discrete Zn-based phases), indicating that a different equilibrium phase than merely τ may be forming with Cu concentrations at the level added. The enrichment of the grain boundary with copper is clear, based on line profiles of copper composition (Figure 4.15), but the presence of the discrete particles is cause for concern. With the objective being to change to composition (and hopefully to corrosive nature) of grain boundary phases that form, additional particle formation could potentially induce new types of corrosion mechanisms. Similarly, the Ag-containing samples reveal grain boundary particles that are more discrete and equiaxed in nature (Figure 4.16) than the drawn-out β or Zn-based τ phases. Further evaluation of these corrosion concerns will follow in the next sections.

4.5.2.2 Cu Additions

One possible reason for the extreme drop in corrosion performance outlined in the previous section may be additional phases that form in the modified alloys. In the Cu-containing alloy, S-phase was present at grain boundaries as well as within the matrix which may have contributed to its poor exfoliation test performance. This study
will endeavor to determine the threshold for S-phase formation in a Cu- and Zn-modified 5083 alloy, thereby determining if a τ-phase containing Zn and Cu will form without additional S-phase formation. While the mechanism for localized corrosion due to S phase formation is unlike the grain boundary weakening mechanism discussed throughout this paper, the concern is valid. The dealloying effects of the intermetallic S, whether actually confined to the phases or local dealloying of the surrounding matrix (both of which occur to some extent [33]), there is a measurable weakening of the alloy that would contribute to failure under stress at lower levels than expected. Since the S phase formation might also be homogeneously distributed throughout grain interiors, some degree of transgranular failure could be expected that is not generally a concern when evaluating SCC resistance.
**Figure 4.14**: Composition map of 5083+Cu showing enriched grain boundary region as well as a distinct Cu-containing phase.
**Figure 4.15**: Linear composition profile across a grain boundary of 5083+Cu.
Experiment

The three alloys examined for this portion of this study were cast in 2 in x 2 in x 5 in graphite molds; the base material was a standard 5083 alloy to which minor additions of Zn and varying amounts of Cu were added. The shrinkage cavities were scalped off and each casting was given a hot work reduction of 75% at 450°C (identical to the alloys of the previous section), but were given a cold work reduction of 80%. The heavy amount of cold work was applied in order to reduce grain size and maximize grain boundary area for TEM observation. Each sample was then given a rapid ‘flash anneal’, at 500°C for 10-15 minutes. This treatment has shown favorable recrystallization results in other modified 5083 alloys [34]. Samples were then severely...
sensitized in order to allow a more complete formation of grain boundary phases. TEM observation was carried out on samples dimpled to 30 μm and ion milled at 6 kV, 1 mA, at 12°, with a finishing mill at 9°. Examination was done on Philips electron microscopes, micrographs and diffraction images on a CM200 (LaB₆), and high resolution images and composition maps on a CM300 FEG equipped with EMiSPEC. In order to facilitate a more complete grain boundary phase formation, the samples were subjected to an aggressive sensitization treatment - 350 hours at 165°C. The final compositions of the modified alloys are listed in Table 4.5.

**S-Phase Formation**

Examination of the three samples indicate that an "extra" phase is present in the grain interiors in the "high"-Cu sample (Figure 4.17). Energy-dispersive spectroscopy (EDS) gives a slight peak at the Cu energy level (Figure 4.18), although this peak is not significant enough to make conclusions on the composition of these precipitates. Previous work on aluminum alloys containing Mg and Cu gives an indication that the compositions cast should be near the S-phase equilibrium [26], but the transition from the α+τ to an α+τ+S phase field is not defined for a 5083+Zn+Cu composition. The phase equilibrium transition is likely between Cu levels of 0.075

<table>
<thead>
<tr>
<th></th>
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<th>Mn wt%</th>
<th>Zn wt%</th>
<th>Cu wt%</th>
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<td>.58</td>
<td>.073</td>
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<td>4.4</td>
<td>.51</td>
<td>.58</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Table 4.5**: Final compositions of re-cast 5083-based alloys with 0.6 wt% Zn and varying low levels of Cu.
and 0.15 wt% in a 5083+Zn alloy, however, based on observations that indicate that no copper-containing matrix phases are present in the “low”-Cu sample while very small and widely dispersed copper-containing phases are present in the “medium”-Cu sample. 0.013 wt% Cu appears, therefore, to be very near the transition point between the two phase fields. Proof that this phase is indeed S-phase is gained through the use of high-resolution transmission electron microscopy (HRTEM). Figure 4.19 shows a HRTEM image of one of the Cu-containing precipitates present in the high-Cu sample. The resulting fast Fourier transform of this image correlates with previously published work on S-phase precipitates in Al alloys [35].

**τ-Phase Formation**

The second goal of this section of the study was to determine whether or not Cu would contribute to the compositional makeup of the expected τ-phase forming along
Figure 4.18: EDS spectra of grain boundary phase in low-copper (a) and high-copper (b) sample contain observable levels of copper and zinc.
grain boundaries. As was shown in Figure 4.18, EDS spectra indicate the grain boundary phase that forms contains some finite level of both Zn and Cu. Further confirmation is gained through compositional mapping via EMiSPEC; Figure 4.20(a-c) indicate that, in addition to the expected enrichment of Mg and Zn, there is also an elevated level of Cu at the grain boundary even for the low-Cu sample. It can be inferred, therefore, that Cu, like Zn, has a propensity to contribute to the makeup of the resulting grain boundary phases in high-Mg aluminum alloys even when added at very minor levels. Compositional maps do not, however, confirm the crystalline structure of the observed phases. Diffraction data aids in clearing up this remaining question; the measured d-spacings between observed patterns (Figure 4.21) and those published in JCPDS file 19-29 [32] correlate extremely well; within a small margin of measuring error, they are essentially the same as those listed in Table 4.3(b). This gives us strong evidence that the structure of the phase is indeed τ phase, in this case Mg_{32}(Al,Cu,Zn)$_{49}$. It is interesting to note that the phase present is not necessarily the stable τ phase in all observations.

Figure 4.19: High-resolution TEM image of one aspect of an “additional phase” precipitate. Associated Fourier transform (inset) of CCD image correlates very well with S-phase published work.
Figure 4.20: Digital image of the grain boundary phases and associated composition maps of selected grain boundary area. EMiSPEC maps show relative levels of selected elements; "brighter" areas indicate higher concentration. Note the presence of copper in addition to the expected levels of magnesium and zinc in not only the high-copper sample (a), but also in the medium- (b) and low-copper (c) samples (continued next page).
JCPDS file 39-951 [36] indicates that a metastable phase exists of the same stoichiometry \((\text{Mg}_{32}(\text{Al},\text{Zn})_{49})\) as the Zn-containing \(\tau\) phase, but of quasicrystalline icosahedral symmetry. Figure 4.22 demonstrates that this quasicrystalline phase is present in some areas of the modified 5083 alloys as well. A more detailed description of these observations will be made in the next subsection.

4.5.2.2.1 Quasi-Crystalline Phase Formation

The previous section discussed the qualitative composition of the grain boundary phases that form in the presence of copper, but the evolution of the grain boundary phases that form was not described. This section of the study will discuss a time-dependent phases phenomenon whereby the "high" copper levels in these modified alloys can lead to the formation of a quasicrystalline phase of icosahedral symmetry. The sensitization time for this modified alloy will be varied in order to provide some indication of the kinetics of formation of these phases of nontraditional symmetry.
Figure 4.21: Diffraction pattern (b) of grain boundary phase (a) gives d-spacings which confirm τ-phase through correlation with published JCPDS file.

Figure 4.22: Several grain boundary phase observations (a) yielded microdiffraction patterns that demonstrated the presence of a quasicrystalline metastable phase. Note the tenfold symmetry of the pattern.
Experiment

The modified alloys observed herein have been processed to a fine grain size through the application of a hot work cycle followed by an 80% cold work reduction. The processing sequence was discussed in the previous section for these Zn- and Cu-containing alloys. Samples were also given a flash recrystallization treatment at 500°C for 10 minutes, cooled, and sensitized at 165°C for intervals of 25, 175, and 350 hours. Foils for transmission electron microscopy (TEM) were prepared in the same manner as outlined in previous sections, by dimpling to 25 μm and ion milling to perforation in order to maintain the integrity of the secondary grain boundary phases.

Observations of foils at lower magnifications and associated diffraction patterns were obtained on the Philips CM200, with compositions being confirmed by utilizing the microscope’s energy-dispersive spectroscopy (EDS) capability. High resolution TEM (HRTEM) work was carried out on the Philips CM300 FEG equipped with a CCD camera.

Discussion

It has been demonstrated that zinc additions to high-Mg alloys will preclude formation of β phase precipitates along grain boundaries in favor of Zn-containing τ phase precipitates of Mg_{32}(Al,Zn)_{49} stoichiometry [30]. Further modifications to the grain boundary phase composition can be accomplished through minor additions of copper, which, like zinc, will combine in a τ phase structure containing magnesium and aluminum. While the amount of copper added to an alloy system which will form the Zn-containing τ phase must be very small in order to avoid bulk precipitation of S phase precipitates, even minor amounts of copper (<0.10 wt%) will find its way into the compositional makeup of the grain boundary τ phase [37]. Proof of this quaternary
makeup has been demonstrated through compositional mapping, although little has been done in terms of correlating the crystalline structure of this quaternary phase with previously studied and reported $\text{Mg}_{32} (\text{Al,Zn})_{49}$ ternary phases.

The formation of these phases, although occasionally seen in the interfacial regions between the prominent $\text{Al}_8\text{Mn}$ particles in the 5083 alloy system, are most often seen as continuous or semi-continuous phases along grain boundaries and only following an extended period of exposure to a moderately elevated temperature. For this experiment, the large amount of cold work followed by a flash recrystallization treatment was implemented in order to refine grain size and subsequently increase the amount of observable grain boundary area upon which secondary $\tau$ phase precipitates could form. Additionally, different sensitization times at 165°C were used, extending to 350 hours, in order to allow the secondary phase ample time to reach a stable state.

Several orientations of the $\text{Mg}_{32} (\text{Al,Zn,Cu})_{49}$ phase that formed at 25 and 175 hours are shown in Figure 4.23. In this experiment, the only such experiment to systematically sensitize the samples, the 25 hour treatment was far less effective at forming grain boundary phases than 175 or 350 hours. This observation was manifested in the difficulty in locating observable phases following the 25 hour treatments. For this reason, subsequent samples (discussed in future sections) are invariably sensitized to 175 hours. As seen in the dark field TEM image, the phase is elongated in the grain boundary interfacial region; the associated diffraction patterns index to those published in related JCPDS files for $\text{Mg}_{32} (\text{Al,Zn})_{49}$. Figure 4.24 shows the orientation relationship between the grain boundary phase and the $\alpha$-aluminum matrix. The simulation in Figure 4.24(b) is a matrix of aluminum with a precipitate of the expected Im3 symmetry of the $\tau$ phase, a body-centered cubic structure with a lattice parameter of 1.42 nm [19]. The simulation and diffraction pattern indicate an orientation relationship $[010]_a \parallel [001]_\tau$ and $(010)_a \parallel (1-10)_\tau$. 

174
Figure 4.23: Dark field image (a) of T phase on a grain boundary. Associated diffraction patterns (b,c) of different orientations properly index to related JCPDS files for Mg$_3$(Al,Zn)$_4$. 
While the extended sensitization treatments were designed merely to allow more complete development of the stable grain boundary phase, it became apparent that the phase that was prevalent in the samples aged to 350 hours at 165°C were, in fact, quasi-crystalline in nature (Figure 4.25). The physical appearance of the phases investigated were similar to the crystalline τ phase precipitates seen in the samples aged to lesser times, but diffraction patterns of all phases observed were limited to two-, three-, and five-fold symmetries along zone axes, indicative of an icosahedral quasi-crystalline structure. Numerous axes were investigated via HRTEM, a 2-fold example of which is shown in Figure 4.26, in order to confirm the observed common zones in the phase through simulated diffraction patterns. It should also be noted that a very limited number of the phases observed along grain boundaries in the alloys aged 175 hours also revealed five-fold symmetry, indicating that a morphological change in

![Figure 4.24](image)

**Figure 4.24**: Diffraction pattern (a) of α-aluminum matrix and Al-Mg-Zn-Cu precipitate. The simulation (b), based on an Mg_{32}(Al,Zn)_{49} precipitate in aluminum, agrees well with the observed pattern.
crystallinity may be occurring near the 175 hour point when sensitizing at 165°C. By all accounts, the contrast appearance and morphology of the quasicrystalline phase was nearly identical to that seen in the other grain boundary phases observed. Figures 4.26 and 4.27 show a high resolution (HRTEM) image of a quasicrystalline phase at the interface of two manganese particles and a grain boundary, a very common location for the β and τ phases seen thus far in this study.

The mere presence of a quasi-crystalline phase is not entirely surprising in that icosahedral structures have been well documented in Mg$_{32}$(Al,Zn)$_{49}$ alloys of near-stoichiometric composition that have been rapidly quenched [38]. It has been postulated that long range quasi-crystalline order is possible during rapid quenching due to the packing of icosahedral clusters of atoms aggregating in body-centered cubic lattice positions [39]. While the behavior observed in the sensitized 5083 alloys is not due to
Figure 4.26: (a) Filtered high resolution image of a quasicrystalline phase, the simulated diffraction pattern (fourier transform) of the blocked area in the quasicrystalline phase apparently exhibits 2-fold symmetry, as shown in (b).

A rapid quenching of the alloy, stable quasicrystalline phases in aluminum alloys are not without precedent. A stable ternary complex \( \text{(Al}_6\text{CuLi)} \) [40] has been observed in lithium-containing phases in aluminum alloys, following either slow solidification during conventional casting operations or heat treatments of a supersaturated solid solution [41]. Further description of this phase, which may substitute magnesium for lithium \( \text{(Al}_6\text{Cu(Li,Mg)} \) indicates that it acts in a manner similar to that seen in the 5083-based alloy reported in this paper, that is, a quasi-crystalline T2 phase precipitates along grain boundaries in peak-aged and overaged tempers [42]. Additional reports of a metastable quasicrystalline phase have been reported for magnesium alloys with zinc and aluminum [43]. Obviously, the main constituent of the matrix is now magnesium,
Figure 4.27: Quasicrystalline phase forming along a grain boundary at the interface between two $\text{Al}_6\text{Mn}$ "pinning points" (a). High resolution image (b) demonstrates an alignment of fringes (coherency) between the Q-C phase and the $\text{Al}_6\text{Mn}$ particle.
rather than aluminum, but of particular note is the similarity of the quasicrystalline phase that forms. It has an overwhelming propensity to form at grain boundaries, as does the phase seen in aluminum alloys; the composition of the phase, based on EDS analysis, is Mg – 43 at% Zn – 19 at% Al. This is essentially a τ phase composition, as is the phase seen in the modified aluminum alloys, but the phases were formed through a rapid quench of the alloy when casting. Again, though, the quasicrystalline grain boundary phase in the magnesium system is not an equilibrium phase. Unlike the modified 5083 alloys, which transformed over time into a quasicrystalline phase, this phase will transform into the equilibrium Mg31(Al,Zn)49 following annealing at moderately elevated temperatures.

4.5.2.3 Silver Additions

As has been indicated in previous sections for a Zn-modified 5083 alloy with various minor additions of copper, a threshold level exists for copper content above which S-phase (Al2CuMg) precipitates are likely to form following particular casting, processing, and sensitization treatments [37]. This threshold level was approximately 0.13 wt% Cu for the compositions given in these sample alloys. Based upon this apparent threshold level, castings were done in a similar manner in order to produce Zn-modified alloys which contained silver in levels that approximated the ideal copper content; i.e. in equivalent at% levels below that of the demonstrated S phase threshold. Again, the casting and processing conditions were repeated as outlined in previous sections – induction furnace melting of base alloys and appropriate additional elements, casting in graphite molds, hot work reduction of 75% at 450°C, and a minor 20% cold work reduction. The composition of these silver-modified castings is shown in Table 4.6. Following the dimpling/ion milling sample preparation used on previous samples,
EMiSPEC mapping of the silver-modified alloys again demonstrates the compositional changes to the grain boundary phase that forms when compared to the Al$_3$Mg$_2$ phase present in unmodified 5083 alloys that contain no silver or zinc. Figures 4.28 and 4.29 demonstrate the presence of silver in addition to the previously observed magnesium and zinc in the grain boundary phase. As shown in Figure 4.30, additional precipitates are prone to form, but it remains to be seen whether or not this additional precipitate structure is detrimental to corrosion performance. While S-phase formation was considered to represent a “threshold level” for Cu addition, the Ag-rich precipitates may not have the same corrosive properties as those attributed to S-phase precipitates in an aluminum alloy matrix.

## 4.5.2.4 Ag- and Cu-Modified Alloys

It has thus far been shown that τ-phase formation can occur not only as a ternary grain boundary phase containing Al, Mg, and either Ag, Cu, or Zn, but also as a quaternary phase containing Al, Mg, Zn, and either Ag or Cu. As a “final” evaluation as to the range of compositions in which τ-phase formation can occur, modified 5083 alloys were cast that contained all three of the “additional” elements – Ag and Cu as
Figure 4.28: 5083 + Zn + "medium" silver. Micrograph (a) and STEM image (b) demonstrate the grain boundary phase, while the presence of silver, along with Mg and Zn, is clear from the composition maps (c).
Figure 4.29: 5083 + Zn + "low" silver. Micrograph (a) and STEM image (b) reveal a grain boundary phase. The presence of silver, along with the expected discernable levels of Mg and Zn, is clear from the composition maps (c).
well as Zn, in compositions listed in Table 4.7. The compositions were designed to evaluate a "low" level of Ag and Cu in the Zn-modified 5083 as well as a "high" level of Ag and Cu. The presence of a grain boundary phase containing all five constituents in samples with both the high levels and low levels are demonstrated in Figures 4.31 and 4.32, respectively. It is interesting to note that during the observations on the low content alloy, the phase was more prevalent in the direct presence of the common Al₇Mn particles located along grain boundaries. These Mn-based dispersoids have been credited with helping to refine grain size in Al-Mg-Mn alloys by pinning grain boundaries [44]; the interface between these particles and the grain boundaries in which they are embedded appears to be ideal for the five-constituent phase to form in the case

![Figure 4.30](image)

(a)  (b)

**Figure 4.30**: The high density of precipitates in the grain interior is present even in the alloys containing relatively low additions of Ag. The presence of a distinct precipitate-free zone is also demonstrated.
Table 4.7: Compositions for a silver-and copper-modified 5083 + Zn alloy.

<table>
<thead>
<tr>
<th></th>
<th>Mg wt%</th>
<th>Mn wt%</th>
<th>Zn wt%</th>
<th>Cu wt%</th>
<th>Ag wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
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<td>.50</td>
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<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>High</td>
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<td>.50</td>
<td>.55</td>
<td>0.10</td>
<td>0.20</td>
</tr>
</tbody>
</table>

of low-level additions. This interface effect is demonstrated in the EDS spectra of Figure 4.33, where relative peak heights demonstrate the presence of Cu and Ag peaks not only on triple points, but also in the direct vicinity of Mn particles (note the Mn peaks on the upper EDS trace). Based on investigations of various samples by this author, the latter case (phases present in Al$\_6$Mn/grain boundary interface regions) was the more commonly observed situation.

As with the high-level Cu additions and each of the Ag additions, additional precipitate formation is quite widespread in the grain interiors of each of the Ag and Cu containing samples. Even for the sample containing low levels of Ag and Cu, the formation of precipitates is clear (Figure 4.34). Note the presence of precipitates with respect to grain boundaries; there is a distinct precipitate-free zone (PFZ) extending 150-200 nm in a perpendicular direction from the boundary. Fine-probe EDS reveals that these particles contain levels of Mg, Ag, and Cu; the size and shape of the precipitates would indicate that these are a variation of the S-phase, a silver-containing metastable precipitate of very similar structure identified as the X'-phase [27]. An additional effect on bulk precipitate structure is shown in Figure 4.34. The hot and cold work
Figure 4.31: 5083 + Zn + "high" copper and silver. Micrograph (a) and STEM image (b) demonstrate the grain boundary phase. Composition maps (c) show that both copper AND silver are present.
Figure 4.32: 5083 + Zn + "low" copper and silver. The images (a,b) and composition maps (c) demonstrate the presence of an Mg-, Zn-, Ag-, and Cu-containing phase embedded in the interface between an Al₆Mn particle the observed grain boundary.
Figure 4.33: 5083 + Zn + "low" copper and silver. Micrographs show (a) an Mn-free triple point and an enriched zone around an Al\textsubscript{5}Mn particle (b). Fine-probe EDS (c) demonstrate the composition of the areas highlighted. The lower spectrum shows the matrix, the middle spectrum shows the triple point highlighted in (a), the upper spectrum shows the Mn-based particle and surrounding phase highlighted in (b).
Figure 4.34: Distinct roll bands (a) of precipitates contain three major types (b): A - an Mg-Ag-Cu precipitate (classified by fine-probe EDS), B - Al$_6$Mn particles, and C - blockier Al$_6$(Mn,Cr) particles. B and C are common in unmodified Al-5083 as well.

cycles have produced a very distinct roll-band structure that is quite dense with precipitates. The majority of these precipitates can be classified as one of three types (Figure 4.34(b)), the Mg- Ag- and Cu-containing (X'-phase) precipitates, the common Al$_6$Mn dispersoids, and the similarly common Al$_6$(Mn,Cr) particles. The latter two particles, it should be noted, are also quite prevalent in unmodified 5083 compositions.

Zn Level Reduction

The formation of variations of $\tau$ phase at grain boundaries has thus been demonstrated, both in terms of structure and composition, for an alloy containing 0.6-0.7 wt% Zn along with the relatively trace levels of Ag and Cu. Concerns have been
raised, however, over the viability of such an alloy as a substitute for standard 5083. More specifically, the castability of an Al-Mg alloys with levels of Zn greater than \( \sim 0.5 \) wt\% (but well below those of common 7000 series alloys) has proven problematic. Based on industry experience, enriched eutectic zones of Al-Mg-Zn (in large-scale pours, where concentration gradients can vary to a greater degree) can be a catalyst for eutectic cracking under some casting conditions [45]. Additionally, the issue of weldability is also a concern due to the same basic premise; that is, behavior during solidification of the weld re-melt zone. For this reason, it was reasonable to cast another group of alloys to ascertain whether a lower zinc level would still have the Zn-enriching effect on grain boundary phases. The compositions for this round of castings are listed in Table 4.8; Zn levels have been reduced to 0.3 wt\% from 0.6 wt\% with similar levels of Cu and, in some cases, Ag. The resulting composition of the grain boundary phase, taken directly from the threaded region of a sensitized sample pulled to failure under slow strain rate conditions, is shown in Figure 4.35. It is clear that, even with the experimentally proven “ideal” zinc level dropped in half, the resulting grain boundary phase is rich in zinc (Figures 4.36 and 4.37). The resulting SCC performance of this potentially more “cast/weld friendly” alloy, along with the performance of the other alloys cast and processed, will be discussed in a future section.

<table>
<thead>
<tr>
<th></th>
<th>Mg wt%</th>
<th>Mn wt%</th>
<th>Zn wt%</th>
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<td>.31</td>
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<td>0.03</td>
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*Table 4.8*: Compositions for a silver-and copper-modified 5083 + reduced Zn alloy.
Figure 4.35: Fine-probe EDS reveals the presence of Zn, Cu and Ag in the grain boundary region.
Figure 4.36: Composition map of grain boundary region showing Zn enrichment and slight copper enrichment.
Figure 4.37: Composition map of reduced-Zn sample; the grain boundary phase is in the $\text{Al}_6\text{Mn}/\text{grain boundary}$ interface.
4.5.3 Activation Energy

When evaluating the behavior of modified alloys with respect to grain boundary phases that form, an important factor in this phase evolution is the transport of solute atoms to the grain boundaries. A novel approach to gaining information on atom transport within alloys modified with zinc, copper, and silver is to perform creep tests in which the strain rate will be a function of, among other factors, the ability for solute atoms to allow viscous glide of dislocations. The ease with which this atomic re-ordering can occur will be reflected in the activation energy for the creep deformation process. It should be noted that this information does not give an indication of actual Mg transport to grain boundaries, which is a product of energy reduction; the creep testing of this section is merely a reflection of bulk atom transport by lattice or grain boundary diffusion.

Experimental

Sections of each alloy, taken from processed sections of alloys fully processed and evaluated in previous sections, were cut in 5 x 5 x 15 mm samples with the long axis oriented in the long transverse direction of the processed bulk material. Samples were identical in concentrations of Mg and Mn, the test elements present are comprised of the levels in Table 4.9. Each sample was slowly heated to a beginning temperature

<table>
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<tr>
<th></th>
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<th>Zn wt%</th>
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<tr>
<td>2 (Q)</td>
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</tr>
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<td>3 (Q)</td>
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</tr>
<tr>
<td>4 (Q)</td>
<td>3.9</td>
<td>.43</td>
<td>0.59</td>
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<td></td>
</tr>
</tbody>
</table>

Table 4.9: Creep test sample compositions for activation energy determination.
of 600 K, at which point the sample was loaded in compression to a stress of 30 MPa for the duration of the test. In order to “back out” the associated activation energy for viscous glide of each sample, the temperature was varied in steps between 600, 615, and 630 K and allowed to equilibrate prior to recording the associated strain rate at each temperature. The following equation is utilized:

$$\varepsilon = A\sigma^N e^{(-Q/RT)}$$

where $\varepsilon$ is the strain rate, $A\sigma^N$ is a combination of material factors along with the stress and stress exponent, $Q$ is the activation energy, and $R$ and $T$ are Boltzman’s constant and temperature, respectively. In order to ascertain strain rates, plots such as that shown in Figure 4.38 were produced for each sample. Following the establishment of

![Graph showing the relationship between time and total strain](Figure 4.38)

**Figure 4.38**: Example figure of slope curve during temperature jump testing - vertical lines display the time when temperature was stepped up or down by 15 K.
a "steady-state" strain increase vs. time at each temperature, the temperature was raised or lowered to the next incremental value until several recordings could be made for each condition at varying levels of strain. Inherent in this type of measurement are differences between structure and dislocation density at each strain level. Ideally, a new steady-state strain rate would be achieved immediately following an instantaneous step increase or decrease in temperature, allowing a direct ratio between two values of strain rate and temperature. This is, of course, not possible, so a reasonable accommodation was made by following the same heatup and cooldown steps for each sample and assuming similar dislocation structures over the moderate range of strains associated with the equilibration process, between 2-12%. By plotting (Figure 4.39)

Figure 4.39: Activation energy for standard 5083 is represented by the slope of the curve; best fit for this data is 155 kJ/mol.
ln(strain rate)*R vs. 1/T for each temperature step, the slope of the linear best-fit curve of the data points is the measured value for activation energy for the sample tested. In the standard Al-5083 sample, the value of the slope (and hence Q) is approximately 155 kJ/mol. This is in reasonable agreement with published values for Al-5.6%Mg in the viscous glide region of 149 kJ/mol [46] as well as with the reported activation energy for Mg diffusion in Al of 130.5 kJ/mol [47].

A comparison of the activation energies for each of the alloys is shown in Figure 4.40. Again, the use of the technique measured above cannot be wholly reliable in terms of the exact numbers gained (Table 4.10). The reason for this is that the use of these creep tests as a mechanical probe of atomic mobility is not straightforward. The precise mechanisms of creep deformation remain an active topic of debate in the literature. For example, dislocation creep is usually associated with stress exponents greater than three, and activation energies close to that for either self diffusion or solute

<table>
<thead>
<tr>
<th>Alloy (+ wt%)</th>
<th>Activation Energy for Creep Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5083</td>
<td>155 kJ/mol</td>
</tr>
<tr>
<td>5083 + 0.6 Zn + 0.08 Cu + 0.05 Ag</td>
<td>192 kJ/mol</td>
</tr>
<tr>
<td>5083 + 0.6 Zn + 0.08 Cu</td>
<td>167 kJ/mol</td>
</tr>
<tr>
<td>5083 + 0.6 Zn</td>
<td>185 kJ/mol</td>
</tr>
</tbody>
</table>

Table 4.10: Measured activation energies for modified alloys compared with standard 5083.
Figure 4.40: Representation of activation energies based on results of temperature step tests.
diffusion. The present experiment is designed to relate the activation energies to solute diffusion, but this can only be accurately inferred if the material is behaving as a Class A material, or alloy. An increase in values is demonstrated in each of the modified alloys, indicating that the kinetics of atomic transport during the formation of grain boundary phases are rendered more difficult in terms of energy barriers that must be overcome. One must be cautious, therefore, when designating differences in activation energy to particular mechanisms of creep deformation. While the intent of the experiment was to investigate possible differences in solute drag of Mg-rich atmospheres

Figure 4.41: Detail of primary creep transient (plastic strain only) demonstrates pure metal-type behavior as evidenced by the immediate plastic response.
around dislocations, the characteristic shape of the creep curves did not indicate that these alloys did not demonstrate alloy-type behavior, but rather pure metal behavior. The evidence for this behavior lies in the shape of the primary transient curve, the detail of which is shown in Figure 4.41. Class I, or alloy-type, behavior should not demonstrate an instantaneous plastic response to a stress jump [48]. While the magnitude of this instantaneous response differed based on the composition of the material, each did display some degree of instantaneous response. Additionally, stress jump and stress drop tests allowed a calculation of associated strain hardening exponents for each creep tested alloy according to the relationship:

\[ n = \frac{\Delta \ln \dot{\varepsilon}}{\Delta \ln \sigma} \]

where the measured stress and strain rates both before and after the jump give an indication of strain hardening exponent \( n \). Whereas Class I behavior should give an \( n \) value of \(~3\), these alloys produced \( n \) values of \(~5-6\), once again indicative of pure metal behavior [49]. This is evidence that that solute drag is not the limiting deformation mechanism for the conditions tested. The activation energies measured, therefore, can only be attributable to some form atomic mobility or lattice friction in the material, and not directly to a solute drag model and subsequent Mg mobility.

4.5.4 Slow Strain-Rate Testing

The identification of the phase morphology at the compositions and tempers described in the previous sections is important to the understanding of associated microstructures that can be expected when casting and processing these alloys. The real merit of modified alloys cannot fully be appreciated, however, unless these microstructures can be effectively correlated with physical properties of interest. That being said, this chapter is focused mainly on the performance of these alloys with
regard to the nemesis of high-Mg 5000 series alloys—stress corrosion cracking. To that end, the test most important for this section of the study is the constant extension rate test (CERT). Several factors make this a test that is highly germane to the SCC conundrum; first, the test can be performed under simulated marine conditions, with samples continuously exposed to an aqueous NaCl environment, and second, it produces an extraordinarily quantitative measure of performance in this environment with regard to strength. Rather than a simple pass/fail criterion or grading system that is subject to observer opinion, CERT gives a full stress-strain curve and associated strength and elongation values over the entire time interval to material failure.

The merit of CERT for understanding SCC in Al-5083 has been aptly demonstrated by the comprehensive work of Searles [50] in which the performance of 5083 under SCC conditions was correlated with the level of sensitization and hence the degree to which the β phase formation had developed. Figure 4.42 demonstrates the resistance (or lack thereof) of a standard 5083 alloy subjected to various times at a temperature moderately close to the solvus line of β phase equilibrium. As shown in the figure, the most extreme SCC vulnerability occurs at 189 hours at 175°C. Based on this work, the sensitization treatments given to the modified alloys tested for SCC will be based on this most-extreme condition for SCC susceptibility in alloys of near-5083 composition.

Experimental

The following sets of experiments are performed on material that has been machined to the cylindrical tensile bar dimensions given in Chapter 2 (Section 2.4.2). The material is based on compositions listed in previous sections taken from the fully processed ingots. Again, the processing conditions following casting in graphite molds included a 75% hot work reduction at 450°C followed by a 20% cold work reduction.
Figure 4.42: The effect of sensitization time at 175°F on total elongation to failure demonstrates a clear minimum for a variety of corrosion conditions.

For geometric considerations, it should also be noted that cold working reductions were limited to 0.005in/pass in the long transverse direction (perpendicular to hot rolling direction) in order to lengthen the stress axis of the samples. Tensile samples were then pulled in the same long transverse direction, in order that the elongation of grains that occurred during hot rolling was once again perpendicular to the stress axis, maximizing the grain boundary area subjected to tensile separation. This orientation prevented elongated grains oriented along the tensile axis from giving a falsely elevated indication of SCC resistance. All samples tested under sensitized conditions will have been exposed to a treatment of 165°C for 175 hours. It is assumed that this will give us a sensitized state that is most detrimental for SCC resistance in Al-5083, and as such
will give a direct comparison of the modified alloys to the baseline data for 5083 performance. Samples tested under “marine” conditions are pulled while constantly exposed to 0.5M aerated NaCl solution. An extremely important factor in each of the CERT experiments performed in an aqueous NaCl environment is that, in order to allow the kinetics of SCC to be the main contributing factor to strain failure, the strain rate was invariably set at $10^{-6}$/sec.

**Compositions**

In keeping with the strategy of the previous section, compositions of interest will be based on Al-5083 modified with some level of zinc in order to facilitate the formation of $\tau$ rather than $\beta$ at grain boundaries. Since the solubility of both copper and silver in these grain boundary phases has also been demonstrated, various minor additions of these alloys will also be tested in order to determine the composition which best resists failure due to SCC in the extremely sensitized condition.

Table 4.11 gives the compositions for a set of castings that contains zinc levels that zinc additions aid in resistance. Based on the CERT observations of Figure 4.43, however, this positive effect is overcome under more severe sensitization conditions.

<table>
<thead>
<tr>
<th></th>
<th>Mg wt%</th>
<th>Mn wt%</th>
<th>Zn wt%</th>
<th>Cu wt%</th>
<th>Ag wt%</th>
</tr>
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<tbody>
<tr>
<td>S 1</td>
<td>3.9</td>
<td>.52</td>
<td>.20</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>S 2</td>
<td>4.3</td>
<td>.50</td>
<td>.55</td>
<td>0.12</td>
<td>0.04</td>
</tr>
<tr>
<td>S 3</td>
<td>3.9</td>
<td>.55</td>
<td>.20</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>S 4</td>
<td>4.4</td>
<td>.53</td>
<td>.30</td>
<td>0.06</td>
<td>0.03</td>
</tr>
<tr>
<td>S 5</td>
<td>4.1</td>
<td>.49</td>
<td>.58</td>
<td>0.073</td>
<td></td>
</tr>
<tr>
<td>S 6</td>
<td>4.2</td>
<td>.50</td>
<td>.60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 4.11**: Compositions for various modified alloys tested via SSRT.
Figure 4.43: SSRT results of modified alloys vs. standard 5083.
Consider the electrochemical characteristics of isolated intermetallic phases $\beta$ (work performed by Searles [50]) and $\tau$ illustrated in Figure 4.44. On the top diagram, $\beta$ demonstrates a distinct passive region with a plateau or breakdown region not demonstrated by $\tau$ phase. Additionally, although the axes differ in units, the corrosion rate (current density) is considerably higher for $\tau$ than for $\beta$. While not explaining the initial positive results on surface corrosion testing outlined earlier in this chapter, this electrochemical characteristic certainly explains the poor performance of Zn-based $\tau$ phase under SCC conditions.

**Copper Additions**

Based on the effect that zinc alone might have on $\tau$ phase corrosion, it seems reasonable to conclude that if copper has a moderating effect on $\tau$ phase corrosion rate, there is a minimum level at which the dissolved copper content in $\tau$ phase will be high enough to begin to offset the highly corrosive nature of the phase under the conditions described. For the levels of zinc in the vicinity of 0.6 wt% in these modified alloys, this apparent minimum level is somewhere just above 0.04 wt%. There is certainly evidence that copper is having a positive effect on corrosion resistance, as evidenced by the increased ductility in the samples that contain a moderate level of copper. This effect begins to diminish, however, as levels begin to exceed 0.12 wt%. Consistent with our microstructural observations, there is a change in precipitate structure as copper begins to exceed these levels. The formation of $S$ phase particles becomes apparent above these levels, an effect that might well be causing corrosive conditions of a differing nature.

Further analysis of this apparent and very narrow copper window is investigated at a lower zinc content, compositions of which were given previously in Table 4.8.
Figure 4.44: Electrochemical potential of isolated $\beta$ and $\tau$ phases.
Silver Additions

In the samples that performed the best under the imposed SSR conditions, silver was consistently present at levels of 0.05 wt%. No explanation has been given thus far as to the strategy behind these additions and the possible role that silver might play in the development of SCC resistant phases. While it may be that the anodic potential of the $\tau$ phase that develops shifts with significant amounts of silver, it would seem based on extensive reports on Al-Cu-Mg-Ag alloys in the available literature that a more profound effect is occurring with regard to matrix precipitation kinetics. While the diffusion rates of the additional elements added to the modified alloys may not be affected significantly through Ag additions [52], it can be expected that precipitation nucleation and growth at the earliest stages might be rendered more rapid. In a phenomenon termed cluster hardening, the affinity of silver to readily form vacancy clusters [53] may lead to more rapid development of the more common phases in the alloys in question, depending, of course, on composition levels. It is commonly reported in the case of the aforementioned Al-Cu-Mg-(Ag) alloys to contribute to hastened formation of $T\alpha$ [54], $\Omega$ [55, 56], $\theta$ [53, 57, 58], and/or $X$ and $S$ [27, 59] phases in their incipient stages. Not only is this cluster hardening apparent in the sharp increases in hardness vs. aging time over non silver-containing alloys, but closer inspection reveals that in many cases the phases actually form oriented on different planes than are normally observed.

This silver effect would likewise have a contribution to the grain boundary phase formation and growth characteristics of our modified alloys. By hastening the formation of matrix phases (lowering the effective solvus temperature for post GP-zone nucleation and growth, it might be expected that more precipitation might occur locally to grain boundaries, effectively limiting the diffusion of solute to form grain
boundary phases. Of particular note is the high affinity of magnesium for silver atoms in solution in formation of these clusters [53], an effect that would be expected to lower the free Mg available in grain boundary regions.

The upper limit for silver additions was dictated by the high degree of excess precipitates that form in the matrix in the presence of silver. Some degree of incipient nucleation of clusters in grain boundary regions would seem to be beneficial for limiting the growth of grain boundary phases. In order to maintain the integrity of strengthening mechanisms in standard 5083 alloys (by limiting the formation of phases that are not otherwise beneficial to the properties of the alloy), it is desirable for the purposes of this study to limit the formation of excess precipitates in the grain interiors.

Zinc Reduction

As was outlined briefly in the latter portion of the last section, there is some concern over the level of zinc that is being added to the alloy with regard to possible cracking issues during solidification. This solidification cracking deals not only with the solidification of full-sized industrial ingot castings, but also of localized re-solidification following a weld pass. To address these concerns, tests were performed on castings that were within the “ideal” windows for copper and silver levels, but with the zinc level reduced from 0.6 to 0.3 wt%. As was demonstrated via EMiSPEC, the grain boundary phases that form in fully sensitized samples are still rich in zinc, indicating that zinc is playing its role in terms of β suppression even at the reduced concentration. Figure 4.45 demonstrates the performance of these alloys during SSRT in an aqueous NaCl environment, pulled to failure at a strain rate of $10^{-4}$/sec. As expected based on earlier testing, the “window” for ideal copper level is again realized, with the 0.10-0.12 wt% concentration showing the highest degree of resistance to failure. Copper in lower and higher concentrations did not perform as well. Somewhat disconcerting,
Figure 4.45: SSRT results of modified alloys with Zn level dropped to 0.3 wt%
however, based on the total elongation to failure in each of these tests, was the overall performance when compared to the other alloys tested. Even the sample that demonstrated the highest degree of strain to failure was less resistant than standard 5083, not nearly the improvement that was expected based on the chemistry and the results of previous tests.

At first glance, one might wonder if, in fact, the lower zinc level played a role in the decreased performance. This possibility can be discounted to some extent when a comparison with a sample pulled to failure in air is compared to those in the aqueous NaCl environment - the loss in ductility is relatively minor (Figure 4.46). When taking a closer look, the samples with the reduced Zn levels demonstrate a measurably higher yield strength than those tested before. This series of observations forces us to rethink some of the completed test results in terms of pre-test conditions. To be more specific, the "flash anneal" at 500°C may not, in fact, be recrystallizing the material to the extent desired in modified alloys with higher alloy concentrations. For these same alloys, it must also be considered that the "excess" η or X' phases that have been shown to form may not be re-solutionizing to the extent desired. In brief, the material tested may, in several cases, not be reduced from a hardened state to the extent that was assumed prior to testing. While it is expected that 5083 will quickly recrystallize under the 500°C conditions, the same may not be said for the modified alloys. The decrease in test ductility is due not to SCC failure, but mainly due to simple ductile failure at a lower strain level as a result of increased stress due to increased hardening. Notice the measurable change in hardening rate shown in Figure 4.47 between standard 5083 and the modified variants; following sensitization treatments the yield strengths and hardening rates for the modified alloys are increased. In an unsensitized condition, the slight hardening rate is more likely due to minor room-temperature aging along with additional solute strengthening. Along with the increases in precipitation-hardened strength, there is an associated loss of ductility that may account for a significant in
Figure 4.46: Standard 5083 shows a large drop in total elongation under CERT conditions. The modified alloy has less initial ductility, but more of this ductility is retained with respect to SCC.
Figure 4.47: Stress/strain curves for sensitized vs. unsensitized alloys pulled in air at 10^3/second. Inset shows detail of yield point and associated increase in yield strength for modified alloys.
It is somewhat tricky to associate the increased hardening rate with decreased ductility; for two similar alloys with different hardening rates, one would expect the increased hardening rate to result in a more uniform distribution of strain. This is particularly true in the gauge section of a carefully machined tensile sample. This uniform distribution leads to an increased resistance to the alloy reaching an “unstable” state (Considere’s criterion), whereby necking occurs and failure results due to the increased stress on the decreased cross sectional area. It should be noted, however, that this ductile instability is all but absent for the SSRT results observed. Failure occurs at or near the ultimate stress, rather than at some engineering stress value that is greatly reduced due to necking in the gauge section. Another important factor to consider from Figure 4.47 is the strain rate used to pull samples was increased to $10^{-3}$/sec from $10^{-6}$/sec. Figure 4.46 demonstrates that modified samples lose a certain amount of ductility as compared to 5083 when tested in air; one factor to be considered is that perhaps the corrosion rate for these modified samples is actually quite high in the untreated air of the CERT laboratory environment. The ductility seen in the modified alloys of Figure 4.47 removes this possible “humid air” effect as a plausible mode of failure [60]; $10^{-3}$/sec is far too fast for SCC failure to occur, but the total elongation for the samples pulled at the faster rate is actually decreased slightly (although all are in the similar range of 12-14%). If SCC in laboratory air was occurring when being tested at $10^{-6}$/sec, we would expect ductility to increase as the samples are pulled at a rate ($10^{-3}$/sec) which is too fast to allow an SCC-failure mechanism to occur.

With regard to the issue of recrystallization response and the associated solutionizing that will occur at elevated temperatures, it is important to examine the effect of an increased recrystallization time on alloy performance during SSRT testing. Several of the alloys, including those with reduced zinc levels, were given an extended recrystallization treatment of 75 minutes at 500°C. SSRT samples were machined and
given the same sensitization treatment as previously tested alloys. The results for the reduced Zn samples, pulled in aqueous NaCl at a strain rate of $10^{-4}$/sec, are shown in Figure 4.48. The elongation performance is quite different than that seen in Figure 4.45; the modified alloys with an “ideal” level of copper perform better than 5083, as was expected. By comparison, the 5083 subjected to the extended treatment fared slightly worse (9% down to 7.5%). Furthermore, the two modified alloys with ~0.11-0.12 wt% copper demonstrated the aforementioned sudden fracture rather than true SCC step-wise failure.

Looking at the changes in SSRT performance based on the length of the recrystallization treatment, it can be seen from Figure 4.49 that 5083 behaves in a different manner than any of the modified alloys. For the extended recrystallization treatment, the 5083 loses ductility, both when tested in air and when tested in aqueous NaCl. Earlier in this paper, Section 3.6.1 demonstrated the change in Al$_6$Mn precipitate structure following exposure to elevated temperatures, particularly in a highly saturated state. Although we cannot be certain of the degree of saturation prior to the recrystallization treatment, it can be inferred that the extended time at an elevated temperature would have a hardening effect on the material along with an associated loss of ductility. Another important factor at play involves the original goal of using a “flash” recrystallization treatment. Following the cold work reduction, the short exposure to 500°C was initiated in order to recrystallize heavily worked regions while being short enough to limit grain growth. The extended treatment would not be expected to limit such grain growth, and, in fact, would contribute to a high degree of grain growth. This behavior is clearly demonstrated in Figure 4.50(a), which utilizes orientation imaging microscopy (OIM) to determine crystal orientation maps of selected sample areas. Figure 4.50(a-c) are all generated via OIM from low-zinc SSRT samples given a recrystallization treatment at 500°C for 10 minutes or 75 minutes. The grain orientation shown is perpendicular to both the rolling direction and the SSRT tensile
Figure 4.48: SSRT (aqueous NaCl) results of modified alloys with Zn level dropped to 0.3 wt% - recrystallized for 75 minutes.
Figure 4.49: Increasing the recrystallization treatment from 10-15 minutes to 75 minutes decreases ductility in 5083 both in air and in aqueous NaCl (a), but increases ductility (SCC resistance) in modified alloys (b-d).
Figure 4.50: OIM images of sample demonstrate the change in (a) grain structure as the recrystallization treatment is increased for 10 to 75 minutes at 500°C.

(continued next page)
Figure 4.50 (con't) : (b) shows grain boundary misorientation which includes low angle boundaries of 1-11°, while (c) shows a histogram of the grain boundary misorientations for the areas mapped.
axis. It can be seen from this figure that while the grain size and shape has changed considerably with the excess heat treatment, there still exist grains that contain large unrecrystallized areas. 4.50(b) is a map which also contains white areas to represent changes in orientation of between 1-11°, grains heavily decorated with white areas are indicative of heavy dislocation density. The extended treatment did not, in fact, produce fully recrystallized samples. In terms of grain boundary misorientation, Figure 4.50(c) reveals that there is no tremendous shift in grain misorientation from low to high angle following the treatment. A weighted curve shown on each histogram indicates that, if anything, grain boundary misorientation is, on average, slightly higher for the grains that have not been subjected to the extended recrystallization treatment. Clearly, then, the change in behavior is attributable more to precipitate structure and solutionizing effects than to grain structure changes.

In the case of the modified alloys, we would expect a similar behavior as outlined above. The main difference, of course, is the presence of additional solute or precipitates which also have an effect on final behavior. As shown in Figure 4.49(b-d), the ductility gained by a more complete recrystallization and re-solutionizing treatment more than overcomes the loss in ductility seen in standard 5083. The extended treatment not only improves the curious lack of ductility in the reduced-Zn samples (to levels greater than standard 5083), but even improves the ductility of other modified alloys which had already shown favorable SCC resistance.

Further evidence of this premise is manifested in the shape of the stress-strain curve prior to failure. Figure 4.51 demonstrates a “representative” curve for simple ductile vs. SCC failure under SSRT conditions. Notice the stepped characteristic of an SCC failure – embrittled and corroding material fails quickly but crack propagation only advances to “clean” material, or material where the grain boundary either does not have a developed phase or where the area containing the grain boundary phase has yet to become dissolved or weakened. As the corrosion process continues, the failure
Figure 4.51: Characteristic shapes of failure regions of tensile samples. SCC failure demonstrates a “stepped” series of stress drops rather than the gentledownward curve of engineering stress.

zone continues to step along the cross section of the material as stress concentration in the remaining material is stepped up. The result is a decreasing trend of engineering stress jumps until total failure occurs. By contrast, the simple ductile failure is more of a very slight downward trend of engineering stress followed by a more sudden failure.

While the samples that did fail by more of a simple ductile mechanism lost a moderate degree of ductility when tested in aqueous NaCl compared with a test in air, indicating that there is some contribution of SCC to total failure, an examination of the failure zone can demonstrate that total elongation to failure is not entirely indicative of the resistance to SCC. Examples of the two types of behavior were demonstrated previously in Figure 4.46. Note the amount of retained ductility (in relation to the
sample pulled in dry air) in the modified sample. Despite the fact that SCC conditions are identical, the failure zone does not exhibit the characteristic SCC profile. A ductile failure of this type demonstrates that the material is, in fact, more resistant to SCC than the elongation to failure data would indicate. In other words, despite the highly representative nature of the SSRT behavior in aqueous NaCl with respect to SCC performance, a detailed understanding of ductile behavior in the absence of a corrosive environment is highly germane to an overall evaluation.

Clearly the important experimental observation from these CERT experiments is that Zn-based \( \tau \) phase is not as resistant to "true" SCC as would be believed from preliminary surface-effect type corrosion tests (grain boundary lining, exfoliation). The fact that a potentially degrading grain boundary phase, \( \beta \), can be replaced by \( \tau \) phase is the important item of note. The importance of \( \tau \) phase is that, in certain composition ranges, it is resistant to SCC failure in even the most extreme sensitization conditions. This optimum composition window is based on the copper level — too little does not overcome the aggressive corrosion effect of Zn, too much introduces additional S phase on grain boundaries and in grain interiors. This "optimum" copper window for the composition ranges tested, based on modified 5083 chemistry, is illustrated in Figure 4.52. The baseline data (dotted line) in the figure is the value for sensitized 5083 pulled to failure in aqueous NaCl at a strain rate of \( 10^{-6}/\text{sec} \). The reasons for this increased resistance due to minor copper levels is not immediately clear. While it is apparent that there is an improvement over the aggressively corrosive nature of Zn-based \( \tau \) phase (\( \text{Mg}_{32}(\text{Al,Zn})_{49} \)), this improvement is not readily obvious if modeled as a simple galvanic couple between the grain boundary phase and the matrix. Figure 4.53 illustrates the electrochemical potential of isolated intermetallic samples of not only the Zn-based \( \tau \) phase, but also a Cu-containing phase that is isomorphous (isostuctural) with \( \text{MgZn}_2 \), the \( \eta \) phase [61]. The corrosion potential does shift slightly, but the corrosion rate is still considerably higher over the foreseeable galvanic coupling range.
Figure 4.52: An apparent optimum, or "ideal", copper window exists with respect to SCC failure for low level additions in Zn-modified 5083 alloys.

between α-Al and this intermetallic than that of β phase (Figure 4.44). While it important to note that the potential of a Cu-based η-type phase may not be an accurate representation of Cu-based τ phase, it does illustrate that an expected shift in an Mg-Zn phase due to Cu is not tremendous. Further work into isolating actual Cu-containing τ phase, which is a complex undertaking due to the narrow compositional equilibrium range, is warranted in order to more accurately investigate the actual shifts in electrochemical potential due to Cu additions.
Figure 4.53: Electrochemical potential of isolated Al-Mg-Zn τ phase. Zn-free Cu-Al-Mg phase (isostructural with MgZn₂ η phase) potential is also shown.
4.5.5 Phase Formation Summary

1. Zinc additions of 0.68-0.70% to 5083-based Al-Mg-Mn alloys change the chemistry of the secondary phase which forms along grain boundaries, from the binary Al-Mg β-phase to the ternary Al-Mg-Zn τ phase.

2. The τ-phase is more resistant to corrosion than the β phase in surface corrosion tests (absent of any applied tensile stress), evidenced by preliminary exfoliation test performance and by the lesser degree of degradation of the secondary phase following electropolishing of TEM foils.

3. TEM foil preparation of samples plays an important role in retaining crystallinity in secondary phases. The electropolishing process can severely degrade secondary phases, a phenomenon that supports the anodic corrosion behavior of secondary phases in Al-Mg-based systems; non-corrosive forms of foil preparation allow a more thorough analysis of crystal structure.

3. The formation of S phase precipitates in material of this composition begins to form at compositions of Zn-modified 5083 alloys with Cu levels near 0.15 wt%. As expected, Zn will precipitate along with Mg at grain boundaries, but the resulting τ phase that forms also contains elevated levels of Cu, even when the original composition of the alloy contains Cu in levels down to or below 0.075 wt%.

4. Long sensitization times reveal the presence of a grain boundary phase of quasi-crystalline structure with icosahedral symmetry. This QC phase is of similar composition
to the Cu-containing quaternary \(\tau\) phase, indicating that the structure is not only present following controlled rapid quenching, as has been reported by other authors, but may also be a stable state following extended sensitization treatments.

5. Like previously modified Zn- and Cu-containing 5083 alloys, Ag can be added to alter the composition of grain boundary \(\tau\) phases that form in sensitized Al alloys that have Mg levels in excess of the accepted limit for \(\beta\) phase formation.

6. In addition to the quaternary \(\tau\)-phase, a five-constituent phase can form that contains Al, Mg, Zn, Ag, and Cu, as demonstrated by composition mapping.

7. In a sample containing a lower level of Ag and Cu (0.10 wt\% and 0.05 wt\%, respectively), the grain boundary phase was most common at the Al\(_{0.6}\)Mn dispersoid/grain boundary interface.

8. Additional precipitate formation is quite prevalent and, for sensitized samples, has a morphology more commonly seen in heat-treatable alloys, with distinct zones of precipitate formation in the grain interiors surrounded by PFZs in the vicinity of grain boundaries.

9. SSRT indicates that Zn-based \(\tau\) phase samples are more susceptible to early failure than standard 5083. Support for this susceptibility lies in the electrochemical potential of Al-Mg-Zn \(\tau\) phase, which demonstrates an extremely high current density under the expected anodic conditions. Tests on cast intermetallic phases also demonstrate this behavior, along with a decrease in corrosion rate for Zn-free \(\eta\)-type AlMgCu phase. While not conclusive based on these curves, SSRT also indicates a change in SCC susceptibility based on copper level in which an optimum window exists for maximum benefit in the composition ranges tested.
References


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CHAPTER 5

SUMMARY

Under the vast umbrella of study concerning "improvements" to aluminum alloys, the previously discussed work has given some insight into one small section of this area of study — that dealing with Al-5083 and minor derivatives of this popular alloy. It has been demonstrated using a variety of techniques that this alloy is capable of an increased level of performance not only through minor chemistry changes but also through changes to the processing techniques used to produce an alloy that is ready to be put into service in a wide range of applications.

Strengthening Issues

The most important strengthening mechanism in these alloys is solid solution strengthening due to magnesium supersaturation. While not deviating from this principle, additional strengthening mechanisms have been evaluated that will be additive to the contribution of magnesium, the level of which has remained constant throughout the copious amounts of modified alloys cast. These additional strengthening mechanisms were based on maximizing the particle distribution within the system due
to alloying elements, whether through maximizing the efficiency of already-present elements or by adding new elements. In terms of existing alloys, the distribution of manganese particles ($\text{Al}_6\text{Mn}$) can be significantly enhanced through post-solidification heat treatments. While the solubility of manganese in aluminum is quite small, a substantial fraction of manganese does not solidify as a eutectic during cooling from the melt. This remaining manganese has a high reversion temperature that it will not dissolve during hot working operations, meaning that any additional $\text{Al}_6\text{Mn}$ particle distribution that can be precipitated prior to hot work will provide additional pinning points for overall grain refinement. The ideal temperature for precipitating manganese is actually a temperature well below the Al-Mn solvus line, both in terms of nucleation and in the speed of growth of $\text{Al}_6\text{Mn}$ precipitates. For the compositions studied in this work, that temperature was approximately to 900°F; generally lower not only than that usually given for a homogenization treatment, but also for initiation of hot work processes.

Continuing with additions to these alloys for strengthening purposes, zirconium and scandium additions were investigated both independently and when added in concert. The effect of adding the two together was synergistic in effects on bulk properties, not only from an overall strengthening vantage but also in terms of alloy stabilization. While this study demonstrated marked and systematic increases in the aforementioned properties as levels of Sc were raised, one might wonder why 5083-based alloys with higher concentrations were not investigated. The clear drawback to additions of rare earth elements such as scandium to a "low cost" alloy are in the vastly increased alloy end price; the limit of reasonable alloy price increases were approached in the levels investigated in this study. At present, additions of Sc beyond 0.10 wt% would most likely be well outside the marketability of 5000 series alloys in most applications, even for the impressive increases seen in bulk properties. As such, it is important to demonstrate the remarkable changes in properties based on such additions when added even at such low levels.
Corrosion Issues

The underlying premise behind SCC failures in Al-Mg, while the mechanisms are not universally agreed upon, is still directly attributable to the migration of magnesium to grain boundaries and the subsequent Mg enrichment. With that, an attempt has been carried out to identify those alloying elements that also have an affinity for grain boundary segregation, and will modify said grain boundary enrichment through their presence in the alloy even while limited to relatively small concentration levels. A successful example of this strategy has certainly been demonstrated with zinc additions, in which zinc not only migrates but indeed changes the entire nature of the phase that forms, from β to τ phase. While copper and silver do not have the robust proclivity for altering phase transformation behavior that is possessed by zinc, both demonstrate a high degree of solubility in the resulting τ phase. The noble nature of copper demonstrates an ability to temper the aggressive, corrosive nature of Al-Mg-Zn based τ phase when added at moderately low levels, below the threshold for S phase formation in grain interiors. Both copper and silver may also have an effect on solute transport in a modified alloy; measured activation energies in modified alloys indicated that creep deformation was slowed in the presence of extra alloying elements when compared to standard 5083.

Modified Alloy Sequence

Based on the summary presented above (which in turn is based upon the material presented in this document), the 5083-based alloy that demonstrates the highest level of performance both from a corrosion and from a strengthening standpoint is an alloy
modified with additions of Ag, Cu, Zn, Zr, and Sc. Of these modifications, Zn would be the only alloying element to exceed 0.12 wt%, at a still relatively minor level of 0.3 wt%. Overall, this is a reasonably minor change to the bulk alloy chemistry, but measurable results in service performance would certainly be expected.

In producing the “ideal” 5083-based alloy, the following sequence of events and behavior might be expected. Following the casting process of the modified alloy, an appropriate heat treatment would be employed in order to precipitate manganese particles in a complete and finely dispersed manner. This preheat treatment would be affected not only by initial manganese levels, but also by impurity levels that will affect precipitation of Al₆Mn particles; most notably iron and silicon. The level of chromium in the system will also have an effect on Mn-based particle dispersion. Regardless of the above factors, however, we know that the time/temperature relationship for the heat treatment applied is important not only for the rate at which the particle distribution develops, but also on the overall size of particles in the final dispersion. Temperatures in the range of 900°F not only give a fine dispersion of moderately-sized particles, but are also near the “nose” of the solid solution decomposition curve, meaning that manganese atoms are coming out of solution at a faster rate.

Following the preheat and lay-on of the ingot to begin the hot working process, a fine dispersion of both Al₆Mn particles and Al₃(Sc,Zr) particles will aid in grain and subgrain structure refinement as the material is reduced at elevated temperatures. This effect will be most apparent during the cold work stage, when no recrystallization or recovery processes are occurring and grains and subgrains will be refined to smaller and more equiaxed geometries. The resulting structure will provide immediate yield and ultimate tensile strength increases as the material is put into service in a variety of applications. Additionally, stabilization treatments or minor temperature increases during the final processing sequences will precipitate a relatively undeveloped, but still observable, substructure of η phase precipitates in grain interiors, providing a further increase in strength levels.

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While in service, the material will continue to strengthen as the zinc and copper continue to precipitate naturally in grain interiors. Most importantly, however, the presence of silver, copper, and zinc will, along with magnesium, precipitate at grain boundaries. In an application where the material has an extended life span, minor to moderate temperature exposures or fluctuations that would otherwise lead to β phase formation on grain boundaries will instead lead to the formation of τ phase. Under conditions where a tensile stress is present (whether through residual or applied stresses as dictated by the application) and environmental conditions are ideal for ionic transport, it can be expected that the alloy containing τ phase of the previously identified “ideal” composition (copper level within the appropriate optimum window), in the place of SCC-prone β, will be more resistant to stress corrosion crack propagation and eventual failure.
CHAPTER 6

CONTINUING ISSUES

While the author has made a concerted effort to comprehensively address the issues contained herein, the work presented is but the “tip of the iceberg” in terms of improvements to aluminum alloys, even for the specific class (Al-5083) and, indeed, even for the exact compositions proposed. With regard to the last point, further study and evaluation of modified 5083-based alloys, the topics suggested in this final section are summarily discussed.

Strengthening Issues

While a great deal of credible research is published on the effects of manganese particles and their role in bulk properties of Al-5083, it would be worthwhile to pursue the effects of dedicated preheat treatments on final properties of interest. Work is presently being carried out to apply the preheat treatments outlined in this document to alloys slated to undergo a full processing treatment and subsequent testing. It is more admissible to discuss the effects of preheat treatments on post-processed material in
order to define the beneficial effects. Changes to the as-cast microstructure, while interesting, are only speculative in nature when making projections on final properties.

Additionally, preheat tests for manganese content were performed on alloys independent of those studied for scandium and zirconium distribution. It is unclear the extent to which Al\(_{(Sc,Zr)}\) particles will coarsen over the length of an extended preheat. It is possible that the particles could coarsen beyond the stage where their contribution to final microstructural properties is limited to dislocation interactions, and actually have an effect on grain boundary migration through pinning mechanisms. It is also possible, however, that the effectiveness of these particles as refiners could be reduced if they lose interfacial energy through decreased coherency.

One of the main goals of manganese distribution studies was to potentially maximize the refining effects of hot and cold work processes. In the area of superplastic forming (SPF), a more direct study of the preheat effects on final properties would be of great interest. Studies into this very area are in progress at the present time.

One of the important characteristics of 5083 and other similar 5000 series alloys is the inherent weldability of the material. Very little has been discussed with respect to this and related properties, although it is certainly of concern in a vast number of potential applications. It can be assumed that the positive effect that scandium has on solidification grain refinement and resistance to hot tearing [1, 2] in weld material would also apply to these alloys, but these factors have not been investigated. Perhaps more of concern is the effect of the additions of zinc to the system and the potential for hot cracking. It is not clear if remelting in a weld zone might lead to potentially harmful coarse eutectics that reduce weld zone integrity, whether by mechanical stress or by corrosion mechanisms. This issue was to some extent addressed through reduction of zinc levels.
down to as low as 0.3 wt%, which still exhibited a positive effect on β suppression, but it remains to be proven experimentally whether welding behavior of the modified alloys has in any way been compromised.

**Corrosion Issues**

Perhaps first and foremost in this study of corrosion in 5083 has been the endeavor to minimize the deleterious effects of elevated magnesium levels. Several minor chemistry changes have been shown to have positive effects on corrosion resistance, but the extent to which these alloying additions can limit β phase formation has been limited to standard magnesium levels. It is quite possible that the level of magnesium can be elevated still further, providing an even greater solid solution strengthening effect, without being any more susceptible to SCC than a standard 5083. No study was carried out to further the alloy modification process by evaluating alloys cast with higher magnesium levels, leaving the door open for development of 5000 series alloys that may find use in extremely high-performance applications.

Although work was carried out in order to help quantify bulk grain boundary phase corrosion characteristics, this work remains largely undiscovered. As was mentioned in the last section, welding concerns have not been largely addressed in the present work. Studies of β and τ phase formation in the heat-affected zone (HAZ) following weld passes were undertaken by TEM investigation of foils obtained from specific HAZ locations (Figure 6.1). It is shown that phase formation is not limited to material that has been sensitized at moderate temperatures for extended lengths of time, but can also occur over the relatively short thermal transient of a weld pass (Figure 6.2). Further study into this area is certainly worthwhile.
Figure 6.1: Differences in 5083 microstructure between areas A and B near a weld. The distance separating A and B is about 1.5 cm.
The difficulty of isolating multi-constituent bulk phases for direct study is considerable, although developing techniques in the Fontana Corrosion Center utilizing microcapillary cells for potential measurements will undoubtedly facilitate further characterization should this investigation be pursued. Convincing work on the corrosion mechanisms in unmodified 5083, carried out by Searles [3], followed proper potential measurements of isolated $\beta$, giving confidence that similar characterization could be performed on the modified phases. With appropriate potential measurements, careful biasing of actual tensile samples under SCC conditions can be utilized to effectively “shut off” or “turn on” the SCC mechanism – compelling evidence for galvanic dissolution of grain boundary phases and the conditions that exacerbate it. In addition, prior work on sensitized 5083 indicated that a range of SCC resistance is evident for differing sensitization treatments. The focus of this particular study was consistent in that it

Figure 6.2: The presence of grain boundary phases in a sample of a Zn-containing 5000 series alloy that have precipitated in the HAZ of a weld.
used the worst-case sensitization treatment for Al-5083 as a model treatment for laboratory-induced aged (sensitized) conditions that do not necessarily reflect in-service industrial conditions. It would be interesting (and certainly painstaking) to probe further into the effect of sensitization levels on the ideal modified alloys to determine if this sort of time- and temperature-dependent effect of sensitization on SCC resistance is as acute as that of Al-5083. It was shown that grain boundary phase formation and evolution is still occurring over extended periods of time — evidenced by the existence of quasicrystalline phases in Zn- and Cu-modified material. Investigation into the effect that such phases might have on bulk characteristics is an area of study that certainly has room to be explored more fully.

Finally, regardless of the mechanism or combination of mechanisms that lead to SCC failure under various conditions, it cannot be argued that atomic transport of alloying elements to grain boundary regions is the one major factor that is consistent for all alloys. The transport kinetics of solute elements in these alloys was investigated through creep testing experiments of various compositions, although this effect would require a highly concerted effort to begin to back out the contributions of each of the different elements for varying composition levels. With regard to the activation energy results, it should be mentioned that these results are an aid to the understanding of atomistic kinetics, but are hardly conclusive. Nonetheless, while many modes of atomic transport will lead to viscous glide of dislocations in these complex solute systems, it is clear that a change in kinetics occurs for the alloys even with the low concentrations of "additional" solute that have been proposed and reported over the course of this study.
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